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**From volcanic ash to allophanic dust :
understanding phosphorous behaviour in Dominican soils**

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**From volcanic ash to allophanic dust: Understanding phosphorus
behaviour in Dominican soils**

**A dissertation submitted in partial fulfilment of the requirements
for the degree of
Philosophiae Doctor (PhD) in Soil Science, Bangor University**

by

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Abstract

The economy of the Commonwealth of Dominica is primarily agrarian based with banana production as one of the key export commodities, notwithstanding its preferential loss in the European Union market. However, banana productivity like most other crops has been severely impacted by a general low native soil nutrient status coupled with low application rates of phosphate (P) fertilizers in particular. The latter can be partly attributed to the low purchasing power on the international market as is evident in the long term trends of increase prices for nitrogenous and phosphate fertilizers.

The volcanic soils of the Commonwealth of Dominica were first studied in a relatively detailed way in 1967 with these soils showing high phosphate retention capacities. As a consequence, although P application is an integral part of profitable agricultural systems, improving soil fertility and plant nutrient management is a complex challenge. This challenge is amplified by the fact that a high ability to adsorb P is one of the characteristics of volcanic soils making P sparingly available for plant uptake. Hence although the world's high reserves of phosphate ores are declining the demand for P fertilizers in the humid tropics are constantly increasing. If not managed properly, increase and continued input of P fertilizers and manure P may eventually lead to environmental rather than agronomic concerns.

This research examines the influence of soil properties from some major agricultural soils in the Commonwealth of Dominica in order to obtain an improved comprehension of soil fertility limitations with the goal of developing nutrient management and farm developmental strategies geared towards increased crop production and overall farm productivity. In this regard special attention is given to the use of pyroligenous acid as a low molecular weight organic acid (LMWOA) in catalysing the dissolution of secondary P minerals. Hence the aim is to understand how native P stocks as well as applied fertilizer can potentially become more plant available thus reducing P fertilizer applications to a required minimum.

DEDICATION



“To my immediate and extended family for all their unconditional love and devoted support given during the realization of this work”

..... May the King of Kings and Lord of Lords continue to shower HIM blessings upon you all.....



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ABOUT THE AUTHOR

Mr. Al-Mario Casimir is an agronomist by training employed by the Ministry of Agriculture, Forestry and Fisheries, Government of the Commonwealth of Dominica. A graduate of the Saint Mary's Academy (1988), and a former student of the Clifton Dupigny Community College (1988 - 1989), Mr. Casimir got involved in agriculture through the school summer attachment programme during the period 1984 - 1987. He formally joined the division of agriculture in 1989 under the Tropical Fruits and Spices Project as vote's clerk. In 1991 he travelled to the Republic of Cuba to pursue undergraduate studies in agronomy. He returned to the division of agriculture in 1998 as team leader of the Western agricultural extension region but that would only be for a short stance because he would soon travel to the Dominican Republic in 1999 to further pursue post graduate studies in agricultural diversification. He returned in 2001 and started assisting in revitalization efforts towards alternative agricultural technologies such as organic input manufacture and organic crop production.

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Lome IV Convention. The thesis presented and approved in May 2001 was entitled “Growth and Productive Responses of Radish (*Raphanus sativus* L.), Coriander (*Coriandrum sativum* L.), and Beans (*Phaseolus vulgaris* L.) to Mineral Fertilizers and Cow, Chicken, and Sheep Manure combinations in Nigua, Dominican Republic.

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Mr. Casimir intends to contribute to the efficient production of locally grown organic products through the generation and transfer of technologies which are more inclined to natural conditions, less destructive to the environment and public health as well as to stimulate the interest for future studies within the context of organic agriculture. He intends to promote the production of organic food by looking to expand the pattern of production, increasing productivity and reducing the seasonal variation of production thus leading to increased trade investment, equitable sharing of benefits and improved networking among primary producers.

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Acronyms and Abbreviations

$\mu\text{g m}^{-3}$	Micro gram per cubic metre
μM	Micro molar
AAS	Atomic Absorption Spectroscopy
ACP	African Caribbean and Pacific
AFS	Atomic Fluorescence Spectroscopy
Al	Aluminium
ANOVA	Analysis of Variance
As	Arsenic
BMP	Best Management Practice
BTU	British Thermal Units
C	Carbon
Ca	Calcium
Cd	Cadmium
CEC	Cation Exchange Capacity
CND	Counting the Number of Drops
CO ₂	Carbon Dioxide
Cu	Copper
DAP	Di-Ammonium Phosphate
dm ³	Cubic Decimetre
DOC	Dissolved Organic Carbon
ECM	Ectomycorrhiza
EM	Ericoid Mycorrhiza
EU	European Union
Fe	Iron

FFS	Farmer Field School
GCOD	Government of the Commonwealth of Dominica
GFAAS	Graphite Furnace Atomic Absorption Spectrometry
GIS	Geographic Information Systems
H ⁺	Hydrogen Ions
H ₂ PO ₄ ⁻	Di-Hydrogen Phosphate Ions
ha	Hectare
HPO ₄ ²⁻	Mono-Hydrogen Phosphate Ions
ICPAES	Inductively Coupled Plasma Atomic Emission Spectrometry
ICPMS	Inductively Coupled Plasma Mass Spectrometry
I _{max}	Maximum Intensity
IPM	Integrated Pest Management
K s ⁻¹	Kelvin per second
K	Degrees Kelvin
kg	Kilogram
Kn/m ³	Kilonewtons per Cubic Meter
LDCs	Less Developed Countries
LMWOAs	Low-Molecular Weight Organic Acids
LOI	Loss-on-Ignition
Mg	Magnesium
mM	Milli-molar
Mn	Manganese
Na	Sodium
NGO	Non-Governmental Organization
NUE	Nutrient Use Efficiency

°C	Degrees Celsius
OECS	Organization of Eastern Caribbean States
P	Phosphorus
PCI	Participatory Crop Improvement
PES	Payment for Eco-systems Services
PESq	Partial Eta Squared
Pi	Inorganic Phosphate
PLA	Pyroligneous Acid
Po	Organic Phosphate
PR	Phosphate Rock
RAE	Relative Agronomic Effectiveness
RCF	Relative Centrifugation Force
REDD	Reducing Emissions from Deforestation and Degradation
SIDS	Small Island Developing States
SOC	Soil Organic Carbon
SOM	Soil Organic Matter
SPSS	Statistical Package for the Social Sciences
TSP	Triple Superphosphate
TXRF	Total Reflection X-Ray Fluorescence
U	Uranium
UNESCO	United Nations Education, Scientific, and Cultural Organization
VAM	Vesicular-Arbuscular Mycorrhiza
VOC	Volatile Organic Compounds
Zn	Zinc

CHAPTER 1

GENERAL INTRODUCTION: JUSTIFICATION AND OBJECTIVES OF THE STUDY

1.1 General Introduction

Increasing agricultural production by improving soil fertility and plant nutrition uptake, together with the optimisation of biotic and abiotic production factors is a complex challenge (FAO, 2011). Excessive use of nutrients, inefficient management of cropping systems, and the inefficient use of residues and wastes result in losses of plant nutrients from agroecosystems (Ju et al., 2007; Goulding et al., 2008; Potter et al., 2010; Lemaire et al., 2014), which can mean an economic loss for the farmer (Johnston et al., 2001). On the other hand, inadequate application of nutrients and residue mismanagement can create a depletion of the stock of plant available nutrients (Grote et al., 2005; Jones et al., 2013; Bahr et al., 2014; van der Velde et al., 2014), which could also result in long-term economic loss for the farmer (Johnston et al., 2001; Jat et al., 2012).

Biomass production inevitably removes plant nutrients from the soil and if farming systems are to be productive as well as sustainable, these nutrients have to be replaced by whatever sources are available (Syers, 1997; Fließbach et al., 2007; Bockstaller et al., 2008; Fragoulis et al., 2009; Cordell et al., 2011). Considering the importance of soil fertility and plant nutrition to agricultural production, it is vital to establish the relationship between yield, use of plant nutrients, economic feasibility and environmental quality (Goulding et al., 2008; Sharpley et al., 2013; Withers et al., 2014, 2015). Given the projected growth of world population, the development of soil fertility and plant nutrition management strategies to increase the productivity of farming systems is a major challenge for food security and rural development (Cohen, 2003; Grote, 2014; Scholz et al., 2014).

Restoring, maintaining and increasing soil fertility are major agricultural priorities, particularly in many less economically developed parts of world where soils are inherently poor in plant nutrients, and the demand for food and raw materials is increasing rapidly (Syers, 1997). This is a major challenge for small island developing states (SIDS) like the Commonwealth of Dominica given its vulnerable and small and open based agrarian economy. In these SIDS, there is a need to intensify crop production (Bommarco et al., 2013) to meet demand for food by increasing farm productivity through improved agronomic and husbandry practices combined with restored socio-cultural values (FAO, 2011). Because agriculture is primarily a soil-based industry that extracts nutrients from the soil profile, effective and efficient approaches to slowing that removal and returning nutrients to the soil will be required (Gruhn et al., 2000; McMahon and Read, 2013; Maaß et al., 2014; Scholz et al., 2014) notwithstanding the release of nutrients from parent material into the soil by weathering.

Within the socio-cultural context of agricultural development, researchers uphold the view that soil fertility and plant nutrition management depends largely on prevailing economic and social conditions (Sánchez and Salinas, 1981; Maene, 2001; Jama and van Straaten, 2006). Farmers' decisions depend on their economic situation and their socio-economic environment, on their perception of economic signals, and on their acceptance of risks (Bruulsema, 2009). Inevitably, in developing productive agricultural systems one of the major constraints that will have to be overcome is the issue of a fertile soil that provides a sound basis for food production within the constraints of climatic conditions (Oenema, 2011; Zhang, 2011; Bommarco et al., 2013). To this end it is imperative to advocate and develop an integrated soil-crop systems management approach which focuses and considers all possible soil quality improvement measures. Ultimately, the approach will need to deliberate on integrating the utilization of various nutrient resources and matching nutrient supply to crop requirements (Withers et al., 2014, 2015), and integrating high yielding cultivation systems (Zhang, 2011).

Phosphorus (P) is a macronutrient that is essential for plant growth and development. It is also required in relatively large amounts for the synthesis of secondary plant metabolites (Melten et al., 2009; Ramakrishana and Ravishankar, 2011), since P has essential functions as a constituent of nucleic acids and phospholipids (biomembranes) and plays a key role in the energy metabolism of cells. However phosphorus availability is among the most severe limitations for agriculture in tropical soils (MacArthur and Knowles, 1993; Armstrong, 1999; Hinsinger, 2001; Solomon et al., 2002; Shen et al., 2011; Sugihara et al., 2012) owing to low native soil P and high P fixation capacity by aluminium (Al) and iron (Fe) oxides (Solomon et al., 2002; Takahashi and Anwar, 2007; Shen et al., 2011; López-Arredondo et al., 2014; Verde and Matusso, 2014). Phosphorus is a highly reactive element, and as such, does not exist in the elemental form in the soil, being primarily in insoluble forms, and partly unavailable to plants (Stewart and Tiessen, 1987; Schachtman et al., 1998; Pant and Reddy, 2001; Daroub et al., 2000; Hinsinger, 2001; Jaggi et al., 2005; Dib et al., 2006; Ramaekers et al., 2010; Yang and Post, 2011; Smith et al., 2011; Yang et al., 2014a).

In fertile soils a significant portion of the total P is in moderately soluble forms, which acts as a ready reserve to replenish the pool of soluble P as it is depleted (Johnston and Syers, 2009; Yang and Post, 2011; Crews and Brookes, 2014). Continuous cultivation with little or no P input not only decreases the plant available soil P pool, but also influences the structural composition and bioavailability of P in these tropical soils (Solomon et al., 2002; Negassa and Leinweber, 2009), thus affecting long-term productivity and sustainability of these cropping systems. Low efficiency of plant P uptake is a major problem associated with P application (Takahashi and Anwar, 2007; Chien et al., 2011; Veneklaas et al., 2012; Sulpice et al., 2014; López-Arredondo et al., 2014). Due to its low solubility and mobility in soil and the fact that even soluble P diffuses very slowly and over short distances, P can be rapidly depleted in the rhizosphere by root uptake, resulting in a gradient of P concentration in a radial direction away

from the root surface (Shen et al., 2011; Barrow, 2015) with some soils requiring regular P application to maintain productivity (Barrow and Debnath, 2014).

There is a growing trend of public, scholastic, and private sector debate which proposes that farmers ought to be encouraged to pursue practices that not only enhance the value of their products but also take into account the issues of environmental stewardship, protection of biodiversity, nutrient management, including social thematic areas (Auburn, 1994; SAI, 2009; Dou, 2011; Sala, 2015). This has led to the advocacy for the growing of food crops with a varied number of approaches to include but not limited to “naturally”, “with low environmental impact”, “sustainable intensification”, “low input farming”, and “biodynamic agriculture”, in addition to “organically grown” and “fair-trade” labels. The latter two approaches have been widely publicised since this is already a lucrative market with tremendous potential fuelled by the healthy lifestyle and wellness agenda, the perceived reduction of environmental pollution, coupled with the ever increasing emphasis on social welfare and capacity building (Becchetti and Constantino, 2008; Beuchelt and Zeller, 2011).

The development of cost efficient and effective alternative inputs with emphasis on the increased utilization of local farm resources to enhance and augment crop nutrient management programmes is considered one key pillar and catalyst in the overall development of sustainable farming systems (Syers, 1997; Fließbach et al., 2007; Bockstaller et al., 2008; Fragoulis et al., 2009), an area of focus which is most relevant to SIDS amidst the agronomic reality that increased use of P inputs is necessary for improved crop performance. Emphasis on P management to increase the productivity of farm land (Crews and Peoples, 2004; Niggli et al., 2009) must be seen as key a developmental priority in stimulating sustainable development goals (SDGs) (Griggs et al., 2013). This priority is based in part on long term trends in increased world prices of fossil fuel based energy and declining reserves of ores containing P, resulting in more expensive nitrogenous and phosphate fertilizers (Cordell et al., 2009).

1.2 Pertinent issues in justification of the study

Even though the total amount of P in the soil may be high, it is often present in unavailable forms or in forms that are only available outside of the rhizosphere (Stewart and Tiessen, 1987; Schachtman et al., 1998; Pant and Reddy, 2001; Hinsinger, 2001; Jaggi et al., 2005; Yang and Post, 2011; Smith et al., 2011) and as such few unfertilized soils release P fast enough to support the high growth rates of crop plant species (Holford, 1997).

In many agricultural systems in which the application of P to the soil is necessary to ensure plant productivity, the recovery of applied P by crop plants in a growing season is very low (Ramaekers et al., 2010; López-Arredondo et al., 2014; Zhang et al., 2014), because a significant percentage of soil P becomes immobile and unavailable for plant uptake (Jiang et al., 2007; Hinsinger et al., 2011) because of adsorption (Bolan, 1991; Prochnow et al., 2006), as well as mineral precipitation (Galvani et al., 2008), or conversion to organic forms (Giles et al., 2014; Crews and Brookes, 2014; Verde and Matusso, 2014).

Phosphorus uptake not only depends on the amount of available P in the soil but also on plant properties (Föhse et al., 1988; Wissuwa, 2003). Differences in external P requirements can be attributed to either a lower internal P requirement for optimum growth or higher uptake efficiency of the plant, determined by both root-shoot ratio and absorption rate per unit of root regarded as the influx (Föhse et al., 1988; Jungk et al., 1990; Zhang et al., 2014).

The Commonwealth of Dominica's edaphic conditions have been greatly influenced by the country's volcanic origin (Spencer, 1902; Earle, 1928; Rouse et al., 1986; Reading, 1991; Goldsmith et al., 2010) and the relatively uniform and recent andesitic–dacitic eruptive history (Wadge, 1985; Whitman, 1989, Samper et al., 2008) has led to variations in rainfall as being the dominant determinant for soil types (Lang, 1967; Goldsmith et al., 2010). Soils of a given type or local classification are in most cases a product of the extent to which volcanic parent material has weathered (Lang, 1967; Rouse et al., 1986; Reading, 1991; Goldsmith et al., 2010).

It is generally accepted that soils which have developed on the deposits of volcanic ash usually have a predominance of non-crystalline alumino-silicates such as allophane, imogolite, and allophane-like constituents in the clay fraction and as such the P sorption capacity is significantly affected by the presence of these minerals (Yoshinaga and Aomine, 1962; Follett et al., 1965; Wada, 1967; Wada and Higashi, 1976; Ross, 1980; Childs et al., 1983; Shoji and Takahashi, 2002; Gérard et al., 2007; Churchman, 2010; Yang et al., 2014a). Nonetheless these soils are considered to be the most productive soil types on a global scale (Ugolini and Dahlgren, 2002; Shoji and Takahashi, 2002; Navarrete et al., 2008; Nugroho, 2010), although phosphorus is usually a limiting nutrient for most crops grown on these soils (Barrow, 2015).

Within the contemporary literature, it is accepted that various extractable forms of Al and Fe which indirectly affect P sorption capacity in acidic soils (Parfitt, 1979, Shoji et al., 1993; Van Ranst et al., 2004; Pizzeghello, 2011; Barrow, 2015) have important implications for P fertiliser management from both productivity and environmental viewpoints (Burkitt et al., 2002; Edis et al., 2002; Bramley et al., 2003; Brock et al., 2007; Haden et al., 2007; Zhang et al., 2009; Mason et al., 2010; Moody, 2011; Webb and Adeloju, 2013; Schoumans et al., 2015; King et al., 2015).

Andesitic soils are widespread globally and are found in many agriculturally important regions such as Europe, Africa and Indian Ocean, Americas, and Asia and Pacific (Shoji et al., 1994; Takahashi and Shoji, 2002; Arnalds, 2004) which closely parallels the global distribution of active and recently extinct volcanoes (Siebert et al., 2010). Approximately 60% of volcanic soils occur in tropical countries (Takahashi and Shoji, 2002). While volcanic soils comprise a relatively small extent of the world's land surface (0.84%), they represent a crucial land resource due to the disproportionately high human populations living in these regions (Shoji et al., 1994). Therefore the extent of P availability is a very prevalent problem on heavily weathered tropical soils to include Oxisols as well as Ultisols.

1.3 Context of the study

Given the necessity for more sustainable phosphorus management characterized by improving the efficiency of inorganic phosphorus as well as the creation of opportunities for the recycling of phosphorus (secondary P), the overall aim of the study is to investigate the behaviour of tropical volcanic soils found on the Lesser Antillean island of the Commonwealth of Dominica with respect to their general chemical constituents, and the expression of different acidic properties affecting P sorption capacities. The study also aims at examining some of the soil characteristics associated with phosphorus availability with a view of developing low cost strategies that would improve and/or stimulate soil phosphorus uptake in these tropical volcanic soils, while at the same time being ever mindful of growing environmental concerns.

The use of commercial P fertilizers is often not cost effective on strongly depleted weathered soils of the tropics (Chien and Menon, 1995; Kpombrekou-A and Tabatabai, 2003; Akande et al., 2005; Jama and van Straaten, 2006), and is associated with low efficiency of use (Shaviv and Mikkelsen, 1993; Major et al., 2010; Oliveira Júnior et al., 2011) as phosphate ions are easily adsorbed by Al- and Fe-oxide minerals (Hinsinger, 2001; Dib et al., 2006; Oelkers and Valsami-Jones, 2008; Cao et al., 2012, Barrow, 2015). Consequently, it has long been recognized that major efforts are needed to develop P fertilizers that are better suited for tropical soils (Sánchez and Salinas 1981; Rajan et al., 1991; Akande et al., 2005; Kumari and Phogat, 2008; Akande et al., 2010; Scholz et al., 2014).

One of the options available to low resource farmers in open and vulnerable small island economies is the utilization of rock phosphate (RP) as a supplement to the more costly triple super phosphate (TSP) and di-ammonium phosphate (DAP) (Oliveira Júnior et al., 2011; Nyambati and Opala, 2014). Per unit of P, rock phosphate is about one third to one fifth the price of simple superphosphate (Sánchez and Salinas, 1981; Nye and Kirk, 1987; Mutuo et al., 1999; Kongshaug et al., 2012). Nonetheless, in some situations rock phosphate may be unable

to support the same maximum yield as water-soluble P fertilisers due to inadequate dissolution of RP even at high rates of application (Kanabo and Gilkes, 1988). In addition there is a growing concern regarding the finite and unrenewable base of this resource in light of its basis for the manufacture of super-phosphate fertilizers which accounts for a significant percentage of global P consumption (Rengel, 1998).

The dissolution of RP can however be augmented by increasing the supply of protons (H^+) and by continuous removal of the dissolved products, calcium (Ca) and phosphorus (P) from the zone of dissolution (Bolan et al., 1997; Kaleeswari and Subramanian, 2001; Nying and Robinson, 2006). Therefore, the dissolution of RP is enhanced by low pH, high cation exchange capacity and high capacity for P sorption as well as the maintenance of low levels of solution P (Smyth and Sánchez, 1982; Cabala-Rosand and Wild, 1982; Rajan et al., 1991).

The importance of mycorrhizal fungi in P acquisition is underscored by the fact that fungal hyphae greatly increase the volume of soil that plant roots explore (Smith and Read, 1997). Mycorrhizal infection may affect the mineral nutrition of the host plant directly by enhancing plant growth through nutrient acquisition by the fungus, or indirectly by modifying transpiration rates and the composition of rhizosphere microflora (Marschner, 1995). The increased uptake of P by mycorrhizal plants is mainly due to absorption and translocation of P from distant areas which are otherwise inaccessible to plant roots. Several of these mycorrhizae species such as ectomycorrhizas (ECM), ericoid mycorrhizas (EM), and vesicular-arbuscular mycorrhizas (VAM) take part in these rhizosphere processes. However, ECM and EM fungi produce ectoenzymes which provide host plants with the potential to access organic N and P forms that are normally unavailable to VAM fungi or to non-mycorrhizal roots (Kothari et al., 1990a,b). Hence, sustainable management of P in agriculture requires mechanisms in plants that enhance P acquisition and management schemes that increase soil P availability (Schachtman et al., 1998; Vance, 2001).

Principally, P efficiency can be enhanced by increasing P solubility in soil solution or by reducing P fixation in soils (Hua et al., 2008). To this end, the use of naturally occurring low-molecular weight organic acids (LMWOAs) that are produced in soil as microbial metabolites or plant exudates from dead or living cells represents an alternative perspective in rock phosphate research (Kpombrekou-A and Tabatabai, 2003). Of particular interest to this research study is the potential use of pyroligneous acid, the condensate of exhaust gas derived from the pyrolysis of ligneous/hemicellulolytic material, as a LMWOA in the dissolution of phosphate sorbed to clay minerals and Al- and Fe-oxides, and the potential to enhance P availability (Lashari et al., 2013; Togoro et al., 2014; Benzon et al., 2015).

1.3.1 General Questions

The overarching aim of this study is to examine the influence of soil properties of some major agricultural soils of the Commonwealth of Dominica on soil vulnerability to P fixation leading to low P uptake by plants. Hence the study will explore avenues which could aid in phosphorus management and by extension P security. In this regard, some of the general questions that are being asked include:

- (1) What is our overall knowledge of phosphorus management in tropical volcanic soils and what are our current practices as influenced by our understanding and attitude with respect to developing sustainable food production systems?
- (2) How can we improve the efficiency of phosphorus application as a management strategy for increasing agricultural production without compromising food security, human health and environmental degradation and without creating economic barriers that local producers would not be able to bear?
- (3) How can we manipulate soil chemistry to increase availability of P to forms accessible to plant roots or their symbionts?

(4) Are there products and/or by-products available from natural chemical and biological processes and/or industrial processes which could assist in P nutrient cycling?

1.3.2 Research premise, rationale and hypothesis

The general approach in conducting the research study is outlined as follows:

Premise	Objective	Setting
The quantity and nature of soil available nutrients is heavily influenced by spatial variation in soil type and soil constituents	To investigate variability in soil chemical constituents and nutrient availability status from some major agricultural producing regions.	Harper Laboratory, Environment Centre of Wales. (Chapter 4), general soil analysis exploratory in scope
The expression of andic properties is consistent to the high levels of geo-spatial variability of selected soil chemical characteristics and associated constituents	To determine what soil constituents contribute towards the expression of andic properties in these volcanic soil and how are they expressed geographically	Harper Laboratory, Environment Centre Of Wales. (Chapter 5), dissolution of Al and Fe forms and variability between soil type
The potential to P losses via runoff and subsurface drainage is consistent to the geo-spatial variability of associated soil constituents	To investigate the relationship of soil chemical constituents influencing vulnerability to P losses and what is the potential at the landscape level	Harper Laboratory, Environment Centre of Wales. (Chapter 6), soil P test extraction methods and relationship of soil constituents with P saturation
The distribution of P availability is heavily influenced by the high levels of geo-spatial variability of associated soil constituents	To quantify P sorption characteristics influencing P availability and the relationship between P sorption and soil constituents	Radioisotope Laboratory. Environment Centre of Wales. (Chapter 7), ³³ P retention and CaCl ₂ desorption studies
P availability is influenced by all LMWOAs and the degree of dissolution affected by the geo-spatial variability of soil type	To determine the efficacy of some selected LMW organic acids with particular interest on the use of (PLA) pyroligneous acid.	Harper Laboratory. Environment Centre of Wales (Chapter 8), maize pot trial and maize rhizotube trial using ³³ P.

The study explores the P retention and desorption capacity of volcanic soils as influenced by the presence of Al- and Fe-oxides which give them their characteristic allophanic properties. Essentially, the research proposes that sparing availability of P can be improved by utilizing pyroligneous acid as a low molecular weight organic acid (LMWOA) to accelerate the dissolution of secondary P minerals into soil solution for plant uptake and utilization. The rationale is that compared to the dicarboxylic (oxalic acid) and tricarboxylic (citric acid), pyroligneous acid, similar in chemical composition to the monocarboxylic acetic acid, should be able to undergo release of protons (H⁺) and so induce the dissolution of Fe- and Al-phosphates associated with secondary P minerals and release P sorbed on clays, Al- and Fe-oxides surfaces.

These arguments are based on the fact that carboxylic acids are polar and thus they are both hydrogen-bond acceptors (the carbonyl $-C=O$) and hydrogen-bond donors (the hydroxyl $-OH$). Hence, adding carboxylic acids to soil enhances the dissolution of secondary P minerals thus exposing previously occluded soil P. However, depending on their ionic strength some of these acids may not compete with P for surface binding sites. As a result, the effectiveness of releasing P previously occluded is partially dependent on the organic acid used. Therefore the study hypothesises that:

- Pyroligneous acid is as effective as other LMWOAs in releasing (dissolving) P from tropical volcanic soils with substantial components of hydrous oxides of aluminium (Al) and iron (Fe).
- Pyroligneous acid has agronomic potential as an amendment for increasing plant-available P in these volcanic soils fertilized with mineral and/or rock phosphate.

1.3.3 Research Application

The ultimate goal of this research is to develop practical land use and management programmes guided by an improved understanding of phosphorus activity in these soils. Thus the study aims to obtain an improved comprehension of Dominican soils by assembling data most relevant to the agronomic and environmental management of P fertilizer application.

To this extent, the study establishes a research framework which ought to direct on-island short term and long-term fact-finding soil studies. Hence one of the direct research applications is to gradually incorporate methodologies related to measurable parameters of allophane chemistry into mainstream soil testing programmes given current analytical limitations. More importantly the research establishes a platform whereby more detailed and holistic studies regarding the potential use of pyroligneous acid as an alternative low cost P management strategy can be developed.

To this end, the research attempts to align current challenges with futuristic outlooks within the broader framework of new policy perspectives for Dominican agriculture. This approach is critical and highlights the necessity for innovation in agricultural research, technology development and transfer, taking into consideration the ever present issues of trade liberalisation, increase use of sanitary and phyto-sanitary barriers, food safety, quality, and security, coupled with rising food prices.

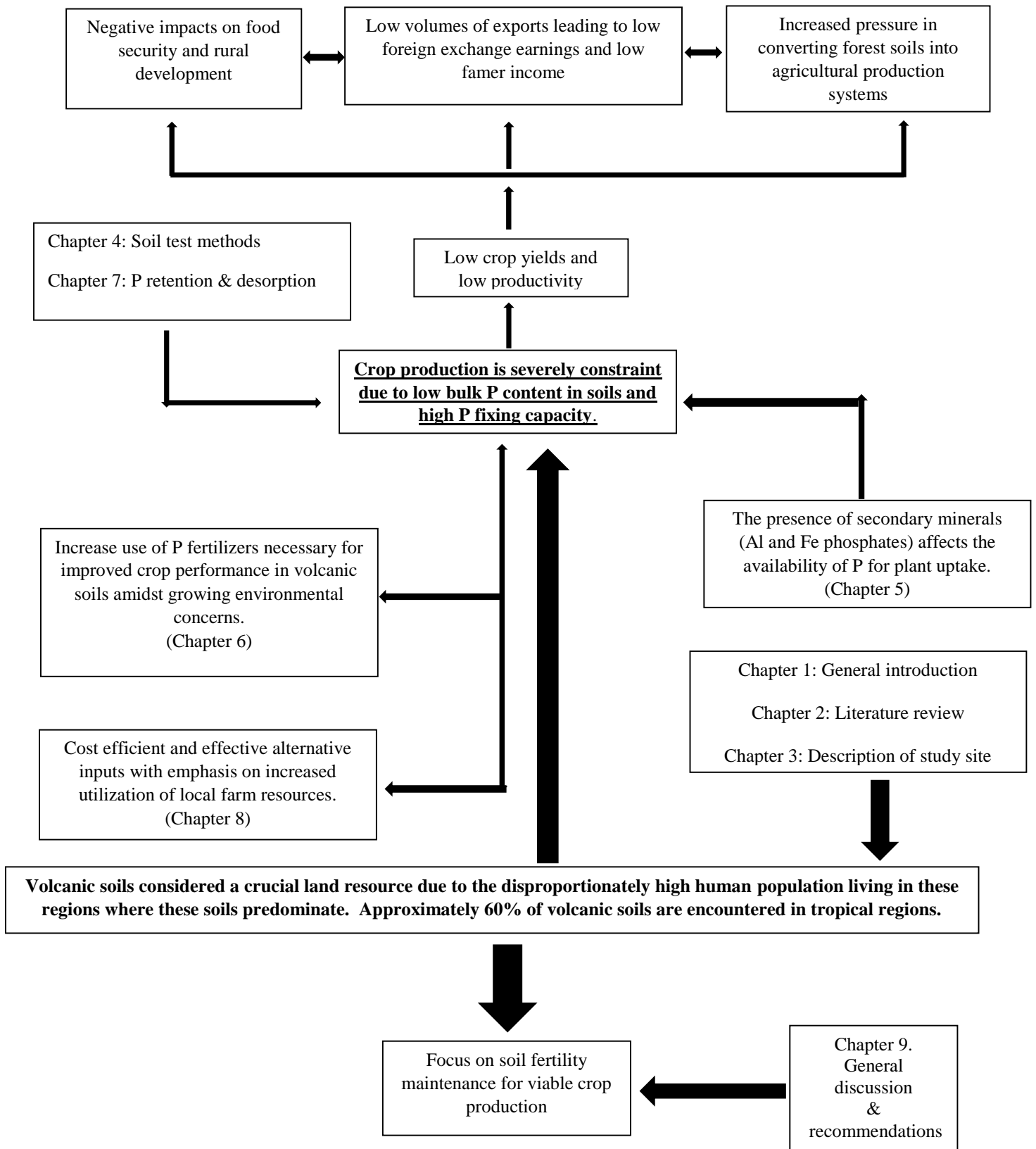
Nonetheless, the Commonwealth of Dominica is ideally located between two European Union (EU) departments (Guadeloupe to the North; Martinique to the South) to take advantage of the opportunities which exist for increasing agricultural trade as a result of increased demand for food. However these opportunities are also associated with increased national, hemispheric and global responsibilities especially as it relates to environmental stewardship. Hence the re-tooling of production technologies which are better adapted at mitigating against potential negative agronomic and environmental impacts must be initiated. This approach is extremely important if the country is to benefit from diversification opportunities into high value products, expansion of niche markets, such as for organic and fair trade products which are gaining consumer acceptance in the current international environment.

The specific overarching goals of this study are summarized as follows:

1. Understanding phosphorus dynamics in Dominican volcanic soils to include mechanisms which dictates phosphorus transformation and movement in the soil and plant.
2. Identifying areas of gaps which need to be addressed at the policy level in order to develop sustainable production systems with emphasis on phosphorus nutrition.

The study is undertaken with a view of developing on-farm technologies which would minimize the challenges associated with P fixation and hence concerted develop programmes geared towards improving soil fertility and plant nutrient management.

Diagram 1.1: Schematic representation of the thesis outline



CHAPTER 2

LITERATURE REVIEW

2.1 Phosphorus Management

2.1.1 *The Importance of Phosphorus in Crop Cultivation*

The 20th century has been described as the century of explosive population growth which resulted in unprecedented impacts (Lutz et al., 2004). In contrast, the 21st century will see mankind live in a world which will be home to at least nine billion people (Tilman et al., 2001; Jenkins, 2003; Godfray et al., 2010; Dawson and Hilton, 2011). However, it has also been argued that we are more than likely to see the end of world population growth and begin to see the century of population aging (Lutz et al., 2004). Producing enough food and other vital resources is likely to be a substantial challenge for humanity (Cordell, 2010; Bommarco et al., 2013; Jones et al., 2013; Grote, 2014; Cordell and Neset, 2014). Moreover the world's terrestrial, freshwater, and marine biodiversity scenarios highlights serious cause for concern particularly as it relates to land use change and the relationship between habitat loss and degradation, species extinction, community structures and shifts in the distribution of biomes (Pereira et al., 2010; Bockstaller et al., 2011).

Phosphorus, together with nitrogen (N) and potassium (K), is an essential plant nutrient which is applied to agricultural soils in the form of fertilizers to maintain high crop yields (Shin et al., 2005; Heinonen-Tanski and van Wijk-Sijbesma, 2005; Schachtman and Shin, 2007; Veneklaas et al., 2012; Verde and Matusso, 2014; van der Velde et al., 2014) and is second only to N as the most limiting element for plant growth (McArthur and Knowles, 1993; Armstrong, 1999; Hinsinger, 2001; Solomon et al., 2002; Shen et al., 2011; Sugihara et al., 2012). Phosphorus has no substitute in food production in either natural ecosystems or in agroecosystems (Childers et al., 2011). An adequate supply of phosphorus to plants is essential for seed formation (Mayer and Shain, 1974; Yoshida et al., 1999; Loewus and Murthy, 2000;

Raboy et al., 2001), root development (Ratnayake et al., 1978; Keerthisinghe et al., 1998) and the maturing of crops with regards to economic yields (Cutcliffe and Munro, 1976; Armstrong, 1999; Ali et al., 2002; Khan et al., 2009). Phosphorus has also been linked to disease resistance and crop quality (Reuveni and Reuveni, 1995; Glenn et al., 2001; Puterka et al., 2005; Marko et al., 2008; Reuveni and Reuveni, 2008), and is also required in relatively large amounts for the synthesis of secondary plant metabolites (Melten et al., 2009; Ramakrishana and Ravishankar, 2011). A marked deficiency of this essential element will provoke reduced fruit quality and storage potential (Ahn et al., 2005; Oke et al., 2005).

Securing the long-term availability of and accessibility to phosphorus is crucial to global food security (Cordell et al., 2009; Childers et al., 2011; Jones et al., 2013; Scholz et al., 2014; Schoumans et al., 2015; Withers et al., 2015). However the major source of phosphorus, rock phosphate, is a non-renewable resource and high quality reserves are becoming increasingly scarce (Butler, 2009; Van Vuuren et al., 2010; Bouwman et al., 2013; Koppelaar and Weikard, 2013; Cordell and Neset, 2014; Schoumans et al., 2015).

While demand for phosphorus increases particularly in Less Developed Countries (LDCs), the world's reserves of rock phosphate are shrinking and distributed over a few countries to include Morocco, United States of America, China and Russia (Cordell et al., 2009; Smit et al., 2009; Dawson and Hilton, 2011; Schoumans et al., 2015). Therefore, in order to increase the productivity of cropping systems, a combination of P efficient crops and P fertilization practices may thus provide a better strategy for sustainable crop production where P availability is a major constraint (Cornish, 2009; López-Arredondo et al., 2014). However, a number of researchers have noted that mineral P fertilizers processed from non-renewable reserves have significantly enhanced crop and livestock production over the past 50 years (Tilman et al., 2002; Cordell et al., 2009; Vitousek et al., 2009; MacDonald et al., 2011) and, as such, the welfare of billions of people globally (Kereiva et al., 2007; Schröder et al., 2011).

Commercial P fertilizers have, however, not only been used to raise the fertility level of formerly poor soils (Manu et al., 1991; Pheav et al., 2003; Vu et al., 2010), but have also allowed people to neglect the reuse of P that humans ingest in the form of food and excrete again as faeces and urine, and also P found in other organic wastes (Haarr, 2005; Childers et al., 2011; Maaß et al., 2014). Consequently, P mainly moves in a linear direction from mines to distant locations for crop production, processing and consumption (Cordell, 2010; Childers et al., 2011), where a large fraction eventually may become either agronomically inactive due to over-application (Withers et al., 2001; Potter et al., 2010; MacDonald et al., 2011; Lemaire et al., 2014), unsuitable for recycling due to contamination (Bolland and Barrow, 1988; Bolland et al., 1988; Chien et al., 2011), and harmful as a polluting agent of the physical environment and surface water bodies (Vance, 2001, McDowell and Catto, 2005; Schröder et al., 2011; Yang et al., 2012; Sharpley et al., 2013; King et al., 2015).

2.1.2 The Presence of Phosphorus in the Soil

In most natural ecosystems, the P cycle is essentially “closed” with minimal short-term losses or gains (Magid et al., 1996; Childers et al., 2011; Karl, 2014; Campbell et al., 2014). In these ecosystems, the amount and chemical nature of soil P are primarily determined by a combination of the major soil forming factors i.e.: parent material, climate, topography, soil biota and time (Adams and Walker, 1975; Walker and Syers, 1976; Vitousek and Sanford Jr, 1986; López-Hernández and Niño, 1993). Moreover, phosphorus transformation in soil occurs with both a dynamic biological cycle and a slow-moving pedologic pathway with the evolution of P forms being ultimately toward P sinks consisting of stable organic P and occluded P (Smeck, 1985; Bahr et al., 2014; Crews and Brookes, 2014; Barrow, 2015).

Accordingly, phosphorus availability is limited by the dissolution rates of inorganic primary and secondary P minerals (Crews, 1996; Shen et al., 2011) as well as different physico-chemical properties of the environment, crop system, and soil in which P adsorption and

desorption reactions occur (Barrow and Debnath, 2014; Giles et al., 2014; Barrow, 2015). These reactions are affected by prevailing temperature, soil organic matter, soil pH, and the type of mineral surfaces in contact with the solution (Oelkers and Valsami-Jones, 2008; Cao et al., 2012). From a crop production perspective, P geochemistry is of agronomic and environmental importance because on the one hand, P as one of the main nutritional elements is essential for sustaining terrestrial and aquatic plants and animals. On the other hand, excess P poses environmental risks because it may cause toxic heavy metal accumulation in soils and eutrophication as well as hypoxia – anoxia processes of surface water bodies (McDowell and Catto, 2005; MacDonald et al., 2011; Schindler, 2012; Yang et al., 2012). Thus one fundamental and intrinsic goal with field crop nutrition management is to optimize crop uptake of available P (Withers et al., 2014, 2015; Schoumans et al., 2015). As a consequence, the forms and dynamics of soil P can however be greatly affected by agricultural management practices which often involve dramatic changes in vegetation cover, biomass production, soil organic matter level and nutrient cycling in the ecosystem (Bünemann et al., 2006; Hanafiah et al., 2010; Childers et al., 2011; Waring et al., 2014; Fang et al., 2014).

2.1.3 Phosphorus Uptake by Plants

Plant roots take up nearly all P as either the primary or secondary orthophosphate anion H_2PO_4^- or HPO_4^{2-} , respectively (Fundora et al., 1980; Syers et al., 2008; Johnston and Syers, 2009; Shen et al., 2011). Primary orthophosphate is the form that is dominant in acid soils and is taken up about 10 times as readily as the secondary orthophosphate form (Johnston and Syers, 2009). At a soil pH of 7.0 there is approximately equal amounts of the two P forms and as the soil pH increases above pH 7.0, the secondary orthophosphate ion becomes the dominant form of available P (Schachtman et al., 1998). Because the concentrations of these ions in soils are in the micromolar range (0.1 – 10.0 μM) (Webb and Adeloju, 2013), high-affinity active transport systems are required for inorganic P (Pi) uptake against a steep chemical potential

gradient across the plasma membrane of root epidermal and cortical cells (Schachtman et al., 1998; Yadav et al., 2005; Richardson et al., 2009; Lucas et al., 2013).

Soil P is found in different pools, such as organic and mineral P. It has been suggested that 20 to 80% of P in soils is found in the organic form, of which phytic acid (inositol hexaphosphate) is usually a major component (Richardson, 1994; Schachtman et al., 1998; Raghothama, 1999; Shen et al., 2011). The remainder is found in the inorganic fraction containing 170 mineral forms of P (Holford, 1997). Pi usually accounts for 35% to 70% of total P in soil (Harrison, 1987). Primary P minerals including apatites, strengite, and variscite are very stable, and the release of available P from these minerals by weathering is generally too slow to meet the crop demand though direct application of rock phosphate has proved relatively efficient for crop growth in acidic soils (Black and Kempthorne, 1956; Nnadi and Haque, 1988; Mutuo et al., 1999; Oliveira Júnior et al., 2011).

In contrast, secondary P minerals including calcium (Ca), iron (Fe), and aluminium (Al) phosphates vary in their dissolution rates, depending on the size of mineral particles and soil pH (Oelkers and Valsami-Jones, 2008; Cao et al., 2012; Rutkowska et al., 2015). With increasing soil pH, solubility of Fe and Al phosphates increases but solubility of Ca phosphate decreases, except for pH values above 8 (Hinsinger, 2001). The P adsorbed on various clays and Al/Fe oxides can be released by desorption reactions (Bolan and Hedley, 1990; Kaleeswari and Subramanian, 2001; Roboredo and Coutinho, 2011; Barrow and Debnath, 2014; Barrow, 2015). All these P forms exist in complex equilibria, representing from very stable, sparingly available, to plant-available P pools such as labile P and solution P (Shen et al., 2011).

Noteworthy of mention is the ability of soil microbes in releasing immobile forms of P to the soil solution and also being responsible for the immobilization of P (Magid et al., 1996; Sumann et al., 1998; Jones, 1998; Rodriguez and Fraga, 1999; Makoi et al., 2010; Giles et al., 2014; Zhang et al., 2014). More soluble minerals such as K move through the soil via bulk flow and diffusion, but P is moved mainly by diffusion (Bhadoria et al., 1991; Schachtman et al.,

1998; Syers et al., 2008). Diffusion involves the movement of ions along a concentration gradient, i.e. from a higher to a lower concentration. Thus, when plant roots remove nutrient ions from the soil solution and the concentration is lowered relative to that in the bulk solution, a concentration gradient develops and nutrient ions move down this gradient (Bowling, 1981; Bolan, 1991; Raghothama, 1999). The extent of depletion at the root surface depends on the balance between the supply from the soil and the demand by the plant. If the absorbing power of the root is large, this creates a sink to which nutrients diffuse (Richardson et al., 2009).

The concentration of nutrients at the root surface depends on the initial state of the system and the balance between rate of uptake into the plant and rate of replenishment from the surrounding soil (Balwin, 1975; Itoh and Barber, 1983; Shen et al., 2011). The amount of P required at the root surface depends on the depletion profile that develops with time. The shape of this profile will depend on the balance between P uptake by roots, the rate at which P is replenished in the soil solution, and the mobility of the phosphate ions by diffusion (Gerke et al., 1994; Syers et al., 2008). Accordingly, nutrient uptake by plants growing in soils depends on the configuration and growth rate of the roots system (Sulpice et al., 2014), the nutrient uptake characteristics per unit of root, and the nutrient supply characteristics of the soil (Itoh and Barber, 1983; Burkitt et al., 2001; Hinsinger et al., 2011).

Changes in plant demand for nutrients are usually linked with changes in internal concentration and often result from alterations in the supply of nutrients to the plant (Burns, 1980). Since the rate of diffusion of P is slow, high plant uptake rates create a zone around the root that is depleted of P (Richardson et al., 2009). Although it is readily mobilized in plants, availability in the soil solution is usually low since much of the phosphorus is tied up in poorly soluble compounds, making the best pH range for phosphorus uptake between pH 6.5 to 7.5 (Peterson and Rolfe, 1982; Clarkson et al., 1992; Tu and Ma, 2003).

While some studies have reported that chemical P fertilizer application only slightly increases the organic P (Po) fractions in tropical croplands (Tiessen et al., 1984; Oberson et al.,

2001; Negassa and Leinweber, 2009), the increase in Po fractions should be important for maintaining the P status in low P input tropical croplands (Zibilske et al., 2002, MacDonald et al., 2011; López-Arredondo et al., 2014). The difficulty in increasing Po fractions, regardless of chemical P fertilization, is considered to be due to the rapid mineralization of SOM in the tropics (Negassa and Leinweber, 2009). Phosphorus deficiency in soils is caused by a general low total P content of the soil or low bioavailability of P (Ramaekers et al., 2010). Because P is highly reactive, it is readily converted to other, less soluble forms (Schachtman et al., 1998; Daroub et al., 2000; Hinsinger, 2001; Yang and Post, 2011; Smith et al., 2011). The particular forms that are created depend on other soil factors such as the soil pH, temperature, moisture, and other mineralogical elements (Stewart and Tiessen, 1987; Pant and Reddy, 2001; Jaggi et al., 2005).

2.1.4 Phosphorus Uptake Efficiency of Plants

The uptake of P poses a problem for plants, since the concentration of this mineral in the soil solution is generally low but plant requirements are high (Mengel and Kirkby, 2001). The form of P most readily accessed by plants is Pi, the concentration of which rarely exceeds 10 μM in soil solutions (Bielecki, 1973; Raghothama, 1999). Decreases in internal concentration tend to increase the concentration gradient across the root boundary and increase the size of I_{max} , which is defined as the maximum rate of nutrient uptake per unit surface area of root, thus enabling more nutrients to be absorbed at a given external concentration (Jungk and Claassen, 1997; Darrah and Roose, 2007). As a consequence, when an adequate nutrient supply is re-established to deficient plants, inflow rates are increased in relation to the initial degree of deficiency (Burns, 1980; Jungk et al., 1990).

Thus, phosphorus-use efficiency depends on soil P status (Rao et al., 1997; Horst et al., 2001; Grant et al., 2005), but measurements of P recovery also depend on crop yield, which can be affected by many factors, including other inputs like nitrogen fertilizers (Aguilar and

Van Diest, 1981; Syers et al., 2008). Therefore, plants must have specialized transporters at the root/soil interface for extraction of Pi from solutions of micromolar concentrations (Schachtman et al., 1998; Yadav et al., 2005; Richardson et al., 2009; Lucas et al., 2013), as well as other mechanisms for transporting Pi across membranes between intracellular compartments (Sulpice et al., 2014; Zhang et al., 2014), where the concentrations of Pi may be 1000-fold higher than in the external solution (Shen et al., 2011). There must also be efflux systems that play a critical role in the redistribution of this precious resource when soil phosphorus content is no longer available or adequate (Raghothama, 1999; Nacry et al., 2005) and as such phosphate (PO_4^{3-}) availability has a strong effect on root system architecture, which may significantly differ from that of other ions (Niu et al., 2012; Péret et al., 2015).

Nacry et al., (2005) indicated that low P induces a biphasic response with, first, an increase in lateral root growth with no effect on primary root elongation, and, later on, a general negative effect on growth of all roots. When the supply of Pi is limited, plants grow more roots, increase the rate of uptake by roots from the soil, re-translocate Pi from older leaves, and deplete the vacuolar stores of Pi (Föhse et al., 1988; Koide, 1991; Gahoonia and Nielsen, 2004). Conversely, when plants have an adequate supply of Pi and are absorbing it at rates that exceed demand, a number of processes act to prevent the accumulation of toxic Pi concentrations (Schachtman et al., 1998). These processes include the conversion of Pi into organic storage compounds (e.g. phytic acid), a reduction in the Pi uptake rate from the outside solution (Raghothama, 1999), and Pi loss by efflux, which can be between 8 and 70% of the influx (Bielecki, 1973). A critical concentration of readily available P must therefore be maintained in order to obtain good crop yields. Crop uptake is generally only 10–20% of the P fertilizer applied in the first year, but a substantial part of applied P accumulates in the soil as residual P (Wolf et al., 1987; Syers et al., 2008). According to Probert (1985), the residual P is the difference between P inputs applied in the form of mineral fertilizer, manure, weathering, and deposition, and P outputs which is generally lost in the form of withdrawal of P in harvested

products, and P loss by runoff or erosion. The residual value of P refers to P that can be taken up by crops for many years, depending on soil P fixation capacity (Takahashi and Anwar, 2007; Cao et al., 2012), soil pH (Bolan and Hedley, 1990; Rajan et al., 1991; Mengel and Kirkby, 2001), crop species (Sánchez and Salinas, 1981; Haynes, 1992, Shaw, 2009) and P application time (Cabala-Rosand and Wild, 1982; McDowell and Catto, 2005; Nelson and Janke, 2007; Bruulsema, 2009).

Plant species differ in their P efficiency that is, the P content in soil needed to reach their maximum yield. The differences in external P requirements can be attributed to either a lower internal P requirement for optimum growth or higher uptake efficiency of the plant which is determined by both root-shoot ratio and absorption rate per unit of root regarded as the influx (Föhse et al., 1988; Jungk et al., 1990). Generally, plant species of low efficiency such as onion, tomato and bean tend to have low influx rates and low root-shoot ratios, (Jungk, 1987; Föhse et al., 1988), whereas plant species of medium to high efficiency tend to have either high influx rates such as rapeseed and spinach, or high root-shoot ratios such as ryegrass and wheat (Jungk, 1987; Föhse et al., 1988; Grant et al., 2001). Therefore P uptake not only depends on the amount of available P in the soil but also on plant properties (Föhse et al., 1988; Wissuwa, 2003; Wasaki et al., 2003; Nacry et al., 2005). To this end, the importance of root architecture in plant productivity stems from the fact that many soil resources are unevenly distributed, or are subject to localized depletion, so that the spatial deployment of the root system will in large measure determine the ability of a plant to exploit those resources (Keerthisinghe et al., 1998; Wissuwa, 2003; Johnston and Syers, 2009; Niu et al., 2012; Péret et al., 2015).

To sustain growth in such limiting conditions, plants have evolved a number of developmental and metabolic responses to adapt both to their internal P_i status and to the external soil P_i availability. These responses include but are not limited to changes in root morphology and architecture (Trubat et al., 2006; Ling et al., 2008; Insalud et al., 2006; Xie and Yu, 2003; Gaxiola et al., 2011), and increases in the synthesis and secretion of organic

acids into the rhizosphere (Koide, 1991; Jones, 1998; Raghothama, 1999; Dakora and Phillips, 2002; Gahoonia and Nielsen, 2004) which enhances the utilization of Pi from insoluble inorganic compounds.

In soil the major limiting steps in the acquisition of P by plants are the mobilization and diffusion of P to the roots, and plants have the facultative capacity to either initiate or cease formation of proteoid roots which is linked to the Pi concentration in the plant (Johnson et al., 1994, 1996; Keerthisinghe et al., 1998; Wasaki et al., 2003). These specialized roots exude high amounts of organic acids (up to 23% of net photosynthesis), which acidify the soil and chelate metal ions around the roots, resulting in the mobilization of P and some micronutrients (Johnson et al., 1994; 1996; Jones, 1998). According to Gahoonia and Nielsen (2004) the presence of abundant root hairs expands the effective root surface area and thereby P uptake. Secondly, root hair release of citrate and acid phosphatase (APase) may enhance the transformation of Po into Pi, and utilisation of organic soil P within the root hair zone (Goldstein et al., 1988; Wasaki et al., 2003). Consequently, due to the synchronised and localised liberation of P and its uptake, the acquisition efficiency is ultimately enhanced.

Notwithstanding, P deficiency is more critical in highly weathered soils of the tropics and subtropics (Sánchez and Salinas, 1981; Cassman et al., 1993; Fageria and Baligar, 1997; Linquist et al., 1997; George et al., 2006), as well as calcareous/alkaline soils of the Mediterranean basin (Salih et al., 1989; Marschner, 1995; Ehteshami, 2011). As such plant root geometry and morphology are important for maximizing P uptake, because root systems that have higher ratios of surface area to volume will more effectively explore a larger volume of soil (Koide, 1991; Lynch, 1995; Kochian, 2012). For this reason the soil microbial community has to play an even more important role in nutrient cycling and availability (Acosta-Martinez et al., 2007; Steiner et al., 2008) and soil microbes such as mycorrhizae are also important for plant P acquisition, since fungal hyphae greatly increase the volume of soil that plant roots explore (Smith and Read, 1997; Feddermann et al., 2010; Heydari, 2013).

2.2 Pyroligneous Acid

2.2.1 Pyrolysis of Biomass

Biomass as a term is used to describe any organic matter (excluding fossil fuels), in which the energy of sunlight is stored in chemical bonds (Babu, 2008). Breaking these bonds by digestion, combustion or decomposition releases the stored chemical energy (Iliopoulou et al., 2007). Furthermore, biomass is the only renewable energy source of carbon which is able to be converted into convenient solid, liquid and gaseous fuels (Demirbas, 2001). Pyrolysis is the fundamental chemical reaction process that is the precursor of both the gasification and combustion of solid fuels, and is simply defined as the chemical changes occurring when heat is applied to a material in the absence of oxygen (Maschio et al., 1992; Iliopoulou et al., 2007; Babu, 2008; Bruun et al., 2011).

Pyrolysis liquids are formed by rapidly and simultaneously depolymerizing and fragmenting cellulose, hemicellulose, and lignin with a rapid increase in temperature (Mohan et al., 2006; Boateng et al., 2007; Czernik et al., 2007; Bruun et al., 2011). The process may be of particular interest in Less Developed Countries (LDCs) that have no indigenous fossil fuels but do have extensive waste biomass resources accumulating from logging for timber and forest exploitation activities, for example, the African Caribbean and Pacific (ACP) countries.

By changing the operating conditions during pyrolysis, modifications of the actual course of reactions can be achieved, resulting in modifications of the final product (Maschio et al., 1992; Boateng et al., 2007; Spokas et al., 2011). The kinetics of the pyrolysis process are influenced by the values of the main process parameters such as temperature, solid residence time, composition of feedstock, particle size and heating rate (Maschio et al., 1992; Babu, 2008; Ratanapisit et al., 2009; Bruun et al., 2011). More importantly and based on the growing concerns with regards to environmental stewardship (Twidell, 1995; Babu, 2008; Sheth and Babu, 2010), waste biomass gasification/combustion can be considered as CO₂ neutral (Collot et al., 1999; Balat, 2006; Iliopoulou et al., 2007; Babu, 2008; Bruun et al., 2011) as CO₂

released during biomass conversion has been previously adsorbed from the atmosphere by plants during photosynthesis (Twidell, 1995; Derimbas, 2001; Balat, 2006).

In addition, the thermo-conversion of biomass is one of the leading near-term options for renewable hydrogen production (Garcia et al., 2000; Rioche et al., 2005; Czernik et al., 2007) as opposed to the current trends of hydrogen production which involves the catalytic steam reforming of methane, light hydrocarbons, and naphtha as well as water electrolysis, partial oxidation of heavy oil residues, or coal gasification. However, these established industrial processes are associated with huge energy consumption and high CO₂ emissions (Wang et al., 2012b). To this effect although hydrogen is recognized as a clean fuel and energy carrier (Rioche et al., 2005) the real environmental benefits will be linked to the ability to produce hydrogen from renewable sources with no net production of greenhouse gases.

Depending on the operating conditions, the pyrolysis process can be divided into three subclasses which are conventional pyrolysis, with the most valuable product being charcoal (Maschio et al., 1992; Ratanapisit et al., 2009), fast pyrolysis, with the main product being a medium British Thermal Unit (BTU) gas rich in hydrogen and carbon monoxide (Maschio et al., 1992), and flash pyrolysis, which is usually carried out at or near atmospheric pressure (Scott et al., 1988), where organo oxygen compounds of low molecular weight are of interest as well as insoluble organics which are mainly aromatics of high molecular weight (Nokkosmäki et al., 2000; Boateng et al., 2007; Bilehal et al., 2012).

According to Scott and Piskorz (1982) and Antal et al., (1985) high heating rates which are employed in flash pyrolysis minimizes the yields of solid pyrolysis products and maximizes those of liquid products. In addition, the atmospheric flash pyrolysis process to produce organic liquids from biomass appears to have wide applicability (Scott et al., 1985; Balat, 2011) whereby the liquid product may be used as a source of low grade fuel directly or may be upgraded to higher quality liquid fuels, or used in other industries such as agriculture.

A number of researchers have highlighted that temperature as the most important factor for the product distribution of pyrolysis (Nakai et al., 2007; Bech et al., 2009; Rakmai, 2009; Othaman et al., 2009; Wei et al., 2010; Ibrahim et al., 2012). Production of liquid goods is maximized at temperatures between 625 K (352°C) and 725 K (452 °C). At higher temperatures, the rather large molecules present in the liquid and residual solids are broken down to produce smaller molecules that enrich the gaseous fraction (Piskorz et al., 2000; Hooi, 2012). For maximum yield of liquid products resulting from biomass pyrolysis, a low temperature, high heating rate, and short gas residence time process would be required (Mohan et al., 2006; Acikgoz and Kochar, 2007; Ratanapisit et al., 2009; Ibrahim et al., 2012; Pattiya et al., 2012). In addition, some reseachers (Bridgwater et al., 1999; Silva et al., 2005; Babu, 2008; Ratanapisit et al., 2009) further reported on the effect of pressure on the yield components and solubility of pyroligenous acid.

Effectively, pyrolysis of biomass is a promising route for the production of useful solid (char), liquid (bio-oil/tar), and gaseous products for the agricultural industry (Doran, 1932; White et al., 2011; Tiilikkala et al., 2010; Kang et al., 2012; Mmojieje and Hornung, 2015) based on globally changing policies and integrated pest management programs (IPM) aimed at reducing pesticide risks on the environment and human health, as well as policies on P nutrient recycling (ESPP, 2015). In addition to being alternate sources of energy (Boateng et al., 2007; Sheth and Babu, 2009) these products are of interest as they are also possible alternate sources of plant nutrients (Yoshimura et al., 1995; Mu et al., 2003; Kadota and Niimi, 2004; Souza et al., 2012). Thus, the development of alternative sources for plant nutritions/soil amendments has drawn great attention from researchers since the 1980's and upgrading of crude bio-oil from pyrolysis of biomass to prepare plant nutrients of high quality has now become an area attracting more research and development efforts (Kadota and Niimi, 2004; Jun et al., 2006; Zulkarami et al., 2011; Lashari et al., 2013; Togoro et al., 2014; Benzon et al., 2015).

2.2.2 Use of Pyroligneous Acid in Agriculture

With regards to pyroligneous acid (PLA) Steiner et al., (2008) highlighted that this technique originated in Japan and has been used for centuries whilst Tiilikkala et al., (2010) accounted that archeological studies have found that pyrolysis liquids were already used in the middle palaeolithic time of the Neanderthal. PLA has been used to increase crop productivity and quality (Jun et al., 2006; Rico et al, 2007; Schnitzer et al., 2010; Payamara, 2011; Yang et al., 2014b; Tsado et al., 2014a,b; Matthew and Zakaria, 2015), breaking seed dormancy and improving germination (Ratanapisit et al., 2009; da Silveira, 2010), and to combat diseases and pests in agriculture (Doran, 1932; Chalermisan and Peerapan, 2009; Tiilikkala et al., 2010; Wei et al., 2010; Mmojieje and Hornung, 2015), and preservation of wood (Nakai et al., 2007; Rakmai, 2009) attributed to the acetic acid content exhibiting termicidal activity (Yatagai, 2002). Pyroligneous acid has also been used as a sterilizing agent, deodorizer, antimicrobial, antioxidative and growth promoting agent (Mohan et al., 2006; Loo et al., 2008; Rungruang and Junyapoon, 2010; Kim et al., 2011) with beneficial effects reported on ornamental plants (Kadota and Niimi, 2004) and areca bamboo palm (Wanderley et al., 2012).

Various studies have shown the beneficial effects of pyroligneous extract applied to soil as an organic fertilizer for the growing of food crops in combination with charcoal (Zanetti et al., 2003; Kang et al., 2012; Lashari et al., 2013), chemical fertilizers, compost as well as animal manures (Steiner et al., 2008) or as a LMWOA soil amendment input (Tsado et al., 2014a,b; Togoro et al., 2014). Of special interest and based on the current global awareness of increased environmental responsibility, Schauer et al., (2001); Hays et al., (2002), and Lee et al., (2005) reported on the measurements of organic compound emission rates for volatile organic compounds (VOC), from residential fireplace combustion of wood during winter months in temperate urban locations. These authors' results have highlighted that emissions from the fireplace combustion of wood have been shown to be major contributors to air pollution and the ambient concentrations of benzene, ethene, and acetylene.

To this end the condensation of wood smoke into pyroligneous acid for agricultural purposes is even more significant within the context of environmental sustainability as it holistically embraces the principle of recycle, reuse and reduce (Nakai et al., 2007; Kang et al., 2012; Matthew and Zakaria, 2015; Withers et al., 2015). Specifically, Spokas et al., (2011) reported that a number of studies have shown that low VOC concentrations ($4\text{-}10\ \mu\text{g m}^{-3}$) can have a significant impact on the wellbeing of plants, impacting seed germination, herbivore resistance, invasive plant responses, and nutrient uptake. In addition, VOCs also control the ability of soil micro- and macro-organisms to participate in abiotic and biotic reactions known to influence soil quality (Insam and Seewald, 2010).

Given growing economic perspectives and technical development, PLA may potentially provide an additional option in P management as many artificial fertilizers which are manufactured and utilized extensively in commercial farm production enterprises, not only impose heavy loads and pollution on the environment but also threatens health (Jun et al., 2006; Wititsiri, 2011). In addition, the cycle for planting vegetables is short and the use of fertilizers has a discernable effect on productivity, especially in highly weathered tropical soils.

Moreover, the long-term application of fertilizers exposes the following problems such as exhaustion of soil organic matter, lower conservation of water and nutrition, deterioration of the soil structure and heavy losses of soil (Tomer and Burkart, 2003; Easton and Petrovic, 2004; Meng et al., 2005; Manna et al., 2005; Steiner et al., 2007). Additionally, the incidence of disease and insect pests increases with excessive continuous-cropping in the pursuit of high yields reflected by the higher the level of vegetable production, and the larger the amount of fertilizer used (Yardim and Edwards, 2003; Lu et al., 2007). Hence, excessive fertilization not only pollutes the soil, water and air but may also retain significant nutrient residues in vegetables, which decreases the quality and security of food supply (Lairon, 2010).

2.2.3 Chemical Composition of Pyroligneous Acid

The synonyms for pyroligneous acid include pyrolysis oils, pyrolysis liquids, wood liquids, wood vinegar, liquid smoke, liquid wood, bio-oil, bio-crude oil and wood distillates (Nakai et al., 2007; Loo et al., 2008). In Japan pyroligneous acid is known as Mokusakueki (Tiilikkala et al., 2010; Dou et al., 2012; Bilehal et al., 2012). It is a complex mixture of water (0.8 to 0.9 dm³ water), acetic acid, methanol, acetone, formic acid, guaiacols, catecols, syringols, vanillins, furan carboxaldehydes, isoeugenol, pyrone and more than 200 organic compounds including phenolic compounds, which are pyrolytic products of lignin and hemicelluloses (Fischer and Bienkowski, 1999; Mohan et al., 2006; Jun et al., 2006; Rakmai, 2009; Wei et al., 2010; Souza et al., 2012; Bilehal et al., 2012; Yang et al., 2014b; Matthew and Zakaria, 2015).

Accordingly, these compounds belong to many different chemical classes: aldehydes; ketones; alcohols; acids; esters; furan and pyran derivatives; phenolic derivatives; hydrocarbons; nitrogen compounds (Sakasegawa and Yatagai, 2005; Nakai et al., 2007; Loo et al., 2008; Ratanapisit et al., 2009; Mun and Ku, 2010). Notwithstanding, the chemical components of wood vinegar varies depending on the wood specie used in the production process (Nakai et al., 2007). According to Ratanapisit et al., (2009) the chemicals found in wood vinegar are attributed to the fact that wood degradation depends on temperature such that hemicellulose will start to degrade at temperatures of (373-533 K (100-260°C), then followed by the thermal degradation of cellulose at temperatures of 513-623 K (240-350°C), with lignin changing at temperatures of 553-773 K (280-500°C). From an analytical point, condensate PLA is high in low-molecular weight acids (formic and acetic), alcohols (methanol) and aldehydes (formaldehyde and acetaldehyde) (Focht, 1999; Diebold, 2000). Some of the largest constituents are acetic acid (0.5–12.0% by weight of total condensate), formic acid (0.3–9.1%), methanol (0.4–2.4%), formaldehyde (0.1–3.3%), acetaldehyde (0.1–8.5%), and hydroxyacetaldehyde (0.9–13.0%) (Diebold, 2000; Bilehal et al., 2012).

It has been reported that when the concentration of PLA applied is high, formaldehyde and acids can serve as biocides (Doran, 1932; Mmojieje and Hornung, 2015). Similarly, Hagner et al., (2010) who worked on the effect of PLA on soil organisms and plants indicated that phenols to be one of the most promising group of compounds in PLA acting as biocontrol agents, but various volatile compounds may also play a role. However, at low concentrations the alcohols, acids, and aldehydes contained within PLA may serve as carbon and energy substrates for soil microorganisms, which can be consumed by strains of prototrophic bacteria occurring in the soil (Focht, 1999). In addition, pyroligneous acid is rich in nutritional components (Tsuzuki et al., 1989) that attracts microbes including bacteria and fungus to roots of plants where symbiosis occurs. The positive effects of bacterial and mycorrhizal symbiosis can be attributed to an improved nutritional state (due to N supplied by bacteria and P by mycorrhizae), which in turn leads to increased photosynthetic rates and improved plant growth (Kaschuk et al., 2009).

2.2.4 Effects of Pyroligneous Acid on Soil Microbial Activity

The effect of pyroligneous acid (PLA) application on the alteration of soil microbial activity has received some level of attention in recent years (Ishii and Kadoya, 1994; Fischer and Bienkowski, 1999; Focht, 1999; Yamato et al., 2006; Steiner et al., 2008). These authors generally concluded that the application of pyroligneous acid to the soil is a practical method to improve soil properties and to foster the development of symbiotic microorganisms including vesicular-arbuscular mycorrhiza (VAM) fungi which improves mineral nutrition of the host by increasing P uptake from a P deficient soil. Of particular interest, Focht (1999), Fischer and Bienkowski (1999), and Uvarov (2000) reported that pyroligneous acid clearly intensifies respiratory metabolism of the soil whereby the intensification of respiration is higher in the soil earlier exposed to substances contained in the smoke, whereas lower in the soil not exposed to smoke, which may be indicative of adaptation changes. These authors concluded

that the respiratory quotient is higher in the soil permanently exposed to the smoke, an indication of anthropogenic disturbance resulting from organic factors. Similar conclusions were made by Steiner et al., (2008). However, Tsuzuki et al., (1989) and Kadota and Niimi (2004) reported on optimal rates of application which might be hormonal in action and dependent on crop species. According to Kadota and Niimi, (2004), the apparent high alkalinity of charcoal combined with PLA can induce alkaline pH increase and thus potentially mask the effect of PLA acting solely.

Furthermore, it has been reported that the condensates from smoke contain only small amounts of inhibitory agents but contains easily degradable substances which could be utilized by the microbes for their metabolism (Steiner et al., 2008). Hagner et al., (2010) reported similar results in which the application of birch tar oil (a mixture of PLA and birch tar) at concentrations between 500-1360 L ha⁻¹ had no negative effects on soil microbes, but instead showed a positive effect on microbial activity immediately after application, suggesting that easily utilized substances in PLA were rapidly consumed by soil microbes.

2.3 Rock Phosphate

2.3.1 Factors Affecting Agronomic Performance of Rock Phosphate

Most of the world's phosphate fertilizers are produced from rock phosphate (RP) reserves and almost all of these resources contain some form of the mineral apatite (Black and Kempthorne, 1956; Fundora et al., 1980; Bolan and Hedley, 1989, 1990; Kaleeswari and Subramanian, 2001; Kumari and Phogat, 2008) along with other accessory minerals such as quartz, silicates, carbonates, sulphates, and sesquioxides (Fundora et al., 1980; Kaleeswari and Subramanian, 2001; Kumari and Phogat, 2008). Soil acidity with associated Al toxicity, as well as P and Ca deficiencies, are common growth-limiting factors in highly leached tropical soils (Bolland et al., 1988; Zapata and Axmann, 1995; Chien and Menon, 1995; Solomon et al., 2002; Akande et al., 2005; Takahashi and Anwar, 2007; Akande et al., 2010).

Typically, low crop yields occur on strongly nutrient depleted acid Oxisols and Ultisols (Sánchez and Salinas 1981; Cassman et al., 1993; Fageria and Baligar, 1997; Linquist et al., 1997; Mutuo et al., 1999; George et al., 2006; Oliveira Júnior et al., 2011). These soils often have a strong phosphate fixation character by Al- and Fe-oxides (Solomon et al., 2002; Takahashi and Anwar, 2007; Chien et al., 2011) which leads to low nutrient availability or in forms not accessible to roots (Stewart and Tiessen, 1987; Schachtman et al., 1998; Solomon et al., 2002; Shen et al., 2004; Rutkowska et al., 2015), as well as low efficiency use of water-soluble P fertilizers such as triple superphosphate (TSP) or diammonium phosphate (DAP) by crops (Kumari and Phogat, 2008; Chien et al., 2010; Major et al., 2010).

Inorganic P sources applied to soil range from processed rock phosphate to ground rock phosphate and slightly modified forms of rock phosphate (Chien and Hammond, 1989; Chien et al., 1990; Casanova, 1995; Jama and van Straaten, 2006, Biswas, 2011). The use of commercial P fertilizers is often not cost effective on strongly depleted weathered soils of the tropics (Chien and Menon, 1995; Kpombrekou-A and Tabatabai, 2003; Akande et al., 2005; Jama and van Straaten, 2006), and is associated with low efficiency of use (Chien et al., 2010; Major et al., 2010) as the phosphate ions are easily adsorbed by aluminium and iron oxide minerals (Hinsinger, 2001; Dib et al., 2006; Oelkers and Valsami-Jones, 2008; Cao et al., 2012; Barrow, 2015). Thus in essence, the P of phosphate fertilisers changes in the soil to non-soluble compounds and becomes unavailable and cannot be absorbed by plants (Stewart and Tiessen, 1987; Pant and Reddy, 2001; Jaggi et al., 2005; Dib et al., 2006; Ramaekers et al., 2010). The dissolution of rock phosphate can be increased by increasing the supply of protons (H^+) and by continuous removal of the dissolved products, calcium and phosphorus from the zone of dissolution (Bolan and Hedley, 1990; Bolan et al., 1997; Kaleeswari and Subramanian, 2001; Mengel and Kirkby, 2001; Nying and Robinson, 2006; Roboredo and Coutinho, 2011).

Essentially, the dissolution of rock phosphate is enhanced by low pH, high cation exchange capacity and high capacity for P sorption as well as the maintenance of low levels of

solution P (Smyth and Sánchez, 1982; Cabala-Rosand and Wild, 1982; Rajan et al., 1991). Conversely, low pH may reduce plant growth by several mechanisms especially by increasing Al toxicity and this may confound the influence of pH on rock phosphate dissolution and availability (Rajan et al., 1991). Generally, surface adsorption and mineral precipitation processes contribute to rock phosphate binding to the solid phase from which it may be released subsequently (Delgado and Torrent, 2000; Du et al., 2013). Thus the rate of dissolution of rock phosphate in a given soil is determined by its chemical composition which includes apatite lattice composition, the type of accessory minerals and particle size (Lehr and McClellan, 1972; Chien, 1977a,b; Anderson et al., 1984; Kaleeswari and Subramanian, 2001).

On the other hand, in calcareous soils, soil inorganic P represents the dominant component of the soil P pool (Wang et al., 2010), in which calcite (CaCO_3), dolomite ($(\text{CaMgCO}_3)_2$) and aragonite (CaCO_3) are dominant carbonates (St. Arnaud and Herbillon, 1973; Dib et al., 2006). Hence, carbonate clay contributes to P sorption when it is foremost in the soil, and when large amounts of P are applied (Zhou and Li, 2001). In essence, calcareous soils contain relatively large amounts of inorganic P, but because of P-fixation relatively little is available for crop use (Salih et al., 1989; Marschner, 1995).

Jiang and Gu (1989) highlighted that the characteristics of Ca-P in calcareous soils can be summarized by:



This reaction takes place mostly in the soil parent material. In these soils, reactions with phosphate takes place giving rise to compounds rich in Ca or Mg (Marion and Babcock, 1977; Wang et al., 2010; Al-Ouds, 2011). In essence P efficiency can be enhanced by increasing P solubility in soil solution or by reducing P fixation in soils (Hua et al., 2008; Du et al., 2013). Thus, the addition of organic compounds such as humic and fulvic acids to soil may increase the efficiency of applied P fertilizers in calcareous soils by increasing the fraction of applied P that remains as highly soluble Ca phosphates (Fixen et al., 1983; Havlin and

Westfall, 1984; Bangar et al., 1985; Al-Ouds, 2011; Du et al., 2013). In addition, a number of studies have shown that root infection with VAM fungi can enhance the uptake of P by plant roots by providing a larger absorbing surface for uptake of P due to translocation via external hyphae to the host plant root (Kothari et al., 1990a,b; Li et al., 1991; Smith and Read, 1997; Richardson, 2007; Jansa et al., 2003; Marschner et al., 2011; Ren et al., 2013; Heydari, 2013; Khalil and Yousef, 2014).

Of equal importance Kpombekou-A and Tabatabai (2003) highlighted that the use of naturally occurring low-molecular weight organic acids (LMWOAs) represents an alternative perspective in rock phosphate research. However, Jones et al., (2011) mentioned that most soils frequently contain enough native P for crop production, irrespective that soils may also contain LMWOAs in the rhizosphere that are used by plants and microorganisms for P-nutrient acquisition. Nonetheless, it is generally accepted that LMWOAs application to the soil render soluble P nutrients through dissolution and anion exchange (Jones and Darrah, 1994).

The choice between soluble P fertilizers and RP as a source of P for crops depends on the relative agronomic effectiveness (RAE) to include residual effects (Yeates and Clarke, 1993; Zapata and Axmann, 1995; Casanova, 1995; Akande et al., 2005) and cost (Sánchez and Salinas 1981; Maene, 2003; Jama and van Straaten, 2006; Koppelaar and Weikard, 2013). According to Chien and Menon (1995), Kaleeswari and Subramanian (2001) and Ehteshami (2011), the fertilizer effectiveness of rock phosphate depends on factors relating to RP itself to include mineralogy, chemical reactivity and rate of application, soil factors such as pH, P and Ca status and the mycorrhizal status of plants (Ghosal and Chackraborty, 2012; Heydari, 2013).

To this end, Chien and Hammond (1978), Chien et al., (1990), Asomaning et al., (2006), Chien et al., (2010), and Oviasogie and Uzoekwe (2011) all highlighted that the most informative property of rock phosphate in relation to its agronomic performance is solubility, which is normally measured by neutral ammonium citrate, 2% citric acid, or 2% formic acid. Thus in general, the solubility of rock phosphate increases as carbonate substitution for

phosphate in the apatite structure increases (Chien and Hammond 1978; Chien and Menon, 1995; Kaleeswari and Subramanian, 2001) and as such the degree of isomorphous substitution in the apatite structure is the key factor in determining the chemical reactivity of rock phosphate (Chien, 1977c; Bigi et al., 2007) as well as contact time with soil (Fardeau et al., 1988).

Field studies conducted by Bolland and Barrow (1988) showed that the relative effectiveness of rock phosphate compared with superphosphate on a sandy soil with low buffering capacity for phosphate and for pH decreased as the level of application of the RP increased. These authors reported that simulation studies showed that this behaviour is to be expected when RP is finely ground and when the P buffering capacity of the soil is low. It also occurs at high levels of application when the buffering capacity is much higher (Bolland and Barrow, 1988). However, Mutuo et al., (1999) and Jama and van Straaten (2006) reported that on-farm trials in P-deficient soils in western Kenya demonstrated that local “Minjingu” RP to be as effective as triple superphosphate (TSP, 20% P) at equal P rates, with benefits most pronounced with the integration of agro-forestry technologies (Jama and van Straaten, 2006).

Nonetheless, in some situations rock phosphate may be unable to support the same maximum yield as water-soluble P fertilisers due to inadequate dissolution of RP even at high rates of application (Kanabo and Gilkes, 1988). Despite that, direct application of grounded RP has been proven to be beneficial to crops on acid soils (Black and Kempthorne, 1956; Nnadi and Haque, 1988) however there are only a limited number of climatic and edaphic situations in which rock phosphate will be sufficiently reactive for use as a direct application fertilizer, especially for fast growing annual crops (Yeates and Clarke, 1993). To this end, Black and Kempthorne (1956) emphasised that natural rock phosphate may not be as effective in calcareous or alkaline soils as demonstrated by Ehteshami (2011) because a proportion of these fertilizers become unavailable for plants. The availability of nutrients contained in natural minerals depends on many factors, to include soil types (Jobbágy and Jackson, 2001), soil reaction pH (Barak et al., 1997), soil solution composition (Nakamaru et al., 2000) plant species

(Sánchez and Salinas 1981; Habib et al., 1999; Montenegro and Zapata, 2002) and types and ratios of micro organisms (Leyval and Joner, 2001; Landeweert et al., 2001).

2.3.2 Rock Factors

2.3.2.1 Type of Rock Phosphate

Four types of RP minerals have been classified: carbonate apatite, fluoro apatite, hydroxy apatite, and sulpho apatite (Abouzeid, 2008; Kumari and Phogat, 2008). Pure fluor-apatite contains 42% P_2O_5 (Fundora et al., 1980), and francolite, the carbonate-substituted form of apatite, may contain 34% P_2O_5 (Black and Kempthorne, 1956): (1) Fluor-apatite ($Ca_{10}(PO_4)_6F_2$), is found mainly in igneous and metamorphic environments, for example, in carbonatites, and mica-pyroxenites (Baturin and Bezrukov, 1979; Abouzeid, 2008); (2) Hydroxy-apatite ($Ca_{10}(PO_4)_6(OH)_2$), is found in igneous, metamorphic environments but also in biogenic deposits, e.g. in bone deposits (Abouzeid, 2008; Warren et al., 2009), (3) Carbonate-hydroxy-apatites ($Ca_{10}(PO_4,CO_3)_6(OH)_2$), found mainly on islands and in caves, as part of bird and bat excrements, guano (Abouzeid, 2008), and (4) Francolite ($Ca_{10-x-yNaxMgy}(PO_4)_{6-z}(CO_3)_zF_{0.4z}F_2$), a complex, carbonate-substituted apatite is mainly found in marine environments, and, to a much smaller extent, also in weathering environments (Benmore et al., 1983; Abouzeid, 2008).

Not all the RP resources are readily plant-available and agronomically effective when applied directly to the soil (Bolland et al., 1988; Kumari and Phogat, 2008). In addition, Hammond et al., (1986b) reported that the effectiveness of rock phosphate relative to soluble P fertilizer may be less on soils with high P retention capacity than on soils with the same pH but with lower P retention capacity for short-term crops such as maize. The apatites of igneous and metamorphic origin are generally regarded as less reactive because of their well developed crystalline form (Leon et al., 1986; Kaleeswari and Subramanian, 2001; Kumari and Phogat, 2008) whereas the apatites of sedimentary rock deposits are soft minerals possessing micro-

crystalline structure and are of major commercial importance for direct application in the soil (Fundora et al., 1980; Narayanasamy and Biswas, 1998; Kaleeswari and Subramanian, 2001).

2.3.2.2 Reactivity of Rock Phosphate

Naturally occurring rock phosphate differ widely in their mineralogy and chemistry. The chemical reactivity or solubility of rock phosphate is a measure of the RP's ability to release P for plant uptake. Rajan et al., (1996) defined reactivity as “the distribution of RP properties that establishes the speed of dissolution of the RP in a particular soil under specified field circumstances”. To this effect, RPs with high relative reactivity are best suited for direct application to acid soils with low Ca and P concentrations (Bolan and Hedley, 1989; Kumari and Phogat, 2008). However, according to Hughes and Gilkes (1994) in addition to mineralogy, soil texture is also important in determining the effectiveness of PR application.

Furthermore, RPs in which greater than 65–70% of their total P content is soluble in 2% formic acid are likely to be highly reactive and therefore agronomically effective P fertilisers for direct application to appropriate soils in suitable environments (Gilkes and Bolland, 1997). Robinson and Syers (1990) highlighted that an acid pH is a necessary prerequisite for the dissolution of an essentially water-insoluble RP in soil, because dissolution of the apatite relies on the net supply of protons. In effect, Mackay et al., (1986) highlighted that percent Ca-saturation, P-sorption capacity, and Ca-exchange capacity of the soil are the three most important parameters influencing RP dissolution. However, of particular concern and interest are the studies of Syers et al., (1986) and Rochayati et al., (2011) who reported that concentrations of As, U, Zn and Cd might also limit the direct use of rock phosphate.

The quantity of P that is available for uptake by plants from the soil is related to the concentration of P in the soil solution and P buffer capacity of the soil (Fundora et al., 1980; Hughes and Gilkes, 1994; Babare et al., 1997; Mengel and Kirkby, 2001; Barrow, 2015). Phosphate buffer capacity is defined as the ability of a soil to maintain a constant solution P

concentration in response to plant uptake (Fundora et al., 1980; Mengel and Kirkby, 2001). According to Chien and Hammond (1978), Chien and Menon (1995) and Kaleeswari and Subramanian (2001) increasing carbonate substitution in RPs increases the ease of breakdown of the structure of the apatite thereby releasing P to the soil solution under acidic conditions.

Of concern, Mengel and Kirkby (2001) highlighted that nutrients required by plants in high amounts are present in soil solution in relatively small concentrations such as is the case of P where the soil solution contains in the order of only about 0.5 – 1.0 kg P ha⁻¹ whereas the demand for this nutrient is considerably higher. Thus Babare et al., (1997) suggests that the effectiveness of RP as a fertiliser may be more closely related to the availability of dissolved P, than to the amount of RP dissolved in a soil, with similar conclusions being expressed by Bolan and Hedley (1990) who argued that measurements of the extent of RP dissolution in soil does not necessarily indicate the amount of plant available P and as such the P nutritional status.

2.3.2.3 *Soil Factors*

There are specific soil properties that influence the dissolution of apatite minerals in rock phosphate. They are pH, Cation Exchange Capacity (CEC), Ca concentration, P concentration, P sorption capacity, organic matter content as well as levels of application (Chien, 1977a,b; Anderson et al., 1984; Mackay et al., 1986; Hughes and Gilkes, 1986; Bolland and Barrow, 1988; Chien and Menon, 1995; Ehteshami, 2011). In order to be effective fertilizers, the first requirement is that substantial amounts of apatite should dissolve shortly after application (Hughes and Gilkes, 1984; Gilkes and Bolland, 1997). According to Khasawneh and Doll (1978), the dissolution of RP is enhanced in low pH soils following:



This reaction is for pure fluoro-apatite but a similar reaction applies to all members of apatite groups present in RPs. Apparently, the determinant factor driving the dissolution of apatites is the neutralizing reaction between proton (H⁺) ion concentrations reflected in pH

values (Hughes and Gilkes, 1984; Robinson and Syers, 1990; Kumar et al., 1993; Kaleeswari and Subramanian, 2001) and the apatites in RPs (Lehr and McClellan, 1972; Anderson et al., 1984; Hughes and Gilkes, 1986; Rajan et al., 1991). To this extent, many studies have shown that acid soils and acid generating processes, as well as inorganic and organic acids, all contribute to enhanced RP dissolution at low pH (Fixen et al., 1983; Havlin and Westfall, 1984; Kpombrekou-A and Tabatabai, 2003; Hua et al., 2008; Du et al., 2013). The conditions of low pH, low exchangeable Ca and low P concentrations are common in many tropical weathered soils and thus acid soils are more conducive to RP dissolution than Ca²⁺ rich alkaline soils (Hammond et al., 1986b; Nnadi and Haque, 1988; Bolan and Hedley, 1989; Sale and Mokwunye, 1993; He et al., 2005; Kumari and Phogat, 2008).

In addition, soil P-sorption capacities also effect the dissolution of RP. High P-sorbing soils such as, Oxisols and Ultisols enhance the dissolution of RPs by reducing the P concentration in the immediate surrounding of the RP (Syers et al., 1986; Chien and Menon, 1995; Linnquist et al., 1997; Chien and Friesen, 2000; Sahrawat et al., 2001). Slow release P-desorption from these soils might become important in the long term as associated with a general increase in the relative agronomic effectiveness of the RP, turning a P-source into a P-sink (Rajan et al., 1991; Zapata and Axmann, 1995; Bolland and Gilkes, 1998a,b). However, volcanic soils with the principal mineral allophane on the other hand are ultimate sinks of P with very low release rates (Imai et al., 1981; Borie and Zunino, 1983; Parfitt and Kimble, 1989; Parfitt et al., 1989; Beck et al., 1999; Smithson and Giller, 2002).

A number of field trials have indicated that in comparison to TSP directly applied finely ground low reactive RPs might be more effective on volcanic soils with low P-sorption capacity than on volcanic soils with high P-sorption capacity (Hammond et al., 1986a; Rajan et al., 1991; Chien and Menon 1995; Hua et al., 2008). The direct use of RP generally requires P-deficient acidic soils with pH less than 5.5 (Khasawneh and Doll, 1978; Smyth and Sánchez, 1982; Rajan et al., 1991, 1996; Kaleeswari and Subramanian, 2001) as well as annual rainfall

of greater than 800 mm (McDowell and Catto, 2005). According to Fundora et al., (1980), pH 5.5 apparently seems to be the dividing point predominating between P-Ca, P-Al and P-Fe and the more acid the soil the faster the rate of dissolution.

In effect, high P-sorbing soils like Oxisols and Ultisols enhance the dissolution of RP (Smyth and Sánchez, 1982; Mackay et al., 1986; Robinson and Syers, 1990; Sahrawat et al., 2001) while the initial effect of RP application on high P-sorbing volcanic soils (Andosols) with allophane minerals is generally negative. This effect is partially due to the fact that an acid pH is a necessary prerequisite for the dissolution of an essentially water-insoluble RP, because dissolution of the apatite relies on the net supply of protons (Hughes and Gilkes, 1984; Robinson and Syers, 1990; Kaleeswari and Subramanian, 2001). Initially the dissolved P may be unavailable to plants (Hammond et al., 1986a,b). However, the residual P effect of RP application increases with time on these volcanic soils (Fundora et al., 1980; Rajan et al., 1991; Zapata and Axmann, 1995; Akande et al., 2005). Interestingly, Yeates and Clarke (1993) postulated that the situation is different in coarse textured acid soils where rapid leaching of soluble phosphorus from rock phosphate gives a greater residual effect in the short term.

2.3.2.4 Crop Factors

Some plant species are better at utilising and/or enhancing the rate of P released from rock phosphate (Sánchez and Salinas 1981; Haynes, 1992; Shaw, 2009). In general, the effectiveness of RP is higher for long-term or perennial crops than for short-term or annual crops (Haynes, 1992; Chien et al., 2010) as well as for crops with developed root systems such as sugar cane and pasture (Fundora et al., 1980). Crops vary in their ability to use P from RP sources mainly because the mobilizing capacity of P from various RPs varies with crop species (Habib et al., 1999; Zhu et al., 2002). For example, leguminous species excrete H^+ ions when fixing atmospheric N, which increases the dissolution of the RP (Gerke et al., 1995; Marschner, 1995; Hinsinger and Gilkes, 1995), whilst others such as rapeseed excrete organic acids

(Hoffland et al., 1989; Montenegro and Zapata, 2002). However, Gourley et al., (1994) argued that germplasms should not be described as differing in P efficiency because they differ in maximum yields when P supply is non-limiting and thus the relationship between physiological and morphological characteristics (Chapin III, 1980; Chapin III et al., 1986; Aerts and Chapin III, 2000).

The balance between cation and anion uptake also affects rhizosphere pH, and this can differ between crops (Kirkby and Knight, 1977; Haynes, 1992). Differences in root morphology and mycorrhizal interactions also play an important role in the different abilities of some crops to utilise P release from RPs (Li et al., 1991; Gahoonia et al., 1997). Dobermann (2007) highlighted a number of indices used in the interpretation of nutrient use efficiency (NUE) by crops and pointed out that NUE generally decreases with increasing nutrient amount added whilst crop yield and plant nutrient accumulation/uptake typically increases with increasing nutrient addition and gradually approaches a ceiling.

Of interest are the findings of Baligar et al., (2001) who reported that estimates of overall efficiency of applied fertilizer have been about or lower than 50% for N, about 40% for K, and less than 10% for P. In addition, sub-optimal levels of P can lead to yield losses to the tune of 5% to 15% of the maximal yields (Shenoy and Kalagudi, 2005). From an agronomic standpoint, nutrient efficient plants are defined as those plants, which produce higher yields per unit of nutrient applied or absorbed than other plants, under similar agroecological conditions (Chapin III, 1980; Aerts and Chapin III, 2000; Fageria et al., 2008). More specifically, Shenoy and Kalagudi (2005) defined phosphorus use efficiency as “the ability of crop genotypes to function well under low available-P concentrations”. This concept was highlighted by Randall (1995) who argued that P efficiency depends on two interrelated groups of plant factors that determine uptake efficiency which are uptake of P relative to supply and utilization efficiency that is dry matter production per unit of P taken up.

As such, plants that are efficient in the absorption and utilization of nutrients greatly enhance the efficiency of applied fertilizers (Shenoy and Kalagudi, 2005), reducing cost of inputs (Sahrawat et al., 2001), and preventing losses of nutrients to ecosystems (Baligar et al., 2001). However, Chapin III et al., (1986) highlighted three major difficulties in the application of the concept of nutrient limitation and argued that low nutrient supply does not necessarily imply nutrient limitation. In addition, Randall (1995) highlighted that responsiveness should be distinguished from efficiency to the extent that responsive plants would be most desirable in fertilized, high-input systems, while P-efficient plants, which produce high yields at low levels of P, are likely to be most valuable in low- fertility situations.

According to Baligar et al., (2001), Cao et al., (2007), and Fageria et al., (2008) the inter-specific and intra-specific differences for plant growth and mineral NUE are known to be under genetic and physiological control and are modified by plant interactions with environmental variables. Sattelmacher et al., (1994) highlighted that genotypes may differ in the efficiency with which the nutrients in the plant are utilized to produce yield (utilization efficiency) and/or they may differ in their effectiveness in absorbing nutrients from the soil (uptake efficiency). In addition, there are species and varietal differences in the tolerance level to low soil P, and in the ability to utilize poorly soluble P sources (Smithson and Giller, 2002). Gahoonia and Nielsen (1996) indicated that from a mineral standpoint, a genotype is considered more efficient than others if it mobilizes and absorbs more P from soils and/or makes better use of the absorbed P to produce biomass.

Because the overall efficiency of applied P fertilizer is generally low, as a consequence plants have evolved two broad strategies for P acquisition and use in nutrient-limiting environments: (1) those aimed at conservation of use; and (2) those directed toward enhanced acquisition or uptake (Horst et al., 2001; Vance et al., 2003; Vance, 2008). In effect, processes that conserve the use of P involves decreased growth rate, increased growth per unit of P uptake, remobilization of internal P modifications in carbon metabolism that bypass P-

requiring steps, and alternative respiratory pathways (Schachtman et al., 1998; Raghothama, 1999; Raghothama and Karthikeyan, 2005).

Essentially plants have developed certain traits which enable them to better utilize P within the soil complex. A number of studies have reported on these traits (Loneragan, 1995; Johansen et al., 1995; Randall, 1995; Ahloowalia et al., 1995; Caradus, 1995; Smith, 1995; Welch, 1995; Delhaize, 1995; Ae et al., 1995). According to these various authors these plant traits would include characters that influence root size, root distribution, root morphology, and mycorrhizal association. Secondly, plant characters that increase the solubility of sparingly soluble soil P are also important. Such characters include root exudates, root exocellular phosphatases, and root induced pH changes (Dakora and Phillips, 2002, Nacry et al., 2005; Insalud et al., 2006; Shen et al., 2011).

In addition to these, several other associated plant characters need consideration since they too can influence the rate of P uptake. These include the P status of plant tissues and plant growth rate (Chapin III et al., 1986; Schachtman et al., 1998; Vance et al., 2003). By association, processes that lead to enhanced P uptake include increased production and secretion of phosphatase, exudation of organic acids, greater root growth along with modified root architecture, expansion of root surface area by prolific development of root hairs, and enhanced expression of Pi transporters (Marschner, 1995; Raghothama, 1999; Xie and Yu, 2003; Gahoonia and Nielsen, 2004; Trubat et al., 2006; Ling et al., 2008; Gaxiola et al., 2011).

2.4 Allophane Soil Chemistry

2.4.1 *The Nature of Allophane Mineral*

Allophane is a clay-size aluminosilicate mineral with short-range-order characteristics, product of weathering of tephra materials in Andosols or Spodosols (Wada, 1989; Shoji and Ito, 1990; Parfitt, 1990; Creton et al., 2008; Fiantis et al., 2010). These naturally occurring hydrous aluminosilicate clays are also characterized by the predominance of Si-O-Al bonds (Wada, 1967; Parfitt and Hemni, 1980; Bishop et al., 2013). Because of its small unit particle size and extensive specific surface area allophane has a large propensity for adsorbing organic substances particularly in the presence of Ca^{2+} and Na^+ ions (Yuan et al., 2000; Ugolini and Dahlgren, 2002). Under a humid tropical climate, a leaching process of Ca, Mg, Na and K rapidly transforms volcanic glass and ash into allophane and other secondary products rich in Si and Fe (Woignier et al., 2007; Vacca et al., 2009). Thus, it is a series name used to describe clay-sized, short-range-order aluminosilicates associated with the weathering of volcanic ashes and glasses (Kanno and Arimura, 1967; Wada, 1967; Wada, 1989; Mizota and Van Reeuwijk, 1989; Parfitt and Kimble, 1989; Ugolini and Dahlgren, 2002).

Allophane commonly occurs as very small rings or spheres having an outer diameter of approximately 3.5 – 5.0 nm (Wells and Theng, 1988; Wada, 1989; Ishida and Makino, 1999; Al-Ani and Sarapää, 2008; Kett et al., 2010), and a wall thickness of approximately 0.7 nm (Wells and Theng, 1988; Wada, 1989) composed of a gibbsitic sheet to which O_3SiOH groups are attached on the inside (Wells and Theng, 1988; Yuan et al., 2000), thus their unique morphological, physical and chemical properties (Creton et al., 2008; Georgoulis and Moustakas, 2010). Interestingly, Gérard et al., (2007) showed evidence of the formation of allophane alteromorphs, due to leaching of Si and cations, with preservation of the original shapes of the tephra. In effect, a striking feature in particular of the chemical composition of allophane is its high content of hydrogen (Wada, 1967) which is related to its form (adsorbed H_2O vs. structural OH groups), location (surface vs. internal), and bonding (Al-OH vs. Si-OH).

According to Shoji et al., (1993), Ildefonse et al., (1994), Ugolini and Dahlgren (2002), Creton et al., (2008), and Tsai et al., (2010) these distinctive properties are largely due to the formation of poorly crystalline and non-crystalline materials (i.e. allophane, imogolite, ferrihydrite, Al/Fe–humus complexes) and the accumulation of organic carbon, which is the two dominant pedogenic processes in volcanic ash soils. They could also occur in any environment where sufficient Si and Al exist in solution from which these rapidly forming minerals precipitate (Farmer, 1982; Khan, 2007; Parfitt, 2009). Current usage of the terminology is limited to short-range-order aluminosilicates having Al:Si ratios varying from about 2:1 to 1:1 possessing a spherical or ring-shaped morphology (Wada, 1967; Wada, 1989; Lizcano et al., 2006). As such, limited amount of isomorphic substitution occurs in allophane with the most common type being the substitution of Fe for Al (Al-Ani and Sarapää, 2008). In general 1:1 clays and oxides dominate mostly tropical soils whereas 2:1 minerals dominate mostly temperate soils (Six et al., 2002).

Allophanic Andosols possess Al–humus complexes, but they rarely show any toxicity (Dahlgren et al., 2004a,b; Ito et al., 2009) even when they contain large amounts of Al–humus complexes and soils seldom show acid injury to plant roots (Takahashi et al., 2008). The origin of the toxic Al is considered to primarily be Al^{3+} adsorbed on permanently charged sites of 2:1 minerals (Dahlgren et al., 2004a,b). However, the continuous and heavy application of nitrogen fertilizers and changes in vegetation will acidify allophanic soils which will then come to possess KCl-extractable Al, which is toxic to plant roots (Takahashi et al., 2008). Similarly, where fertilizer NH_4^+ accumulates in the soil at high concentrations, dispersion of clay colloids can be favoured (Haynes and Naidu, 1998). Notwithstanding, the presence of allophanic materials (allophane, imogolite and allophane-like materials) reduces Al toxicity (Ito et al., 2009), and most allophanic Andosols are formed at a soil pH (H_2O) greater than 5, where Al is relatively insoluble and is not released into the soil solution (Ito et al., 2009).

Allophanic soils are dark-coloured young soils derived mainly from volcanic ash (Birrell and Fieldes, 1952; Maeda et al., 1977; Allbrook, 1985; Arnalds, 2004; Madeira et al., 2007a,b; Verde Vilanova, 2009) dominated by allophane and also imogolite or ferrihydrite minerals (Yoshinaga and Aomine, 1962; Anderson et al., 1982; Parfitt and Kimble, 1989; Shoji et al., 1993; Ugolini and Dahlgren, 2002). According to Gérard et al., (2007) the formation of allophane is essentially considered to be a result of mineral precipitation from a weathering solution. However, this assumes that volcanic glass undergoes congruent dissolution, followed by a downward migration and degradation of metal-organic complexes (Gustafsson et al., 1995). In essence, the rapid weathering releases elements, such as Si, Al and Fe faster than crystalline minerals can form, resulting in soil solutions becoming over-saturated with respect to metastable, noncrystalline materials, such as allophane, imogolite, opaline, silica, and ferrihydrite (Ugolini and Dahlgren, 2002; Georgoulis and Moustakas, 2010).

Under humid weathering conditions, the composition of the colloidal fraction forms a continuum between pure Al-humus complexes and pure allophane/imogolite depending on the pH (Ishida and Makino, 1999) and organic matter characteristics of the weathering environment (Farmer, 1984; Mizota and Van Reeuwijk, 1989). According to Delvaux et al., (1989) low Si levels are a feature of the more weathered soils, consistent with the disappearance of allophane. In addition, depending on the SiO₂ content volcanic tephra is classified as acidic, alkaline or intermediate (Shoji et al., 1975; Le Bas et al., 1986). As such, the colloidal fraction of Andosols in humid weathering environments usually tends to be dominated by Al-humus complexes or allophane/imogolite (Ugolini and Dahlgren, 2002). In addition, the formation of complexes between allophane and organic matter in soil would also enhance the retention of heavy metals and non-ionic organic contaminants, so reducing their mobility in the soil column (Yuan et al., 2000; Krull et al., 2004, Bruce et al., 2009). Interestingly, Broquen et al., (2005) indicated that the formation of Al-humates can prevent the synthesis of allophane, and a further process that acts against the accumulation of allophane is the influx of illuvial organic matter

from the surface horizons (Anderson et al., 1982), a process that may be dominant in sands poor in minerals prone to weathering, (Farmer, 1984).

Nonetheless, Buurman and Van Reeuwijk (1984) highlighted arguments refuting the alternative concept that iron and aluminium are transported down the profile as short-range-order aluminosilicates such as proto-imogolite which would thus play an important role in podzol formation, and instead attributed the mobilization, translocation and precipitation of sesquioxides to complexing organic compounds. Similarly, Childs et al., (1983) provided arguments that a different mechanism is also likely to apply in that movement of Al occurs both as inorganic and organic complexes, either simultaneously or in sequence depending on the nature of the soil and its development and climate events. Thus, the mineral fraction of soils has a profound effect on the quantity and quality of organic matter (OM) in soils (Sollins et al., 1996; Parfitt et al., 1997). This effect is due partly to adsorption on clay surfaces by which a large part of the OM is protected from microbial decomposition (Oades, 1988; Yuan et al., 2000; Armas-Herrera et al., 2012) and partly to physical inaccessibility of OM within pores of microaggregates (Tisdall and Oades, 1982; Miyazawa et al., 2013).

2.4.2 Characteristics of Allophanic Soils

In Andosols, which are defined as soils showing andic properties to a depth of 35 cm or more from the surface and having a mollic or an umbric A-horizon possibly overlying a cambic horizon (Mizota and Van Reeuwijk, 1989; Aran et al., 2001; FAO, 2006), the allophane content which is a key colloid of these soils has a strong affinity for trace metals such as Cu and Zn (Latrille et al., 2003), hence the rapid disappearance of phosphate from an equilibrating solution (Borie and Zunino, 1983, Barrow, 2015). On the other hand, the imogolite structure can occur over a short range (Parfitt, 1990), showing instability in the presence of organic substances (Inoue and Huang, 1986; 1990; Huang, 1991; Gustafsson et al., 1995) as well as with increasing pH (Farmer, 1984). Here the spherule wall is composed of a curved Al-O, OH

octahedral (gibbsitic) sheet to which orthosilicate $[(O_3) Si(OH)]$ groups are attached on the inside (Wells and Theng, 1988; Yuan et al., 2000). However, Madeira et al., (2007a,b) and Vacca et al., (2009) highlighted that the occurrence of volcanic parent material does not guarantee the development of andic properties, as these are not defined from a purely mineralogical basis.

In allophanic soils, structural defects within the wall give rise to approximately 0.3-nm wide perforations (Wada and Wada, 1977; Wells and Theng, 1988) where $(OH)Al(H_2O)$ groups are exposed. These groups can acquire protons on the acid side, and lose protons on the alkaline side, of the point zero charge, and hence are responsible for the (pH-dependent) variable-charge characteristics of allophane (Yuan et al., 2000). When $pH < 8.2$ the surface charge of the allophane is positive, whereas for $pH > 8.2$ the surface is negatively charged, and when a cation is added to the system, the point of zero charge shifts towards acid pH (Latrille et al., 2003). This corresponds to an increase of OH^- consumption by the allophane surface or the bulk solution, apart from cation hydrolysis (Latrille et al., 2003). Yuan et al., (2000) highlighted that the surface positive charge decreases, whereas the surface negative charge increases with increasing pH and thus surface negative charges are created when humic acid forms a complex with allophane by a ligand exchange reaction (Sollins et al., 1996). As such, the chemical composition, size, number, and nature of the functional groups and concentration of organic ligands such as humic substances plays a vital role in perturbing the formation of allophane and imogolite, resulting in the formation of ill-defined aluminosilicate complexes and/or hydroxy-Al-tannate complexes (Inoue and Huang, 1986; 1990; Huang, 1991).

Allophanic soils typically have a low bulk density ($< 0.9 \text{ g/cm}^3$) due to the high porosity resulting from spherules remaining discrete, separated from each other by moisture films (Maeda et al., 1977; Iñiguez and Val, 1984; Allbrook, 1985; Wells and Theng, 1988; Aran et al., 2001; Woignier et al., 2007). In addition, the low bulk density of volcanic ash soil is generally explained by the presence of short-range-order minerals and high organic matter

content (Navarrete et al., 2008) which is attributed to the stabilization of soil organic matter in organo-metallic complexes, their association with short-range-order minerals, and physical protection from microbial attack inside soil macroaggregates and microaggregates (Oades, 1988; Yuan et al., 2000; Armas-Herrera et al., 2012). However, Miehl (1991) and Witanachchi (2004) suggested that this property could be due to isovolumetric weathering, whereby the original shapes and volumes of the dissolved minerals are maintained. These soils also have a high water retention capacity (100% by weight at field capacity) and the water content increases with increasing allophane + ferrihydrite for soil horizons with < 6% C (Iñiguez and Val, 1984; Arnalds, 2004; Broquen et al., 2005; Candan and Broquen, 2009; Óskarsson et al., 2012; Arnalds, 2015).

It has been observed that allophanic soils have high shrinkage, and irreversible drying (Birrell and Fieldes, 1952; Warkentin and Maeda, 1980; Wells and Theng, 1988; Kett et al., 2010; Velescu et al., 2010; Bishop et al., 2013). The plasticity characteristics of allophane: high liquid limit, low plasticity index, and decrease of plasticity index on drying, are suggested as a basis for rating the amount and nature of allophane in soils (Warkentin and Maeda, 1974; Maeda et al., 1977). In addition, these soils also have large microporosity, wide limits of plasticity, good aggregate stability and are relatively resistant to water erosion (Armas-Herrera et al., 2013). These soils are also known to exhibit thixotropic qualities (Mizota and Van Reeuwijk, 1989; Óskarsson et al., 2012) and under static conditions will flow (become thin, less viscous) over time when shaken, agitated, or otherwise stressed (time dependent viscosity).

It has been reported that allophane formation is inhibited by organic matter in horizons with >12% C (Aran et al., 2001; Arnalds, 2004, 2015). In effect, the accumulation of organic matter, by illuviation and possible root activity, within upper soil horizons leads to the dissolution of previously deposited allophanes (Farmer, 1984). The turnover of soil organic matter in allophanic soils is slower than that in non-allophanic soils (Aran et al., 2001; Nanzyo et al., 1993a,b; Saggar et al., 1996; Parfitt, 2009). Imogolite-like allophane occurs very

frequently in soil horizons with >1 or 2% allophane, suggesting that it is more stable, or is more readily formed, in soils than other allophanes (Parfitt and Kimble, 1989). Among examples noted, Borie and Zunino (1983) highlighted that volcanic soils of Chile with high allophane content are basically characterized by their unusually high organic matter content and by a microbial ecology dominated by actinomycetes and fungal species some of which synthesize humic-like polymers, and as such the influence of microbial communities on P dissolution.

Nonetheless, Matus et al., (2008) suggested that noncrystalline Al hydroxides and insoluble organically complexed Al rather than allophane (or imogolite) should be considered as the key parameters for OM stabilization in andic soils. Within that context, Fujii et al., (2011) highlighted that in Andosols of Japan, dissolved organic carbon (DOC) fluxes are low throughout the profile because of low DOC production in the O horizon and the high adsorption capacity of amorphous Al- and Fe-hydroxides in the mineral horizons whereas in Spodosol soils, DOC from the O horizon represents a large proportion of C input into the mineral soil. In addition, according to Madeira et al., (2007a,b) the Andosols of the volcanic systems of Portugal show several particularities such as high clay content (<2 μm), high organic C content not only in their epipedon but also at lower depth, containing up to 50 kg C m⁻² within the soil profile (100 cm depth), with increase of allophane content with depth and have a relatively high total iron content and low oxalate Fe content.

These characteristics and interactions with allophane create a soil environment highly reactive from the biochemical standpoint (Van Ranst et al., 2004). This is reflected, among others, in the following properties of such soils: (a) strong stabilization of the indigenous organic matter and of extraneous organic materials and compounds (Zunino et al., 1982a; Aran et al., 2001), (b) high rates of synthesis of microbial humic-type macromolecules (Zunino et al., 1982b; Sollins et al., 1996), and (c) high enzymatic activity (Borie and Fuentealba, 1982). These soils are identified by a distinctly greasy feel when moistened and rubbed firmly between the fingers (Farmer et al., 1985; Wells and Theng, 1988; Mizota and Van Reeuwijk, 1989;

Parfitt, 1990). From an agronomic perspective, these soils are easy to dig and samples crumble easily (Maeda et al., 1977; Parfitt, 2009) and hence their superb productivity.

According to Arnalds (2004, 2015) these soils show characteristic properties of soils dominated by andic materials with allophane contents of up to 30%. Ferrihydrite commonly accounts for 5–15% of the soil and the contents of both allophane and ferrihydrite generally decrease with increasing organic C content of soil horizons, as organic matter inhibits allophane formation (Farmer, 1984; Aran et al., 2001; Arnalds, 2004) and Fe tends to become reduced and lost in poorly drained locations (Childs et al., 1990; Arnalds, 2015). To this end, Buurman et al., (2007) postulated that soil organic matter in allophanic soils is supposed to accumulate due to protection caused by binding to allophane, aluminium and iron. However, Aran et al., (2001) pointed out that the organic C content of humus horizons increases with increasing ratios of pyrophosphate-extractable Al to acid oxalate-extractable Al, a ratio reported by Nanzyo et al., (1993a) to be in the range 0.1–0.4 for allophanic Andosols and 0.8 – 1.0 for nonallophanic Andosols.

2.4.3 Phosphate Sorption in Allophanic Soils

It has been well established that Andosols and other variable charge soils that contain large amounts of allophane and other amorphous minerals, have considerable capacities to bind P (Imai et al., 1981; Iñiguez and Val, 1984; Wada, 1985; Allbrook, 1985; Aran et al., 2001). Phosphate adsorption on tropical and subtropical soils in particular may be closely correlated with iron and aluminium oxides in these soils (Allbrook, 1985; Crews, 1996; Raghothama, 1999; Vance et al., 2003; Auxtero et al., 2008; Sattari et al., 2012), a process which also occurs in temperate podzolic soils as was reported by Cade-Menun et al., (2000).

It has also been observed that organic anions are adsorbed on minerals, such as goethite and gibbsite, and that adsorption increases with a decrease in pH (Parfitt, 1977; Bowden et al., 1980; Barrow, 1984; Sibanda and Young, 1986; Bolan et al., 1986; He and Zhu, 1998).

Furthermore, when anions such as phosphate are adsorbed by soil, or by soil constituents, the extent of adsorption and the charge on the surface depend on several factors. These include pH, the concentration of adsorbing ions, the concentration and properties of the electrolyte, and the nature of the adsorbent (Bowden et al., 1980). The reactions of phosphate with iron oxides depend on the number of reactive surface Fe-OH groups and the crystallinity of the oxides (Goldberg and Sposito, 1985; Parfitt, 1989a,b) and the reactions probably involve rapid, strong ligand exchange, followed by weaker ligand exchange and by penetration at defect sites and pores (Goldberg and Sposito, 1985; Fontes and Weed, 1996), where at very acid pH values, iron phosphate may precipitate (Parfitt, 1989a,b). Likewise, the partitioning of Al between organically complexed and allophanic forms is controlled by pH and soil organic matter content (Cade-Menun et al., 2000; Barrow and Debnath, 2014).

Allophane adsorbs cations and anions from neutral salt solution (Iñiguez and Val, 1984). More specifically, interactions of anions with allophane involve three different reactions to include non-specific adsorption, specific adsorption, and decomposition of the allophane induced specifically by adsorbed anions (Iñiguez and Val, 1984; Lizcano et al., 2006). The reactions of phosphate with allophane can be considered to take place as a rapid, strong adsorption, probably at defect sites, followed by weaker adsorption and by disruption of the allophane structure, leading to precipitation of aluminium phosphates (Parfitt, 1989).

In allophanic soils with very high organic matter, the organo-mineral complex seems to form a rather open microstructure such that phosphate ions at low P additions are adsorbed on relatively low energy surfaces only (Imai et al., 1981). Organic matter can be sorbed by allophane through ligand exchange between the carboxyl functional groups of organic matter and the hydroxyl groups bonded to structural Al exposed on spherule surfaces (Parfitt et al., 1999). Thus P sorption in soils is influenced by the presence of organic matter and other materials and also by slow reactions (Parfitt, 1979; Guppy et al., 2005). Since allophane has surfaces rich in reactive Al-OH and Fe-OH groups, it is to be expected that allophanic soils

behave towards P in a manner similar to that of hydrous oxides (Pardo and Guadalix, 1990) and as such when P is sorbed in allophanic soils, a concomitant release of OH^- , SO_4^{2+} , and SiO_2 takes place (Rajan and Fox, 1975).

However, it is also possible, that some of the OH^- groups may immediately combine with protons from the dissociation of phosphate ions (Pardo and Guadalix, 1990). When larger amounts of P are added, more P-reactive surfaces are exposed; with the loosely bound organic matter being progressively displaced by the phosphate ions (Bowden et al., 1980; Bolan and Barrow, 1984). With the largest P additions, the adsorption is attributed to the nucleation, precipitation and re-crystallisation of aluminium phosphate (Imai et al., 1981). As a consequence, the adsorption capacity of allophane at higher phosphate levels is directly related to the aluminium content (Theng et al., 1982).

The rate of the reaction between soil and phosphate is known to be increased by high temperatures and to be decreased by low water contents (Barrow, 1980) and tends to differ among soil types. Effectively with high rates of reaction the residual value of phosphate fertilizers tend to increase whereas with an extended rate of reaction the residual value of phosphate fertilizers tends to decrease (Barrow, 1980; Rutkowska et al., 2015).

With an accelerated rate of weathering or chemical attack of primary crystalline and short-range-order aluminosilicates, the formation of acid soluble secondary minerals will increase the proportion of acid extractable Al in fertilised soils compared with non-fertilised soils (Taylor et al., 2012). According to these authors, two specific mechanisms are involved: (1) partial dissolution of clay minerals by local areas of temporal high acidity that are associated with fertiliser granules; (2) surface complexation and extraction by the fluoride and residual hydrofluoric acid present in phosphate fertilisers (Taylor et al., 2012). In addition, humified soil organic matter can significantly reduce the amount of phosphate required to maintain a solution concentration necessary for crop growth (Sibanda and Young, 1986), an effect which is more likely to be pronounced in acid soils.

2.4.4 Agronomic Management of Allophanic Soils in Tropical Regions

In soils, secondary clay-size minerals are the most reactive inorganic components, commonly occurring in association with the most reactive organic materials (Bronick and Lal, 2005; Churchman, 2010). Fixation of phosphate in allophanic soils is one of the major factors limiting their agronomic use (Borie and Zunino, 1983; Juo and Franzluebbers, 2003; Dahlgren et al., 2004a,b; Buurman et al., 2007). In general, soils formed on volcanic ash exhibit particular physical, chemical and mineralogical properties which are rarely encountered in soils forming on other parent material (Shoji, 1985; Shoji et al., 1993; Vacca et al., 2009), such as the formation of non-crystalline components and the accumulation of organic matter (Rouse, 1990; Ugolini and Dahlgren, 2002; Dahlgren et al., 2004a,b). With regard to nutrients, volcanic ash soils are both N- and P-limited. Nitrogen limitation does not appear to be severe, because SOM tends to have C:N ratios around 10:1 (Buurman et al., 2007). Nutrient limitation, however, would influence both the decomposition of plant-derived SOM and the production of microbial SOM (Bronick and Lal, 2005; Buurman et al., 2007). Thus, in effect, knowledge of the properties of these reactive materials should enable close predictions of the useful properties of soils, especially for the growing plants (Churchman, 2010).

Andosols commonly show a striking accumulation of organic carbon (Aran et al., 2001), attributed to the stabilization of soil organic matter in organo-metallic complexes, their association with short-range-order minerals, and physical protection from microbial attack inside soil macroaggregates and microaggregates (Mizota and Van Reeuwijk, 1989; Ugolini and Dahlgren, 2002; Buurman et al., 2007; Armas-Herrera et al., 2012). However, plant-derived SOM in allophanic Andosols is strongly degraded and microbial SOM contributes substantially in its accumulation (Buurman et al., 2007). Although C sequestration in Andosols is highly efficient, these soils are vulnerable both to erosion and aggregate breakdown which might induce accelerated mineralisation of soil organic carbon (Armas-Herrera et al., 2012). To this end, the preservation of soil organic matter in these soils is apparently influenced by

processes such as (i) protection of organic matter by complexation with iron, aluminium and allophane, (ii) reduced bacterial activity that results from the presence of free aluminium and iron, (iii) low soil pH, and (iv) poor availability of phosphorus (Naafs, 2004).

Allophanic volcanic ash soils have a large amorphous fine fraction which causes the formation of aggregates of roughly 10-micron size whereby aggregation is mediated by soil organic carbon (SOC), biota, ionic bridging, clay, and carbonates (Bronick and Lal, 2005). Furthermore, Fe oxides affect soil structure by inducing the formation of microaggregates (Six et al., 2002; Juo and Franzluebbers, 2003; Bronick and Lal, 2005). This combination of aggregates and primary particle sizes induces a large amount of small pores and a large water-holding capacity (Buurman et al., 2007; Armas-Herrera et al., 2013). The highest aggregate stability is found in surface horizons. This can be ascribed to the quantity and quality of SOM in these horizons, as the hydrophobic character of SOM possibly reduces the soil's ability to acquire moisture and preserve aggregates from disaggregation (Aran et al., 2001; Armas-Herrera et al., 2013).

These soils are at field capacity much of the year, which implies that all micropores are filled with water causing local anoxic circumstances and inhibits SOM decay (Buurman et al., 2007). The high wilting point is a reflection of both the high specific surface and the discrete spherules of allophane soils (Allbrook, 1985). This is due to the development of hydrophobic surfaces on the spherules which leads to an uneven distribution of water films. Thus, water-stable aggregates seem to be related not only to C content but also to Al and Fe content in underlying horizons (Aran et al., 2001). These volcanic soils exhibit a wide range of agricultural productivity, depending on the degree or intensity of pedogenic development and the colloidal composition of the rooting zone (Dahlgren et al., 2004a,b) making them a highly valuable resource in the pursuit of crop cultivation and agricultural development.

CHAPTER 3

GEOPHYSICAL DESCRIPTION OF THE DOMINICAN ENVIRONMENT AND GENERAL CHARACTERIZATION OF STUDY SITE

“.....APRES BONDIE C’EST LA TER” are the words embedded on the coat of arms of the Commonwealth of Dominica. In the local patois (Kreyol) tongue, a stable natural language that has developed from a fusion of African and French origins, it literally means “AFTER GOD IS THE EARTH” and by extension the soil. These sentiments are deeply rooted in the Dominican spirit, in the everyday life of its country folk, and in the cultural essence of its people, as can be heard in the first stanza of the national anthem as it resonates....

“...Isle of beauty, isle of splendour, isle to all so sweet and fair, all must surely gaze in wonder, at thy gifts so rich and rare, rivers, valleys, hills and mountains, all these gifts we do extol, healthy land, so like all fountains, giving cheer that warms the soul....”

[Lyrics by Wilfred Oscar Morgan Pond (1912-1985) and music composed by Lemuel McPherson Christian OBE (1917-2000)]

Indeed the country has been blessed with a climate benign and bright as is evident in the abundance of flora and fauna, rich biodiversity and a healthy eco-system. As the authors of the national anthem put it“.. *a gem beyond compare..*”. This lush tropical paradise has been nicknamed the "*Nature Isle of the Caribbean*" for its unspoiled natural beauty and in recent times it has also acquired the title of "*The Volcanic Pearl*", for its many active volcanoes with one of the highest concentrations per land mass on a global scale (Le Friant et al., 2002; Lindsay et al., 2003; Lindsay et al., 2005a,b; Staisch, 2008; Rad et al., 2013).

The Commonwealth of Dominica is located between 15°12' and 15°39' North Latitude and between 61°14' and 61°29' West Longitude. The landmass measures 48 km along its north-south axis and 24 km from east-west at the widest point of the island (Evans, 1986). The land area is 750.6 km², with 153 km of coastline, adjoining a 715 km² coastal shelf. It is the

youngest island in the Lesser Antilles, still being formed by geothermal-volcanic activity, as evidenced by the world's second-largest hot spring, Boiling Lake (Lindsay et al., 2003; Staisch, 2008; Fournier et al., 2009; Joseph et al., 2011; Di Napoli et al., 2014).



Fig. 3.1. Map of Caribbean islands positioning the Commonwealth of Dominica and its central location within the Caribbean volcanic arc. Source:

<https://www.google.co.uk/search?q=maps+of+dominica&biw=1264&bih=719&tbm=isch&tbo=u&source=univ&sa=X&ei=jI0AVeHBDIH9UoDbgtgH&ved=0CCIQsAQ>

<http://www.google.co.uk/url?sa=i&rct=j&q=&esrc=s&source=images&cd=&cad=rja&uact=8&ved=0CAYQjB0&url=http%3A%2F%2Fwww.visitdominica.com%2Ftravel.cfm&ei=540AVfqrJcKxUfuRgcAM&bvm=bv.87611401.d.d24&psig=AFQjCNEXh5RRHh0nGmWtmFSbELdPjuc01A&ust=1426186084049663>

3.2 Rock Formation and Geology

The island is almost entirely composed of andesitic-dacitic volcanic rocks from ten volcanic centres of mainly Pleistocene age (Sigurdsson, 1972; Carey and Sigurdsson, 1980; Rouse, 1990; Rao, 1996; McCarthy et al., 2005; Goldsmith et al., 2010; Joseph et al., 2011). Historically, activity on the island has been limited to intense and prolonged fumarolic emanations (Pedroni et al., 1999; Le Friant et al., 2002; Samper et al., 2008; Joseph et al., 2011). The oldest formations are andesitic and basalt andesite breccias and lavas in the eastern and north-eastern part of the island (Sparks et al., 1980; Gurenko et al., 2005; Halama et al., 2006). Overlying the rocks of the basal complex is a discontinuous formation of shoreline conglomerates with coral and algal limestone lenses of Pleistocene age (Sigurdsson, 1972; Reading, 1991; Joseph et al., 2011; Rad et al., 2013). Typically, the weathering profile consists

of a highly organic topsoil ("A" soil horizon), of variable depth, above 15-150 cm of mineral soil ("B" soil horizon) (Lang, 1967; Reading, 1991). Below this lies a layer of saprolite ("C" soil horizon) which grades into progressively less weathered parent material with depth (Reading, 1991).

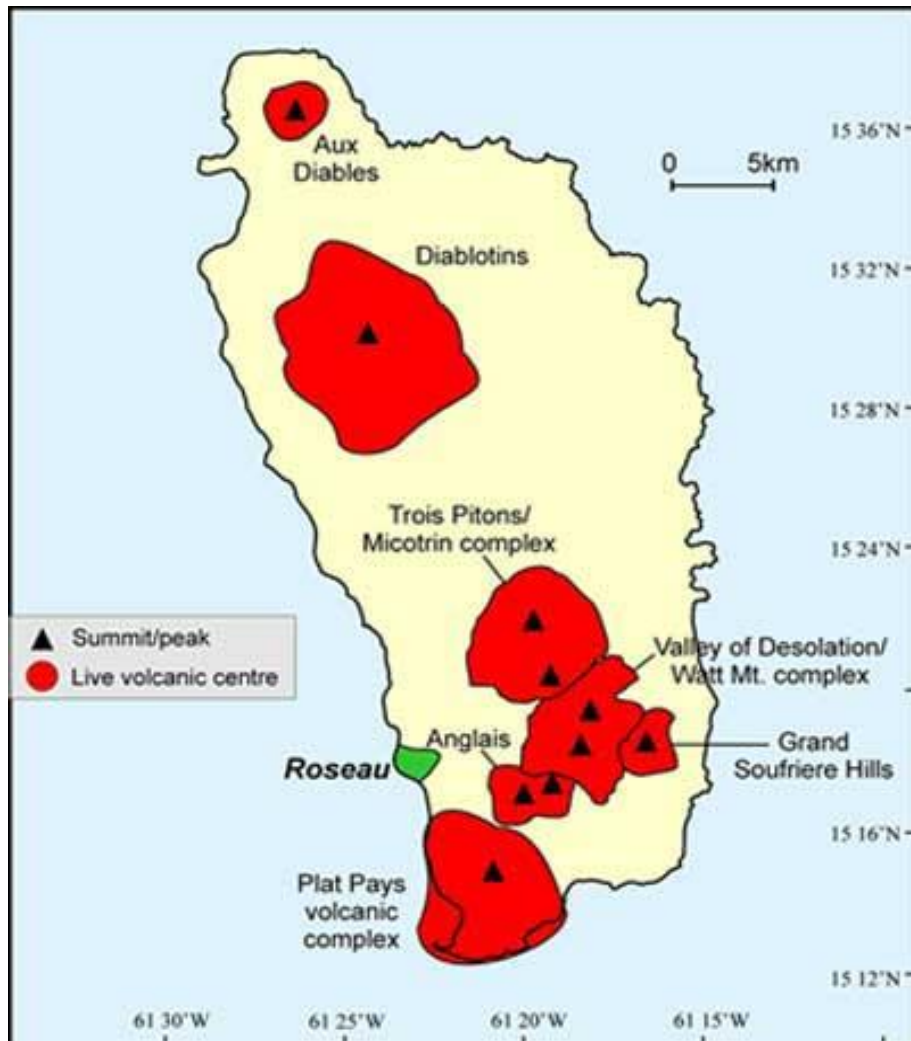


Fig. 3.2. Areas of live volcanic activity of the Commonwealth of Dominica. Source:

<http://www.google.co.uk/url?sa=i&rct=j&q=&esrc=s&source=images&cd=&cad=rja&uact=8&ved=0CAYOjB0&url=http%3A%2F%2Fwww.thedominican.net%2Farticles%2Fauxdiablies.htm&ei=FZIAVdbOGIS8UYeHhKgL&bvm=bv.87611401.d.d24&psig=AFQjCNFV3Tq98B9wvr4E4qk4egnHBOsnwg&ust=1426187129214417>

The island is very rugged and the most mountainous of the Lesser Antilles as a result of youthful volcanic relief (Roobol et al., 1983), mid Pleistocene uplift, rapid erosion primarily by landslides (Reading, 1991), and high drainage densities (Rouse et al., 1986; Rouse, 1990; Rao, 1996). Slopes are steep, frequently exceeding 50°, especially in the southern part of the

island with gentle gradients being largely restricted to structural hollows and narrow interfluves (Lang, 1967; Sigurdsson, 1972; Reading, 1991; Goldsmith et al., 2010).

Erosion is problematic in Dominica’s interior highlands due to a combination of high rainfall, steep slopes, rapid uplift in the Pleistocene and an abundance of poorly consolidated pyroclastic deposits (Lindsay et al., 2003; Rad et al., 2006). However, Rouse (1990) highlighted that the clays of Dominica exhibit unusual geotechnical and hydrological properties due to high water retention capacity, and as emphasized by Rao (1996), only rainfall of exceptionally prolonged high intensity can elevate pore water pressures and induce landslides.

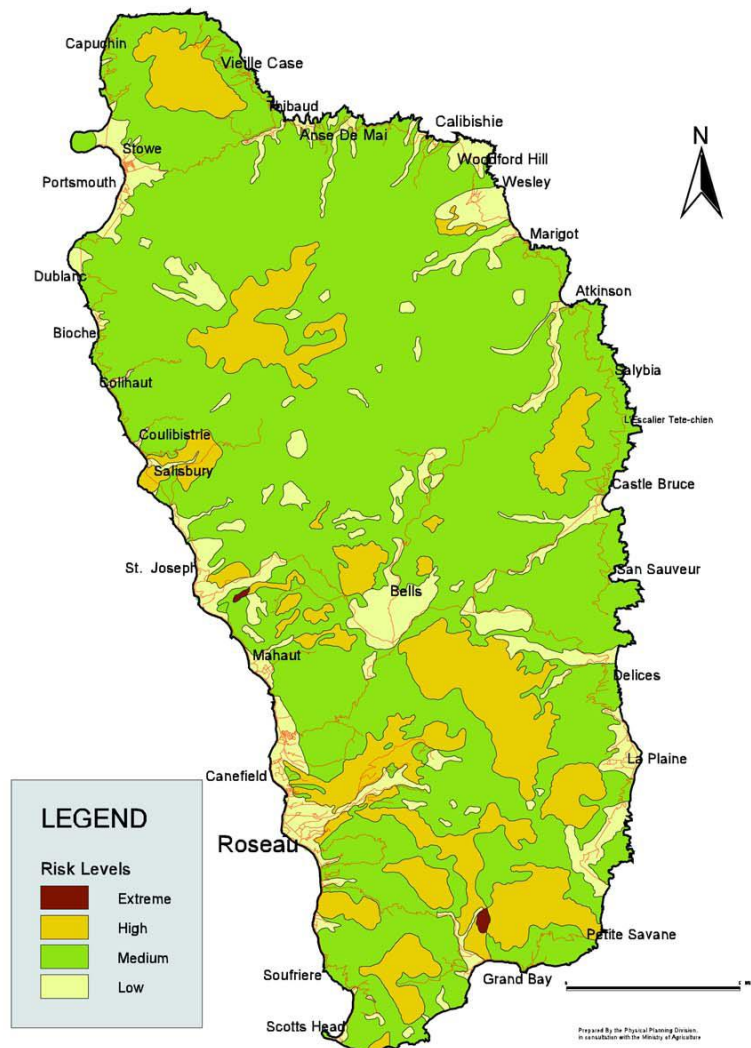


Fig. 3.3. Landslide hazards in the Commonwealth of Dominica. Source: Agricultural Information and Communication Unit (AICTU) of the Ministry of Agriculture, Government of Dominica.

3.3 Topography

There is a common saying among the Dominican people that if Christopher Columbus was to ever make a fifth or even a sixth voyage back to the West Indies, the only island that he would be able to recognize would be the Commonwealth of Dominica for the undeniable presence of its majestic topography! According to Lang (1967), the landscape of Dominica is divided into a small number of constructional types and subdivided according to the stage to which erosion processes have modified their original form.

The island is the most mountainous of all the Lesser Antilles with characteristic lush green, very rugged and steep terrain extending above 1500 m in elevation over much of the country (Shillingford, 1972; Drigo, 2001; Lindsay et al., 2003; Lindsay et al., 2005a,b). The dominant land formations are Morne Diablotin (1730 m), in the northern half of the island and a chain of mountains including Morne Trois Pitons (1424 m), in the southern part of the island and extending to the coast (Drigo, 2001; McCarthy, 2004; McCarthy et al., 2005; Smith et al., 2012). More gently sloping areas can be found primarily in the river valleys, the coastal areas of the northeast and the Bell's Wet area in the centre of the island (CCA, 1991; Drigo, 2001).

Virtually the whole of Dominica is volcanic (Fig. 3.2) which rises precipitously out of the sea but more accentuated on the leeward side of the island (Spencer, 1902; Earle, 1928; Wadge, 1985; Whitman, 1989). Its intermediate igneous and pyroclastic rocks characteristically form composite cones with a steeply sloping central part, what Lang referred to as "the pile", and a more gently sloping outer "glacis" (Fig. 3.4). Lang (1967) further went on to highlight that the initial slopes of the volcano may be smooth, or corrugated by avalanche-like movements of later deposits, or with breaks in slope determined by the presence of underlying earlier topography only thinly mantled by the volcano; but apart from the cutting of benches by wave action virtually all the sculpting of the cone is primarily affected by streams which radiate from the pile.

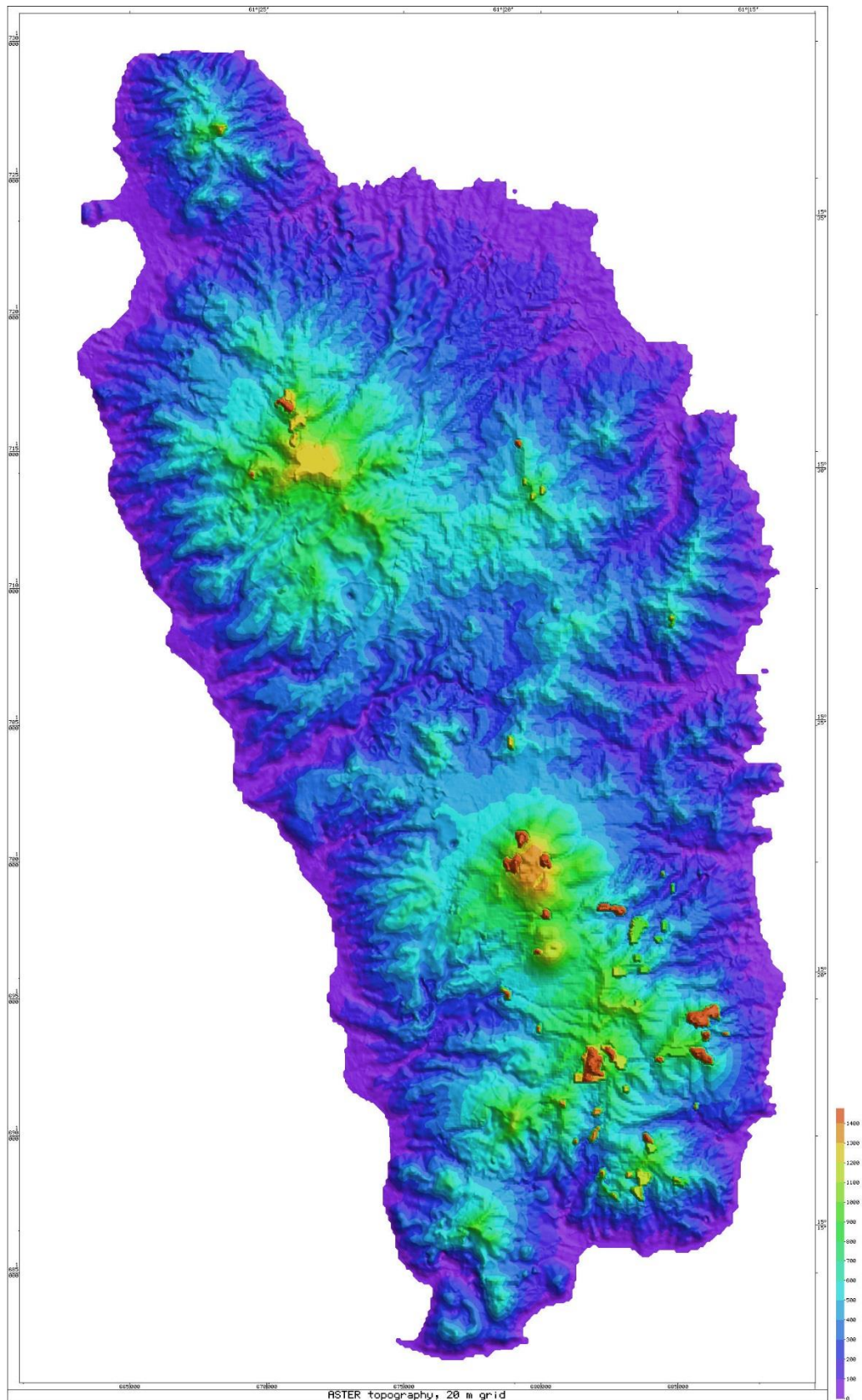


Fig. 3.4. Radar topography of the Commonwealth of Dominica.

https://www.google.co.uk/search?q=topography+of+dominica&biw=1440&bih=763&tbm=isch&imgil=Q4o13UsdXPBguM%253A%253BtYwhHciajCXRLM%253Bhttp%25253A%25252F%25252Fwww.caribbeanvolcanoes.com%25252Fdominica%25252Fradarmap.htm&source=iu&pf=m&fir=Q4o13UsdXPBguM%253A%252CtYwhHciajCXRLM%252C.&usq=__p7L6nJgripmY4skbpBNd2ktTZ3o%3D&dpr=1

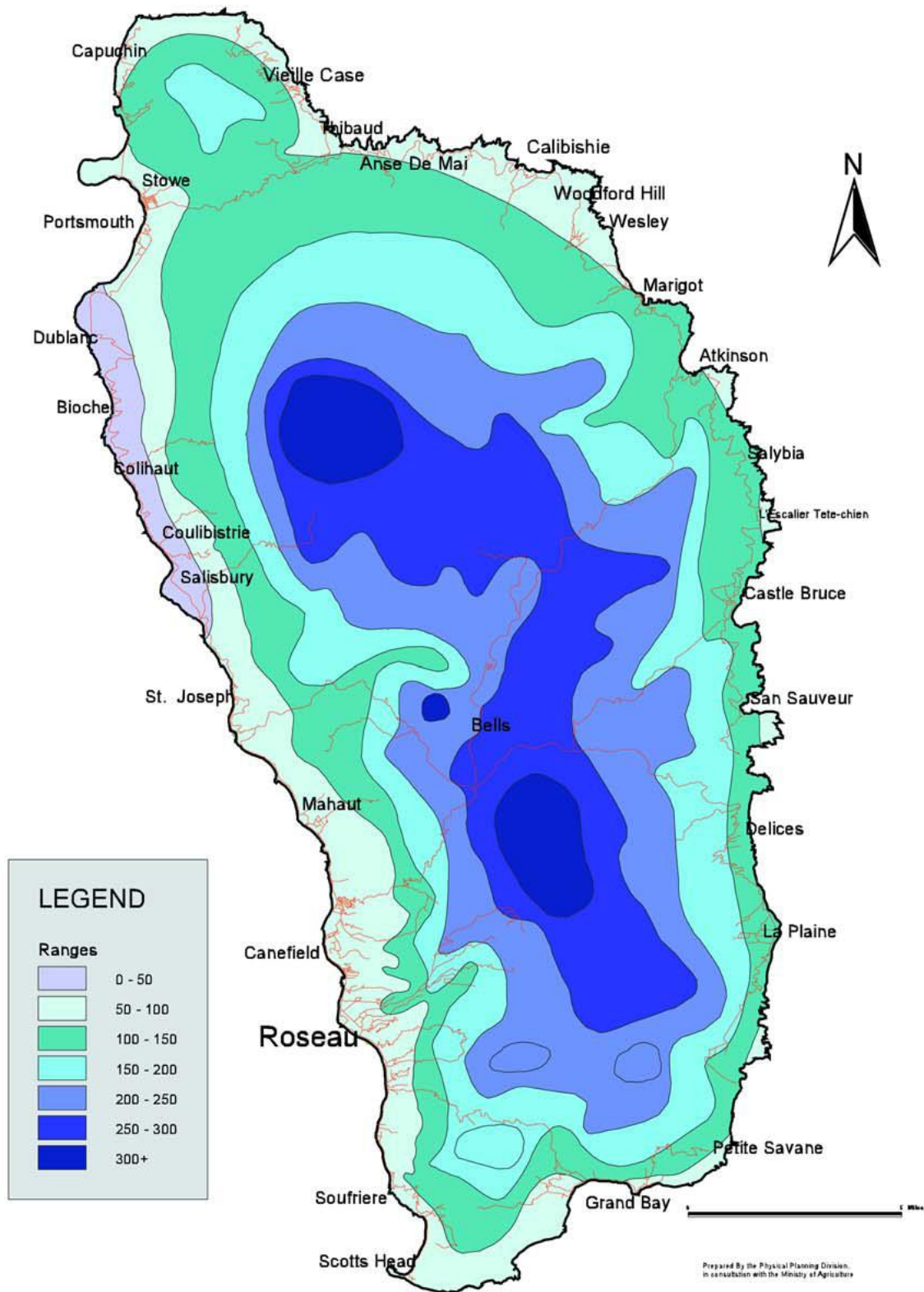


Fig. 3.5. Mean monthly rainfall (mm) for the Commonwealth of Dominica. Source: Agricultural Information and Communication Unit (AICTU) of the Ministry of Agriculture, Government of Dominica.

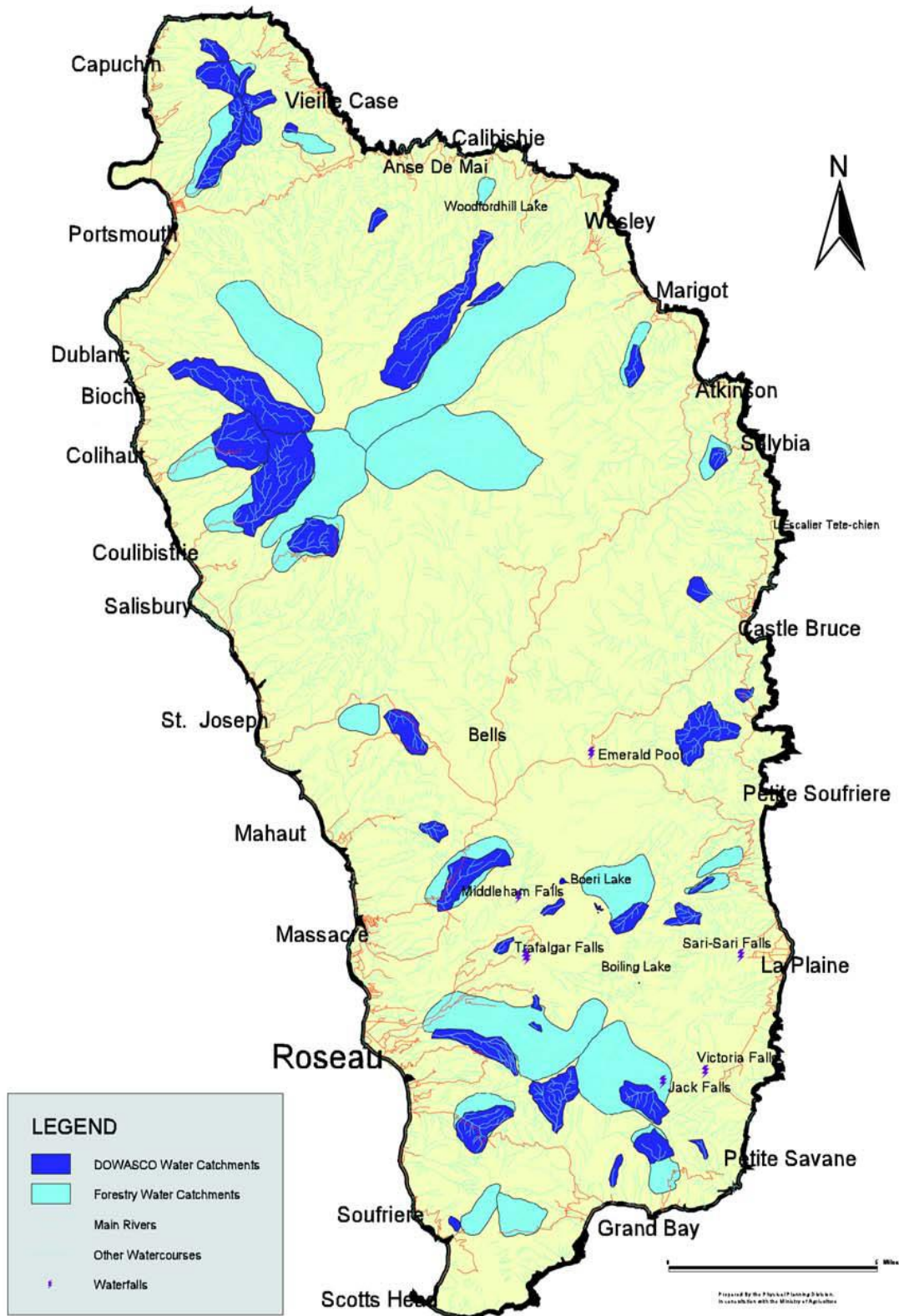


Fig. 3.6. Water Resources for the Commonwealth of Dominica. Source: Agricultural Information and Communication Unit (AICTU) of the Ministry of Agriculture, Government of Dominica.

3.4 Water, climate and hydrology

The island is dominated by a maritime tropical climate, which is characterised by little seasonal or diurnal variation with strong and steady trade winds (Smith et al., 2009a,b; Kirshbaum and Smith, 2009). The island can be classified as humid tropical varying from highly seasonal (west coast) and weakly seasonal (east coast) to perennially wet (in the interior) (Smith et al., 2009a,b; Smith et al., 2012). These variations in the amount and seasonality are reflected in the varied soil types (Fig. 3.9-3.10) and vegetation (Fig. 3.12) encountered in the island (Lang, 1967; Rouse et al., 1986; Goldsmith et al., 2010), and the island's rugged topography results in micro-climatic variability within very short distances (CCA, 1991, Smith et al., 2009a,b).

The main climatic characteristics includes relative humidity of about 95%, seldom falling below 85% in the interior (CCA, 1991), with little seasonal or diurnal variation; and high rainfall (4375 mm yr⁻¹) which is distributed between the wet season (between July and November) and the dry season (between February and June) (Lang, 1967). In essence, the country has a tropical rainforest climate and some areas border on a tropical monsoon climate with characteristically warm temperature and heavy rainfall (Fig. 3.5). Most of the island's ample supply of water (Hart Jr and Hart, 1969) is brought by the North-east trade winds (Fig. 3.6). Although rainfall amounts vary with location, rain is possible throughout the year, with the greatest monthly total recorded from July through November (Fig. 3.7).

Average yearly rainfall along the windward east coast frequently exceeds 5,000 mm, and exposed mountainsides receive up to 9,000 mm, among the highest accumulations in the Caribbean and the world. Totals on the leeward west coast, however, are only about 1,800 mm per year (Evans, 1986; Reading, 1991; CCA, 1991). Average air temperature is 27°C; maximum temperatures are 33°C and 27°C during the day on the coast and in the interior, respectively; minimum temperatures are 18°C and 12°C during the night on the coast and

interior, respectively (Lang, 1967; McSweeney et al., 2010). Relative humidity (RH) is closely tied to rainfall patterns, with the highest values occurring on the windward slopes and the lowest in sheltered areas. On the leeward coast relative humidity ranges between 64% and 74% with a mean annual of 70 percent. At night RH rises, particularly in the interior where temperature drops off markedly. The monthly mean sunshine hours is around 219 with a yearly total just in the range of 2,600 hours (Fig. 3.8).

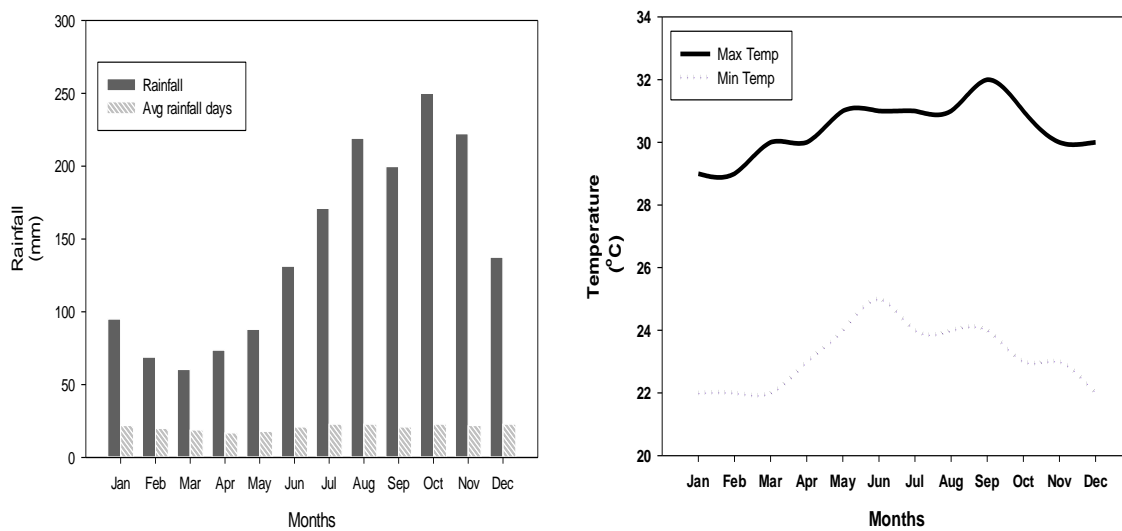


Fig. 3.7. Mean monthly rainfall with average number of rainfall days; and mean monthly temperatures of the Commonwealth of Dominica. Data compiled by the Dominica Meteorological Services. Data consist of 30 years monthly temperature averages for Canefield (West Coast) and Melville Hall (North-east Coast)

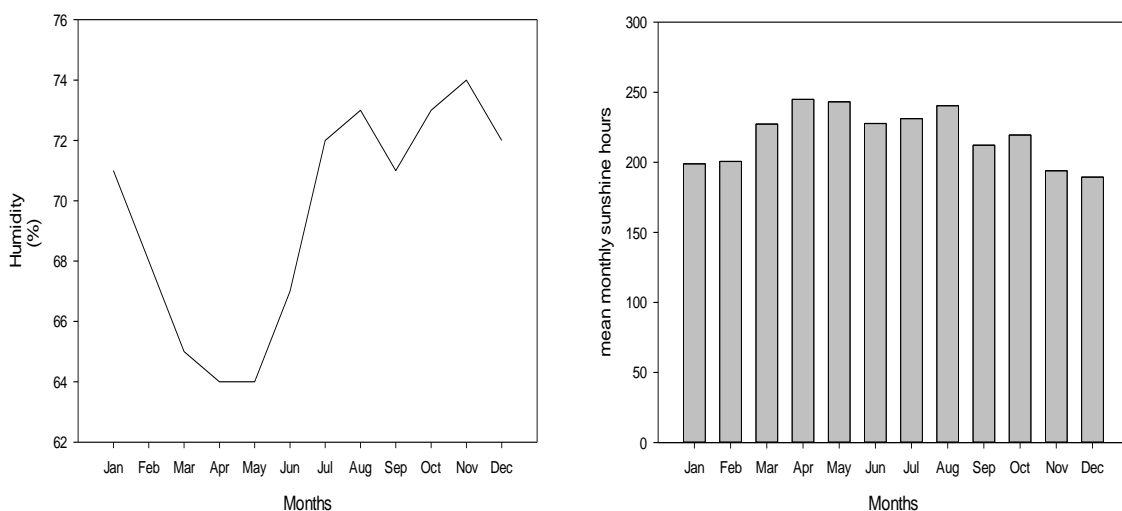


Fig. 3.8. Mean monthly humidity and mean monthly sunshine hours of the Commonwealth of Dominica. Data compiled by the Dominica Meteorological Services. Data consist of 30 years monthly temperature averages for Canefield (West Coast) and Melville Hall (North-east Coast).

3.5 Major soil types of Dominica

Edaphic conditions have been greatly influenced by the island's volcanic origin (Rouse et al., 1986; Reading, 1991; Goldsmith et al., 2010) and the relatively uniform and recent andesitic–dacitic eruptive history has led to variations in rainfall as being the dominant determinant for soil types (Lang, 1967; Goldsmith et al., 2010). Soils of a given type are in most cases a product of the extent to which volcanic parent material has weathered (Rouse et al., 1986; Reading, 1991; Goldsmith et al., 2010). Lang (1967) characterized 75 soil types, with 5 main groups: Deep strongly weathered allophanic and kaolinitic clay soils with good physical properties (51%); shallow soils over volcanic material (32%); montmorillonitic clay soils, usually shallow and with a silica pan (9%); deep weakly weathered sandy soils from volcanic pyroclastic (6%); alluviate soils (1%); other soils (1%). Furthermore, the distribution of soil types (Fig. 3.9-3.10) is largely a function of climatic factors which control the leaching effectiveness (Lang, 1967; Rouse et al., 1986; Reading, 1991).

The soils of Dominica have very high porosities (allophanes and kandoids 64-81%, smectoids 36-54%). The main types of surficial soils and their associated climatic regimes are: (1) montmorillonite/smectoid soils in the western coastlands which have a marked dry season, (2) kaolin/kandoid clays in the rain forest areas with a weak dry season, (3) allophane latosols in very wet mountainous interior, and (4) allophane podzolics in areas with greater than 7000 mm annual rainfall (Walsh, 1980; Rouse et al., 1986; Rouse, 1990).

In effect, the youthful relief and effectiveness of soil erosion are responsible in not allowing the development of allophanes into gibbsite (Fig. 3.9) along the evolutionary sequence of transformation (Lang, 1967; Rao, 1996), with soil depths on slopes commonly reaching 1.5 m but on ridge tops can exceed 3.0-4.0 m. Present day limit of development is affected by the degree of weathering and the intensity of leaching; increasing from seasonally dry to perennially wet.

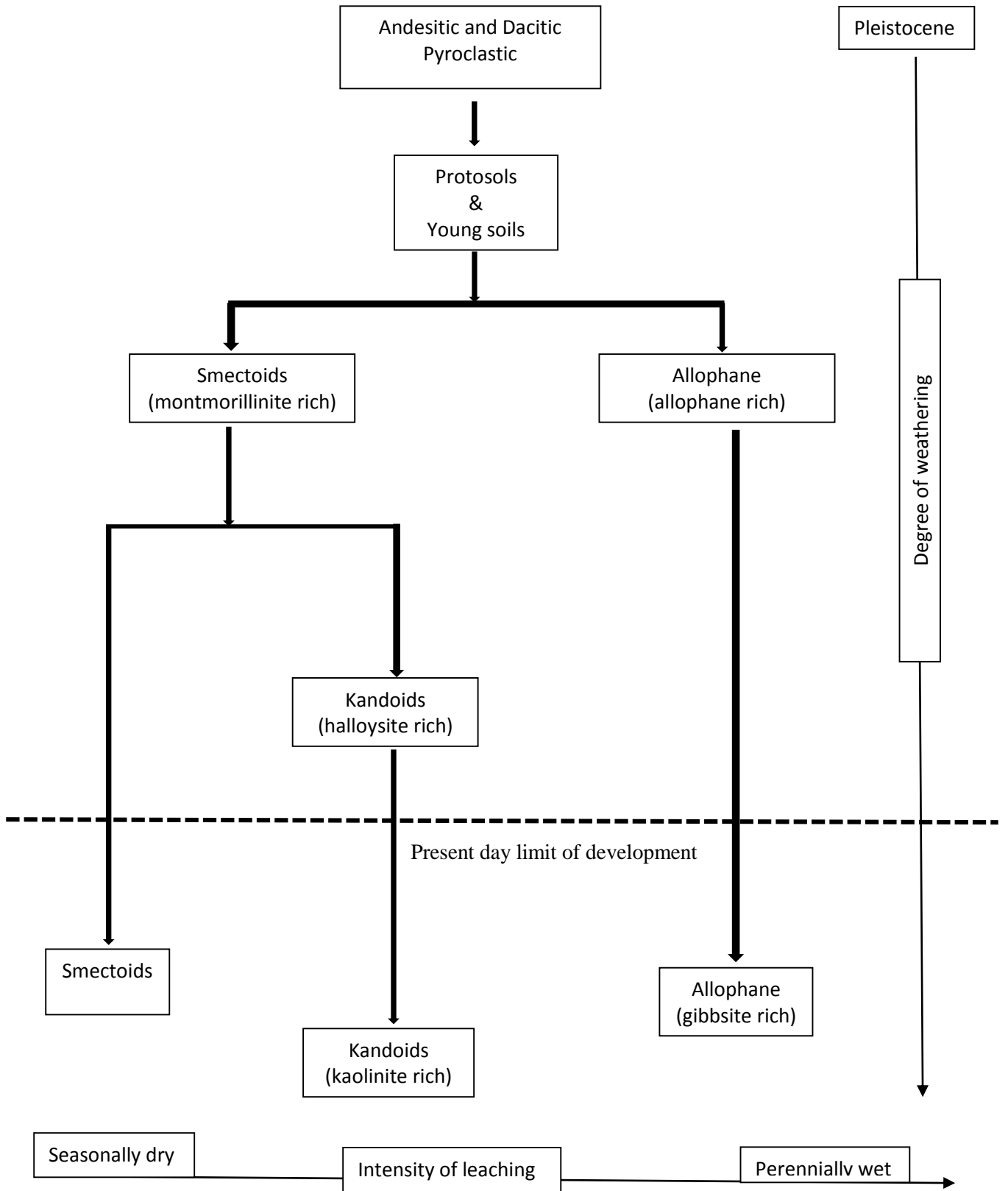


Fig. 3.9 Development sequence of tropical volcanic soils from the Commonwealth of Dominica (Adapted from Lang, 1967).

Soil-forming processes have been active on the island of the Commonwealth of Dominica since the end of the Pleistocene age (Rouse et al., 1986). The location of the island which lies virtually in the centre of the trade wind belt is strongly influenced by the frequent passage of low atmospheric pressure systems (Kirshbaum and Smith, 2009; Smith et al., 2009a,b), and these systems generate strong enough winds that causes mechanical weathering and translocation of particles in rain storms. On 29th August 1979 the island experienced one of the most severe hurricanes in the North Atlantic with wind speeds of over 280 km h⁻¹ and in excess of 200 mm of rainfall within an estimated timeframe of 10.2 hours (Lugo et al., 1983).

The eruption of Morne Trois Piton-Micotrin dated at ~ 28 ka is the largest volcanic event in the Antilles in the last 200 ka (Rad et al., 2013) and in the last 10 ka, seven volcanic centres have been active in the southern part of the island resulting in widespread tephra deposits (Carey and Sigurdsson, 1980; Sparks et al., 1980; Lindsay et al., 2003; Lindsay et al., 2005a,b). This is of extreme importance with regards to the role that acid precipitation following volcanism has on the degree of weathering. Fluorine is known to be found in high concentrations in rainwater on areas subject to degassing of volcanic gases into the troposphere and the formation of Al-fluoride complexes can enhance natural glass dissolution rates by an order of magnitude or more (Vacca et al., 2009) thus affecting the rate of soil formation. Due to its relatively young nature, these volcanic soils developed from these tephra deposits constitute an important resource for agriculture and forestry in Dominica. They exhibit unique properties and high productive potential apparently related to the amorphous materials they contain all which favour for strong root development and vigorous plant growth.

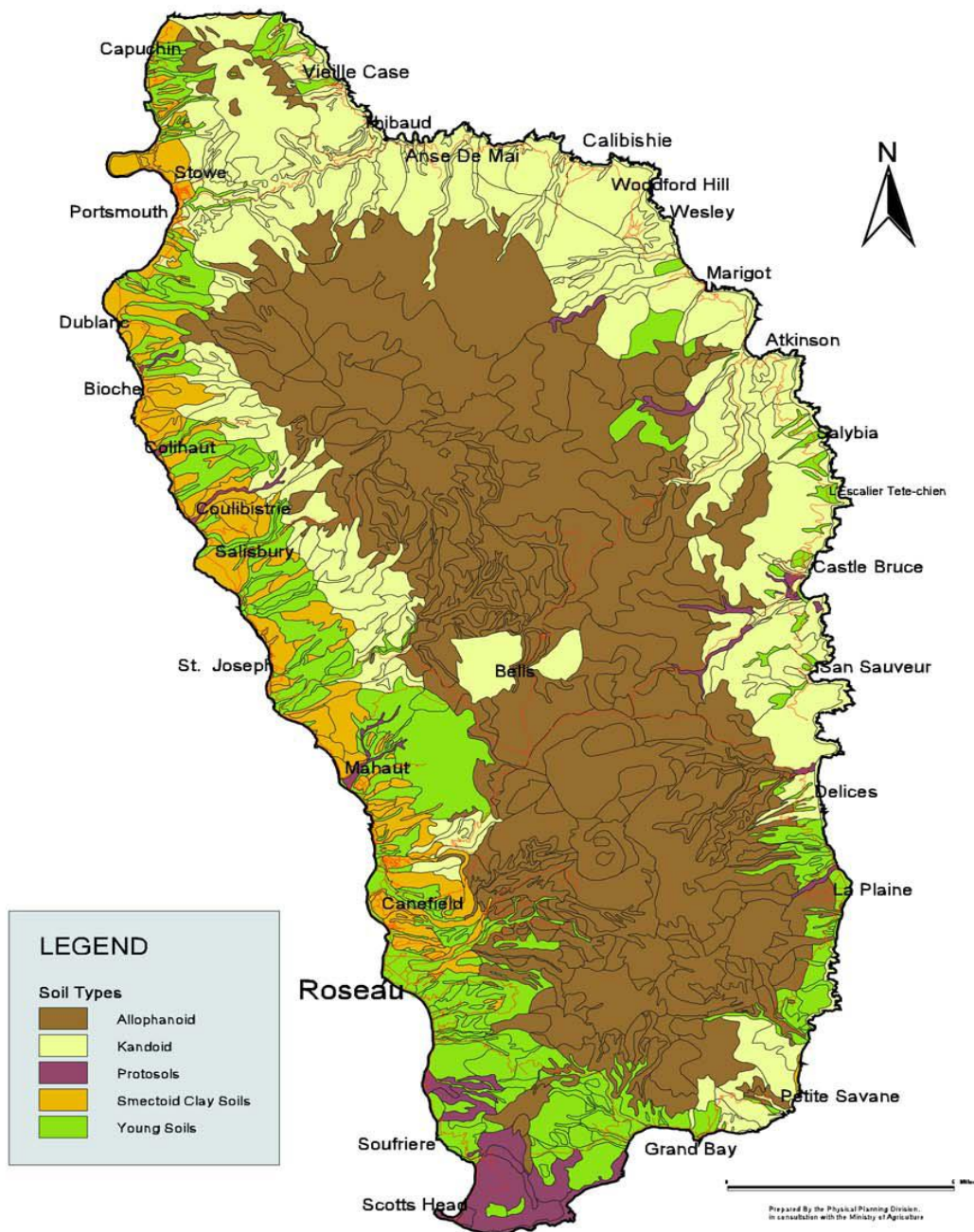


Fig. 3.10. General Soil types of the Commonwealth of Dominica. Source: Agricultural Information and Communication Unit (AICTU) of the Ministry of Agriculture, Government of Dominica.

The kandoid soils, developed from deep, little consolidated pyroclastics, occur in areas of high rainfall (2100-3750 mm) and a short dry season (Lang, 1967; Shillingford, 1972). According to Lang (1967) they show advanced weathering (stages 2+) and the production of kandoid clays. Leaching is moderate and uninterrupted favouring the development of

halloysite and eventually kaolin (Rouse, 1990). They take longer to develop than smectoids and allophanes and are found in the oldest volcanic areas where deep soils have developed. They are very permeable (porosities 0.66-0.79) with low subsoil dry unit weights (6-10 kN/m³) and no hard pans (Rouse, 1990). The nutrient characteristics of these soils are moderately good, for although some macro nutrients tend to be deficient and reports of the presence of manganese in toxic concentrations has been made (Lang, 1967), amendments are not likely to be difficult and reserves of nutrients are present.

Smectoid soils are found in the more seasonal western coastlands with less than 2100 mm rainfall where leaching is low and seasonal base removal incomplete (Lang, 1967; Shillingford, 1972). The resultant montmorillonite in conjunction with a cemented silica hard pan at the base of the B horizon makes these shallow soils very impermeable when wet (Rouse, 1990). Due to poor structure, aeration is generally poor and always relatively susceptible to erosion. These soils are moderately well weathered, usually with between 40-60% readily weatherable minerals weathered to matrix-size (weathering stages 2-4). The properties of these soils are dominated by the expanding lattice clay and the silica pan and often exhibit gley spots or gleying resulting from their self-sealing properties.

Allophane is the most abundant soil type encountered on the island of Dominica and is found in areas of high annual rainfall (4000+ mm) and no dry season where leaching is intense and continuous (Lang, 1967; Shillingford, 1972; Rouse, 1990). These are soils which are fairly well or well weathered with at least 40% of the readily weatherable primary minerals reduced to matrix-size clay minerals (weathering stages 1 and 2+) of allophanoid type.

The allophanoid latosolics are an extensive group and have a number of characteristics which require careful examination. They are normally without layers restricting root development, very highly permeable, of low bulk density and low strength. Although they mainly occur in steep slopes, in general they are remarkably difficult to erode in the natural

state, the surface humic horizon having considerable structural stability (Rouse, 1990; Reading, 1991; Rao, 1995) the root mat being extensive and the permeability very high. However, there is little doubt that if the humic horizon is destroyed the stability of the subsoil is markedly lowered (Lang, 1967). The chemistry of these soils indicates that nearly all the nutrients are concentrated in the organic matter. Therefore, loss of the humic horizon, through poor husbandry practices, would leave only a very efficiently leached subsoil.

A peculiar variant of allophane soil is found in the wettest parts of Dominica (>7000 mm annual rainfall). The allophanoid podzolic soil is the product of extremely high leaching and is characterized by deep litter and organic humic Ah horizons, a bleached highly leached subsoil, and about 0.45-0.50 m depth, a subsoil pan formed by accumulation of a complex of organic matter and amorphous sesquioxides (Rouse et al., 1986). The podzolics are frequently gleyed, with root restrictive pans, low bulk density, extreme poverty of nutrient supply, possibly toxic concentrations of aluminium and relatively low structural stability.

The young soils are immature soils freely to imperfectly drained with a relatively high content of unweathered, readily weatherable, primary minerals (not less than 60%, weathering stages 1 and 2) although allophanoid clay minerals are beginning to form in some quantity (Lang, 1967). These appear to be the stages of development in which glass disappears and the leaching of silica is most important. These soils are found mainly on youthful landscape elements or where thin mantles of recent ash overlies older topography, in all climatic zones.

3.6 Agricultural Potential and Land Use

The Dominican environment can be thought of as four zones, characterized by rainfall limits, each of which, because of climatic and soil characteristics, has its own set of land-use challenges (Lang, 1967). In areas less than 2032 mm per annum, the marked to strong dry season, not less than four months, and the dominance of protosols and stiff clay soils which have developed under these conditions determine the choice of crop. Some modifications are

possible if the high capital cost of irrigation can be borne, but drought resistant crops and conservation of moisture are more practical in these areas where the soil is usually shallow and often seriously degraded through former poor husbandry.

Rainfall areas from between 2032 – 2540 and up 4318 mm per annum are the most extensive zone in Dominica and at the moment is both the most used and the most favourable for agriculture, with a variety of fairly good soils of all clay types except smectoid and all weathering stages (Lang, 1967). To this extent, the concept of intensive agro-forestry systems has been suggested and large areas of relatively good soils remain uncultivated in these zones.

In areas of rainfall between 4318 – 6350 mm per annum, lack of water is not a problem, but excessive wetness may be. Temperatures are conspicuously lower than at the coast since most of the area is at 450 - 900 m altitude and it has been suggested that forestry is the best form of land-use although semi-permanents and tree crops will do well in areas where the rainfall is near 4000 mm.

In general crops will do better on the early weathering stages latosolics at lower elevations and on young soils where, despite high rainfall, unfertilized crops are surprisingly good, for example at Morne Prosper. Rainfall areas more than 6350 mm per annum coincide roughly with the mountain backbone of the island. It has been suggested that, until problems of high rainfall areas have been examined more closely, no further clearing be allowed in this area, with one very specific lowland exception, near Belles in the Layou Valley and on the nearby youthful glacia, where relatively youthful soils and higher temperatures offer more favourable conditions (Lang, 1967). This point of the conservative use of allophanoid podzolics for farming is further highlighted by the designation of protected areas in these high rainfall areas (Fig. 3.11), however there are recommendations for the establishment of field stations to study such productive potential.

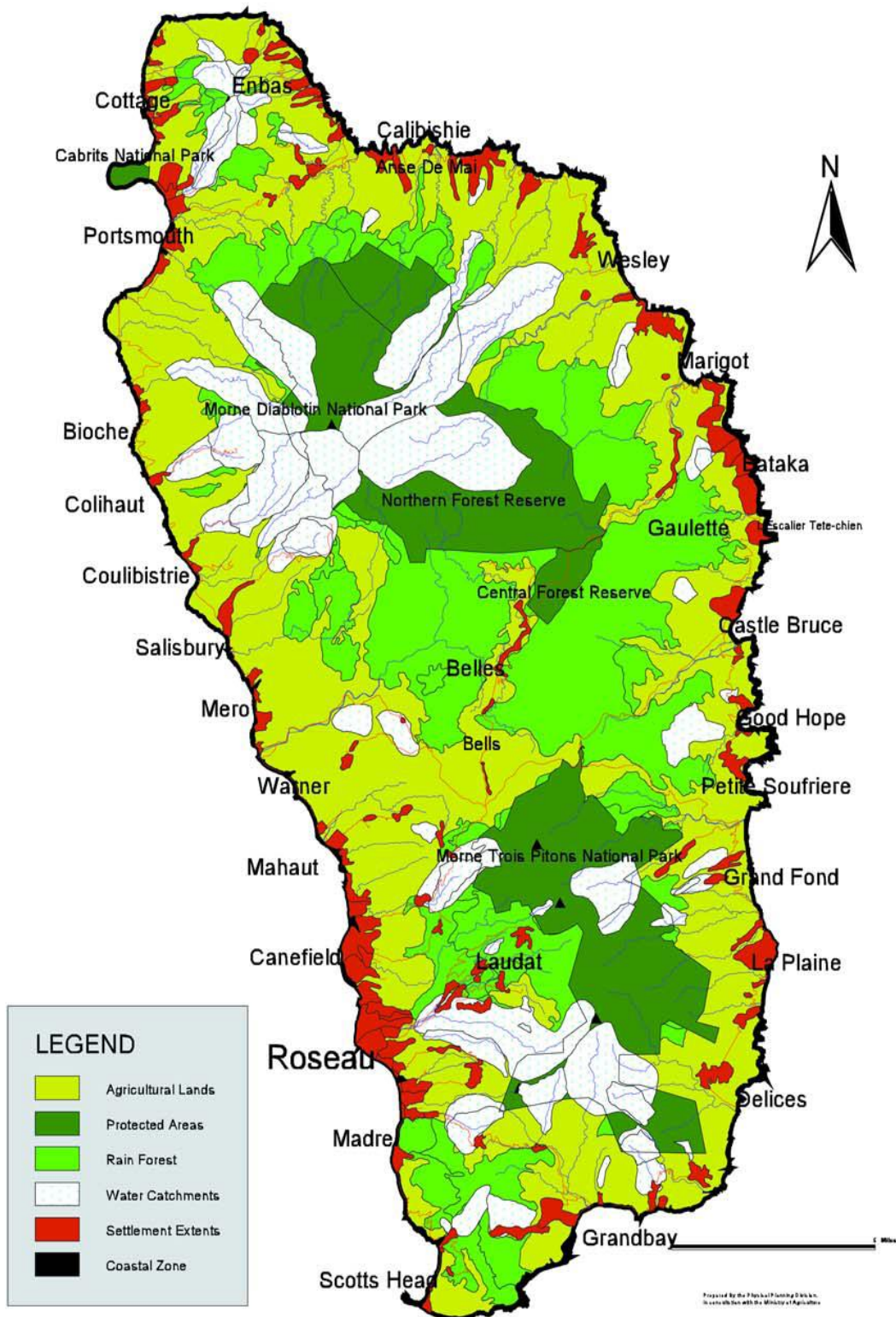


Fig. 3.11. Generalized land use of the Commonwealth of Dominica. Source: Agricultural Information and Communication Unit (AICTU) of the Ministry of Agriculture, Government of Dominica.

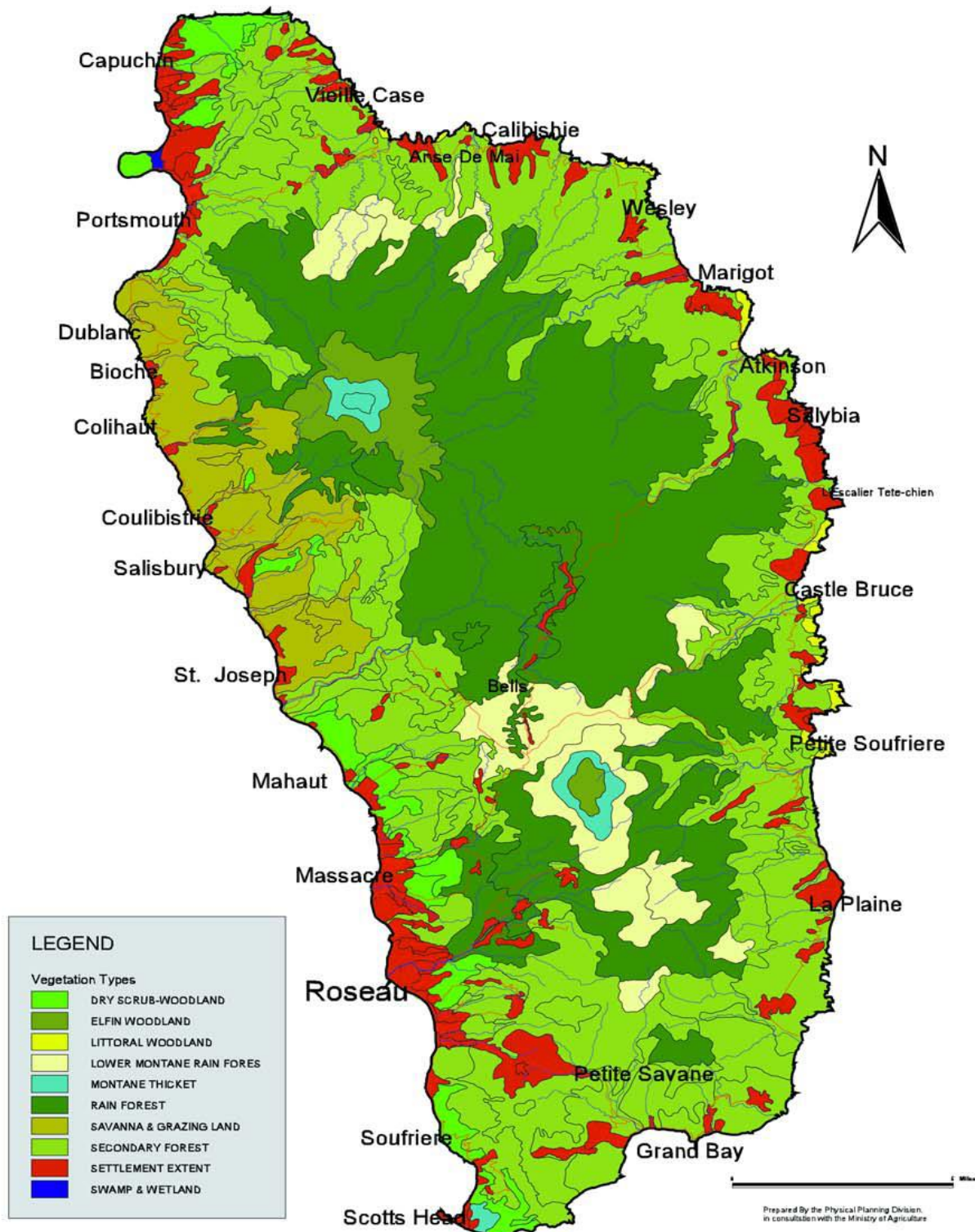


Fig. 3.12. Generalized Vegetation of the Commonwealth of Dominica. Source: Agricultural Information and Communication Unit (AICTU) of the Ministry of Agriculture, Government of Dominica.

3.7 Crop Production and Nutrient Use

The Commonwealth of Dominica is fundamentally an agrarian-based economy. The agriculture sector, despite significant decline in economic performance, continues to play a dominant role in the socio-economic development of the country (Payne, 2008; Peteru et al., 2010). Agricultural trade has been and continues to be a major factor determining food security outcomes in the Commonwealth of Dominica and a key driver of economic activity (Patterson et al., 2004). In recent times there have been increasing efforts towards a gradual conversion from a dependent synthetic input base agriculture to one which relies more on natural processes and one which incorporates more use of natural resources (Chesney et al., 2006; Boys et al., 2014) however that process has been extremely slow and plagued by a number of institutional and political challenges (Claxton, 2011).

Crop production is the primary foreign exchange earner in agriculture, accounting for 78.5% of all agricultural production, led by bananas which still accounts for an estimated 30% of total crop production. Agriculture production accounts for an estimated 12.2 % of total GDP but the sector has declined by an estimated 10.6% over the last two decades (BAM, 2012). The sector recorded an annual average decline of 0.6% from 2002 – 2007 and as a contributor to GDP declined from 18.3% in 2002 to 16.0% in 2007 of which crop production accounted for 11.3%. As at 2013, the WTO reported on agriculture's contribution to GDP as 10.5%. The sector has been subject to sharp fluctuations as it remains vulnerable to the vagaries of nature, as was again experienced on 27th August 2015 by the passage of tropical storm Erika, and other external shocks (trade liberalization). Nonetheless despite its declining role it has lent credible support to the GDP and remains a major driver for economic growth (Payne, 2006; Torgerson, 2010). With 26% of the population living in the rural community and 22% of the working population employed in the sector, a large part of the population directly or indirectly depends on income generated in agricultural related activities (CDB, 2010; BAM, 2012; WTO, 2013).

Trade and food security in the Commonwealth of Dominica are tied together through a variety of linkages rooted in the importance of exports and imports to this small vulnerable and open economy. On the one hand, export oriented economic activity (agricultural export) is a major source of foreign exchange and employment-based income-earning opportunities (linked to both the supply and accessibility dimensions of food security). Banana production is the single largest agricultural activity in Dominica, contributing 35% to agricultural exports and 11% total goods exports in 2009 (BAM, 2012). The banana industry has gone through dramatic structural changes such that in 1999, there were 6055 farmers who exported some 27,255 metric tonnes of bananas to the EU with a value of US \$14.31 million. By 2009, the number of farmers had fallen to 400 and the export tonnage to 5894 metric tonnes with a value of US \$3.21 million (BAM, 2012). On the other hand, imports to include the importation of agricultural inputs (Fig. 3.13), are equally critical to nutritional and stability dimensions of food security, as the country is a net food importer, net agri-inputs importer, and a net importer of agricultural technology.

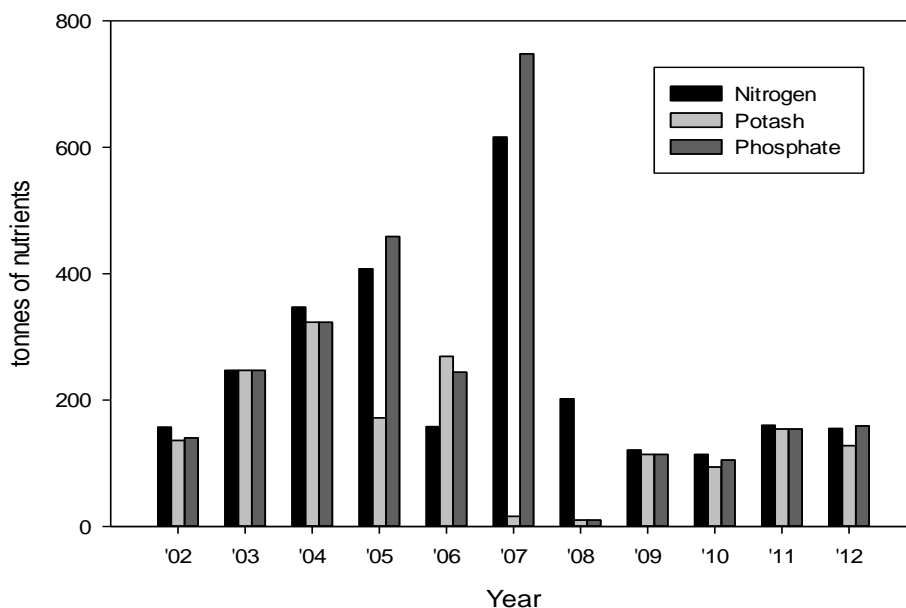


Fig. 3.13. Import quantity in nutrients into the Commonwealth of Dominica for the period 2002 to 2012. Nitrogen = N total nutrients; Potash = K₂O total nutrients, and Phosphate = P₂O₅ total nutrients. Data obtained from the Food and Agriculture Organization official database from questionnaires and/or national sources and/or COMTRADE. <http://faostat.fao.org/> Date accessed: 24 February 2015

The use of mineral fertilizer has drastically declined (Fig. 3.13) due, in part, to the contraction of the banana industry, where it was primarily utilized. To highlight this point, total fertilizer imports in 2007 were valued at US \$1,485,730.00 while in 2010 it plummeted to a mere US \$ 844,779.00 (FAO, 2015). To counteract this negative trend, the Government of the Commonwealth of Dominica (GCOD) has implemented duty concessions on the importation of fertilizers by up to 40% with the objective of increasing food production.

Nonetheless, at present, no integrated plant nutrient management system based on soil and plant analysis exist and farmers are forced to follow broad recommendations for fertilizer application. The extent to which this has affected productivity (Fig. 3.14) has yet to be ascertained but it's clear that more efficient use has to be made of available fertilizer stocks taking into account the use of appropriate types and quantities, as well as proper application techniques. However, the internal dynamic linkages is that increased food security will not be realized unless domestic producers are able to participate in increased trading opportunities and as such the production environment has to be stimulated and conducive to meet the required changes.

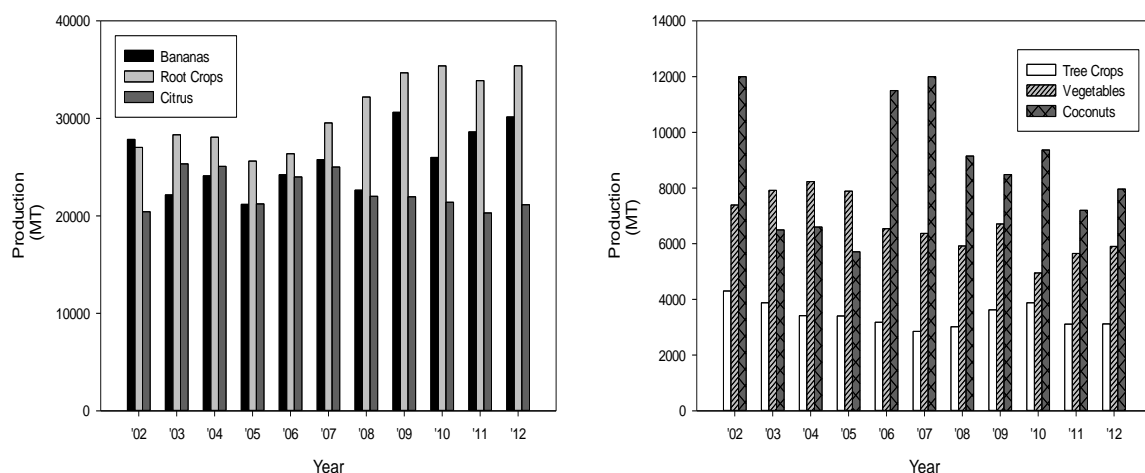


Fig. 3.14. Total production (Metric Tonnes) for some major economic crops from the Commonwealth of Dominica. Data obtained from the Food and Agriculture Organization official database from questionnaires and/or national sources and/or COMTRADE. <http://faostat.fao.org/> Date accessed: 24 February 2015

Nonetheless, within current times (February, 2015), the Government of Dominica has entered into a bilateral agreement with the Kingdom of Morocco to implement a “*Soil Fertility Mapping for Agricultural Development in Dominica and other Eastern Caribbean Islands*”. The project specifically aims to design and develop a Geo-referenced soil information and expert system; GIS-FertiDominica; fertilizer recommendations for major crops, and the establishment of a national fertilizer programme. The project is expected to develop the national technical capacity for maximizing farmer’s profits and enhancing farming efficiency while maintaining good environmental stewardship and re-enforcing the extension system in devising soil fertility and fertilization guidelines for major crops.

As a result, the enabling environment or current lack thereof critically affects the ability of Dominican producers to increase their productivity and/or switch to alternative activities successfully. Therefore, producers that are not able to participate in cost reduction/increased efficiency of operation, in the area where they are currently operating and have not prepared to be effective in alternative areas, could face increased food insecurity. Increases in food productivity globally have been determined largely by technological advances such as soil science and nutrient management, and the Commonwealth of Dominica like most other Caribbean countries have lost research and development capacity over the past two decades.

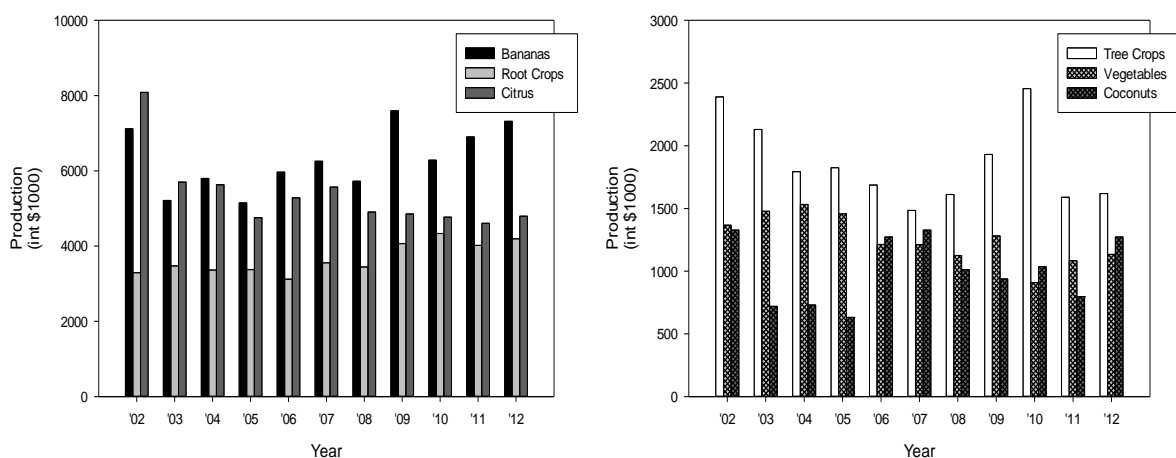


Fig. 3.15. Total production (int \$1000) for some major economic crops from the Commonwealth of Dominica. Data obtained from the FAO official database from questionnaires and/or national sources and/or COMTRADE. <http://faostat.fao.org/>. Date accessed: 24 February 2015

As has been highlighted, the banana sector has played a major role in the economy of Dominica (Fig. 3.15). Such a role has been captured directly in terms of production, employment and income, with significant indirect effects through multipliers (Moberg, 2005). However the banana industry has gone through various cycles of growth and depression over the last two decades and while there has been fluctuations in volumes, there has been a marked decline since 1993 which was a consequence of the loss of preferential treatment on the EU market. An important role of the banana industry in the Commonwealth of Dominica has been its direct contribution to commercial activity and economic growth which can be summed up in terms of trends of production and exports, number of active farmers, persons employed and revenues generated by the industry.

The non-banana sub-sector is dominated by root and tuber crops such as dasheen (*Colocasia esculenta*), yams (*Dioscorea* spp.), sweet potato (*Ipomoea batatas*), and tannia (*Xanthosoma sagittifolium*). The indigenous (Kalinago) people of Dominica have also traditionally cultivated cassava (*Manihot esculenta*) as a staple food crop. Tree crops include citrus (*C.sinensis*, *C.aurantifolia*, *C.paradisi*), coconuts (*Cocos nucifera*), avocado (*Persea americana*) and mangoes (*Mangifera indica*). A host of vegetables are produced but mainly for local consumption. The crop sub-sector also provides raw material for agro-processing and agri-business industries, earmarked to be major contributors to economic development. As a result, the country must proactively align itself to an agricultural development pathway which will see improved soil and land management, improved agricultural land use planning, new and improved agricultural technologies – e.g. phosphate fertilization programmes, increased soil analysis, crop diversification programmes based on land suitability and capacity mapping among others. The failure to do so will increase the risk for future generations in under-valuing the country's remarkable, common resource base and, by doing so, inadvertently allowing it to deteriorate and devolve into a diminished habitat for all Dominicans in the distant future.

3.8 Description of Study Sites

Table 3.1. Information on the soils studied, Commonwealth of Dominica

Location	Parent Material*	Taxonomy*	Land Use	Altitude** (m)	Rainfall* (mm)	Drainage*
Morne Prosper <i>61.18.334 W</i> <i>15.21.309 N</i>	Andesitic lavas compact agglomerates	Allophanoid Latosolic	Semi Intensive cultivated soil	357	4,798	Freely
Soufriere <i>61. 20.747 W</i> <i>15 14.584 N</i>	Andesitic-dacitic ash	Young Soils	natural pasture	60	2, 123	Freely- imperfectly
Castle Bruce <i>61 23.032 W</i> <i>15 24.570 N</i>	Andesitic agglomerate	Kandoid Clay	Semi-intensive cultivated soil	84	3,806	Freely
Pond Casse <i>61.23.344 W</i> <i>15.30.378 N</i>	Andesitic agglomerate	Allophanoid Podzolic	Semi-intensive cultivated soil	515	7,070	Imperfectly- poor
Layou Valley <i>61.23.825 W</i> <i>15.18.016 N</i>	Andesitic lavas	Allophanoid Latosolic	cultivated soil	393	6,384	Freely
Salisbury <i>61.26.432 W</i> <i>15.26.430 N</i>	Andesitic ash	Smectoid Clay	cultivated soil in fallow	65	1,636	Imperfectly- poor

(*Source: Lang, 1967; ** Altitude above sea level)

Rationale underlying the selection of the study sites

The study sites were chosen to best represent major agricultural production catchment areas in the Commonwealth of Dominica. Indeed the chemical characteristics of these soils were not fully known and subject to laboratory analysis. The sites were also selected to best represent climo and topo-sequences within the southern part of the island. It has been suggested within the literature that soil chronosequences, developed in contrasting environments, should more than likely provide useful information on the pedogenetic pathways of soil P (Walker and Syers, 1976). Hence the soils were as diverse as possible within major agro-ecosystems.

Such sequences consist of soils formed on the same or similar parent materials and are arranged in order of development brought about for example by increasing weathering and/or leaching due to greater age, and/or higher precipitation and temperatures and/or decreasing slope (Lang, 1967; Rouse et al., 1986; Reading, 1991; Goldsmith et al., 2010). Such sequences should be highly invaluable for understanding patterns of soil development and soil processes, and for answering nutritional problems associated with Dominican agriculture.

Morne Prosper: The farming community of Morne Prosper is located within the Roseau Valley catchment bordering the Morne Trois Piton world heritage site. Agricultural production is semi intensive to intensive and mainly centers around vegetable and culinary herb production (Fig. 3.16). It remains the single largest vegetable growing area in Dominica. The majority of crop production is performed by women who make up an estimated 70% of the farming population. The average age of the farmers is 40 years and most are full-time farmers with a primary education as their highest level of attainment. The average farming experience is estimated at 20 years. The average size farm is between 0.2 – 0.5 hectares with production being mainly rain-fed on gently sloping land. In a Participatory Rural Appraisal exercise conducted some years ago (2002), most farmers identified soil loss as a frequent phenomenon, especially due to high rainfall and windy conditions. This situation is even more prevalent where cultivation of crops is done down slope (against the contour) and outlet drains (storm drains) are constructed in a similar fashion, a custom that has been traditionally practiced in the area but evidently needs to change in order to reduce soil loss via erosion.

Soufriere: The southern village of Soufriere has been traditionally involved in citrus production with particular emphasis on West Indian limes (*Citrus aurantiifolia*). The village has also been traditionally involved in livestock rearing (cattle) due to the relative flat nature of its terrain (Fig. 3.17). With the introduction of the Citrus Tristeza Virus (CTV) during the late 1990's, the area lost 100% of its citrus productive capacity with most land gradually becoming abandoned. Currently there are renewed efforts in revitalizing this once vibrant productive base with the introduction of CTV resistant root stock material. The average farm size is between 0.3 – 0.6 hectares with production being mainly rain-fed. The majority of crop production is performed by men at an estimated 70% of the farming population. The average age of the farmers is 50+ years and most are full-time farmers with a primary education as their highest level of attainment. The average farming experience is estimated at 25 years.



Fig. 3.16. Landscape and crop production features of the MORNE PROSPER farming catchment highlighting culinary herbs and vegetable production as the base of the cropping system. (c) Irish Potato (*Solanum tuberosum* L.) has been recently introduced as an import substitution crop with similar efforts being geared towards onion (*Allium cepa* L.). Crop production as highlighted can be classified as being semi-intensive to an intensive system of production. Traditional land clearing activities leaving the soil bare (b,f) and coupled with high rainfall has serious implications for nutrient leaching as well as loss of soil.



Fig. 3.17. Landscape and crop production features of the SOUFRIERE farming catchment highlighting natural pasture with dairy cattle rearing. The remnants of a once thriving West Indian lime industry can be appreciated with a few scattered citrus trees still standing (c). The crater of the Soufriere volcano (Morne Plat Pays Complex) is also visible in the background (b). The Morne Plat Pays Complex consist of one of nine active volcanos on the island of the Commonwealth of Dominica.

Castle Bruce: The eastern farming community of Castle Bruce has been traditionally involved in banana production. It has some of the flattest lands in all of Dominica and crops like coconuts, cocoa and bananas were extensively planted in its valley and adjoining hillsides (Fig. 3.18). The community is also home to one of Dominica's 10 water catchment areas. During the recent past (mid 90's - 2001) both the Ministry of Agriculture and the now defunct Dominica Banana Marketing Corporation (DBMC) in particular, made a significant investment to bring approximately 40 hectares under irrigation mainly to enhance productivity in banana. However, of great concern is the apparent lack of measures in place with respect to drainage linked to irrigation schemes. Nonetheless, increased soil salinity is not expected to occur due to the high rainfall experienced during the wetter period of the year. The average farm size is between 0.8 - 2.0 hectares. Crop production is performed by an estimated 60% of male farmers. The average age of the farmers is estimated at 60+ and most are full-time farmers with a primary education as their highest level of attainment. The average farming experience is estimated at 25 years.

Pond Casse: The centrally located farming catchment of Pond Casse is situated at the foot hills of the Morne Trois Piton world heritage site, bordering with the southern forest reserve. The area is relatively flat and is covered with several trees and shrubs (Fig. 3.19). Being in the rainforest buffer zone, it is ideally suited for environmentally benign activities like camping, light farming or other eco-friendly use. Because of its cool environment, the area has a long history with citrus cultivation. However, within recent times, the introduction of roots and tubers (*Colocasia esculenta*) and Anthurium lilies has been a common sight on its landscape. The farming population is made up of 75% men and 25% women. The average age of farmers is estimated at 45 years with about 50% involved on a part-time basis. The average farming experience is estimated at 18 years with the average farm size between 0.4 to 1.2 hectares.



Fig. 3.18. Landscape and crop production features of the CASTLE BRUCE farming catchment highlighting Banana and Coconut production. With relative flat land coupled with a functional irrigation system has led to the adoption of crop production under controlled conditions (greenhouses) as well as the cultivation of non-traditional crops such as sweet corn (f). With topography not being a significant constraint coupled with the abundance of natural pasture and grasses, the farming catchment has also been traditionally involved in beef cattle rearing to supply the domestic market.



Fig. 3.19. Landscape and crop production features of the POND CASSE farming catchment highlighting Banana and Colocassia production. High rainfall coupled with a clay hard pan in the subsoil has seen the proliferation of a number of fern species in this wet and humid environment. Traditional land clearing activities leaving the soil bare and coupled with high rainfall has serious implications for nutrient leaching as well as loss of soil.

Layou Valley: The Layou Valley has traditionally been a high banana and citrus production belt. This farming zone is also home to one of Dominica's 10 water catchment areas. Banana cultivation is still prevalent but in recent times the introduction of roots and tubers (*Colocasia esculenta*) has been gaining momentum in terms of acreage expansion (Fig. 3.20), however significant productive acreages have been left abandoned to semi-abandoned following the decline in the banana industry. Layou Valley is a very broad catchment area, geographically located near the Layou River - the island's longest river (23.55 km). This area is made up of numerous small catchment areas to include Caffé, Clarkhall, and the Hillsborough estate at lower elevations; Goulde and Cassada Garden at mid level and Layou Park, Neiba, Crowne, Chappara and Atlee at the highest elevations. The average farm size is estimated at 2.1 hectares, with farming operations carried out by 77% male and 23% female. Young farmers (>35 years) accounts for an estimated 7%. An estimated 15% of farms are operated by farm families with an estimated 3% being full-time farmers. An estimated 69% of these farmers are between the ages of 35-65 years. The average farming experience is estimated at 15+ years.

Salisbury: The western community of Salisbury has been a major producer of tree crops including, citrus, mangoes, and bananas (Fig. 3.21). This farming catchment was the first of its kind to introduce the technology of protected agriculture via the utilization of greenhouse structures. In addition the catchment was also instrumental in first conducting field trials with the introduction of onions as an import substitution crop. However in recent times there has been a gradual shift in land use more towards dwelling construction. Nonetheless, 70% to 80% of farms are operated by farm families with an estimated 80% being full-time farmers with an estimated 10% being female farmers and an estimated 30% being youth. The farmers are between the ages of 18-75 years farming on an average 2.02 hectare farm; an estimated 65% of these farmers are between the ages of 35-65 years. The average farming experience is estimated at 20 years.



Fig. 3.20. Landscape and crop production features of the LAYOU VALLEY farming catchment highlighting Banana and Colocassia production. In the last two decades there has been a concerted effort in diversifying the productive base primarily driven by pineapple cultivation (f). The topography of the area with relative vast amounts of flat land has significantly favoured the adoption of pineapple cultivation as an alternative economic crop complementary to banana production.



Fig. 3.21. Landscape and crop production features of the SALISBURY farming catchment highlighting open field vegetable production. During the relative dry months of February to May, open field tomato and pumpkin cultivation is a common sight on the landscape. The marked dry season means that rain fed is not viable and as such on-farm irrigation schemes are necessary to compliment crop cultivation.

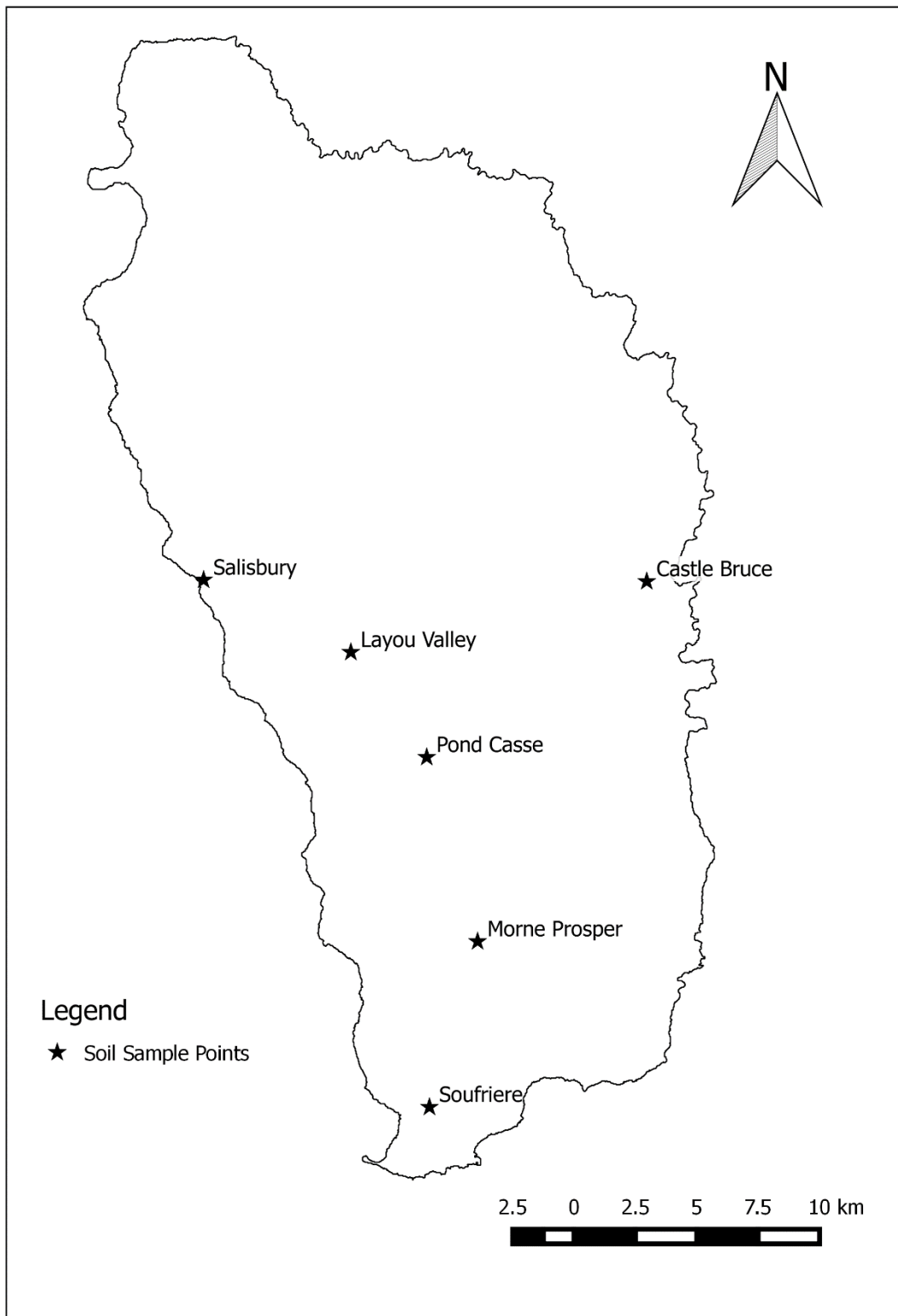


Fig. 3.22. Location of the six soil sampling sites under study. Sites represent some major agricultural production zones within the Commonwealth of Dominica. The sites were also selected to best represent climo and topo-sequences within the southern part of the island

Soil samples were collected during April 2013 (Fig. 3.22). Six sites were selected at which soil samples were taken from surface soil and sub-surface soil from different geographical locations representing different soil types according to the classification of Lang (Lang, 1967). At each site, a soil auger (50.8 mm diameter) was used to take samples from the uppermost 0–0.2 and 0.2– 0.4 m layer at ten different points spaced at 30-m intervals on a zig-zag line transect. The geophysical characteristics of the sample sites were described and soil samples were thoroughly mixed then taken for air-drying and preparation for shipment.

Because the properties that might affect the rate of reaction were unknown, requests to those colleagues who collected the soils specified only that the soils be surface soils (0-0.2 m) and sub-surface soils (0.2-0.4 m), that they be either low in available phosphate and/or unfertilized with phosphate, and that the soils from each region be as diverse as possible.

CHAPTER 4

THE EXPLORATION OF SOIL CHEMICAL AND PHYSICAL PROPERTIES IN THE COMMONWEALTH OF DOMINICA: DEVELOPING BASELINE DATA TOWARDS A NEW BENCH MARK

Abstract: The volcanic soils of the Commonwealth of Dominica were first studied in a relatively detailed way in 1967. The report which followed was part of a wider scheme undertaking soil surveys across all the territories of the British or former British West Indies which commenced in 1947. Since then, a number of contemporary studies in Dominica have been undertaken within the general thematic area of volcanism, geothermal and geochemistry which has added insights to the country's soil properties. However, with the paucity of current information there is an urgent need to develop up-to-date soil datasets which will enable farmers, agriculture technical personnel as well as policy makers to implement land use strategies guided by edaphic information with regards to the soil's productive capacity and limitations. With its unique climatic conditions and given the difficult challenges with regards to its very steep and finely dissected topography, which accounts for a significant percentage of the country's agricultural productive base, the development of soil maps with soil boundaries becomes even more of an imperative in order to guide agricultural development and implement suitable management systems.

In this regard, the objective of this study is exploratory in nature. It aims at developing baseline information on the soil's chemical and physical properties and characteristics distributed across six sites and thus builds the foundation for the rest of the thesis and for future research. The results reveal that the soils are moderately acidic, pH H₂O 5.38 (0.03), have low bulk density, 0.61 g cm⁻³ (0.01) with some showing a high accumulation of organic matter in the top soil, 10.63% (0.84). Soil porosity is good, 0.77 cm³ cm⁻³ (0.004) and water holding capacity is fair, 0.59 g g⁻¹ (0.03). Cation exchange capacity is moderate, 25.51 cmol(+)kg⁻¹ (1.01) and base saturation is low, 13.98% (0.28). There is a significant content of native Al, 20.2 g kg⁻¹ (0.99) while native P status is low, 205.7 mg kg⁻¹ (9.80).

Key words: Acidic, Fertility, Soil Analysis, Dominica

1. Introduction

Soil sampling and analysis is a valuable tool for both the farmer and the agricultural technician as it determines the inputs required for efficient and economic production (Franzen and Cihacek, 1998; Johnston et al., 2001; Jat et al., 2012). A well conducted soil test will help ensure the application of enough soil amendments to meet the requirements of the crop while taking advantage of the nutrients already present in the soil (Peverill et al., 1999; Naidu et al., 2008). The relevance of soil sampling and analysis is well known and documented and it has always been an important management tool in assessing soil fertility and plant nutrient management. In recent times the use of soil audits is being promoted to augment the approaches to plant nutrient management (Johnston, 2011) which will help improve the identification of economically optimum rates of nutrient requirements for sustainable cropping systems.

The economic importance of soil sampling and testing is even greater today in terms of using it as a risk management tool to maintain the soil's productive capacity while still making a profit (Johnston et al., 2001; Grote et al., 2005; Goulding et al., 2008; Jat et al., 2012; Hergert, 2014). The future of food security depends upon the attention paid to soil health and the conservation and efficient use of water (Swaminathan, 2005), and in this regard achieving and maintaining appropriate levels of soil fertility, especially plant nutrient availability, is of paramount importance if agricultural land is to remain capable of sustaining crop production at an acceptable level (Carter, 1993; Peverill et al., 1999; Naidu et al., 2008). Hence it can be fully appreciated that soil sampling and analysis is the first of three equally important steps in managing the nutrients required by plants. The second is the interpretation of the analytical data leading to the third step, recommendations for nutrient additions, as fertilisers or manures, to optimize crop yields while minimizing any adverse environmental impact from their application (Franzen and Cihacek, 1998; Johnston, 2011; Withers et al., 2015).

Doran and Parkin (1994) defined soil quality as “the capacity of a soil to function, within ecosystem and land use boundaries, to sustain productivity, maintain environmental quality, and promote plant and animal health”. Undoubtedly, the productive capacity of a soil thus depends on often complex and sometimes little understood interactions between the biological, chemical and physical properties (Gugino et al., 2009). The ultimate aim of good farm husbandry is to manage the various factors that make up each of these three properties in order to optimize the yields of crops in environmentally-friendly ways.

Agriculture as well as farm husbandry practices (Dumont et al., 2014) inevitably removes plant nutrients from the soil and from the farm. Consequently, if a farming system is to be sustainable, these nutrients have to be replaced by whatever sources are available (Syers, 1997; Fließbach et al., 2007; Bockstaller et al., 2008; Fragoulis et al., 2009). Excessive use of fertilizers especially nitrogenous and phosphate fertilizers may lead to environmental pollution such as eutrophication and nitrate toxicity of ground water (Sharpley et al., 1995; MacDonald et al., 2011; Schröder et al., 2011; Chien et al., 2011; Schindler, 2012; Yang et al., 2012). Therefore, soil testing provides sound information for recommending the application of fertilizers, and correct amount of chemical fertilizers to be integrated with organic amendments for improving the soil health and quality in order to increase farm productivity.

The integrated management of the soil’s physical, chemical and biological properties is only one part of best soil management practice, which also involves consideration of soil organic matter, soil structure, and the maintenance of a thriving soil microbial population. The other part entails the socio-economic dynamics which favours or limits the farmer’s willingness in adopting and/or adapting recommended policy. In addition, the knowledge, attitude and practice of the farmer as well as the agricultural technician (Adhikarya, 1994) thus becomes even more critical in helping address these edaphic challenges confronting agricultural production in small island economies like the Commonwealth of Dominica.

The quantity and availability of plant nutrient elements in the soil usually changes as a result of removal by the growing or harvested crop, leaching, erosion, or the addition of fertilizer, manure or compost (Robinson and Sharpley, 1995; Gruhn et al., 2000). As soil is a dynamic body and undergoes changes, it is advisable to test the soil periodically, within the confines of financial limitations and economic feasibility, for better environmental health and crop nutrition. The importance of soil testing is unequivocally clear, and if the soils of the Commonwealth of Dominica can be tested as often as is technically justifiable and financially viable, it will help in achieving scientific land use plans geared towards sustainable agricultural development in the years to come and thus improving on soil health and productive capacity.

Soil sampling and analysis is meant to be an aid to managing soil nutrients efficiently and to maintain soil fertility for those nutrients like phosphorus (P) in particular that are largely retained in the soil in non-plant-available forms. If the amount of this nutrient in such forms in soil is too low then crop yield could be severely compromised (Grote et al., 2005), but increasing reserves in agricultural soils to very high levels is an unnecessary expense (Wu and Babcock, 1998; Goulding et al., 2008). Thus the concept of increasing plant-available nutrients in the soil to critical recommended levels aided and guided by soil sampling and analysis as well as climatic conditions is of paramount importance.

In this regard, the objective of this study within this wider research is exploratory in nature. It aims at developing baseline information from which more exhaustively designed studies can be developed. As such it is expected that a number of the soil parameters currently being investigated will be correlated to other soil properties. The study further aims at identifying the soil constraints (i.e. acidity, deficiencies and chemical exchange of nutrients) and to better understand soil fertility limitations with the goal of improving nutrient management and developmental strategies geared toward increased crop production.

2. Materials and Methods

2.1 Determination of organic matter, C, N, pH, electric conductivity, particle size and hydro-physical properties, cation exchange capacity, and exchangeable cations.

Soil organic matter was determined by loss-on-ignition (LOI) as described by Ball (1964), Schulte and Hoskins (1996), and Robertson (2011). Soil pH (H₂O and CaCl₂) was analysed on a Hanna®™ pH meter model 209 using a soil-to-solution ratio (w/v) of 1:2, as described by Thomas (1996). Electric conductivity was measured on a Jenway®™ EC meter model 4520 using a soil-to-solution ratio (w/v) of 1:5, as described by Rhoades (1996).

Soil particle and textural analysis was done according to the hydrometer method after sieving through a 2 mm mesh (Bouyocous, 1962) using a Humboldt®™ (H-4241) hydrometer. This analysis together with bulk density determination was conducted at the Produce Chemist Laboratory of the Ministry of Agriculture, Commonwealth of Dominica during a second soil sampling and collection exercise undertaken by the author during the month of February 2014.

Total elemental analysis of the bulk soil (mg kg⁻¹ soil) for Al, P, Ca, K (as major elements) and Fe, Mn, Cu, Zn (as minor elements) was carried out using total reflection x-ray fluorescence (TXRF) on a S2 Picofox Bruker®™ TXRF spectrometer. This method was chosen because it has been shown to offer the capacity of multi-element detection, high detection power, minimization of systematic errors as well as simple and reliable calibration procedures (Gerwinski and Goetz, 1987; Michaelis and Prange, 1989; Maguí et al., 2010), coupled with low elemental interferences (matrix absorption and enhancement effects) (Dargie et al., 1997). Although there are limitations to include the need for recalibration of the spectrometer, an under estimation of P, S, and K, and Na and Mg not detectable (Stosnach, 2005; Stosnach, 2006; Towett et al., 2013), the method has been shown to produce results comparable with those of other commonly used methods such as AAS, ICPMS, GFAAS, ICPAES, and AFS (Maguí et al., 2010; Towett et al., 2013; Cherkashina et al., 2014).

Percentage carbon (%C) and percentage nitrogen (%N) was determined on a TruSpec®™ CN analyser (Leco Corp, St. Joseph, MI) and the C:N ratios were calculated accordingly. Exchangeable cations were determined according to the method described by Bertsch and Bloom (1996), Helmke and Sparks (1996), and Suarez (1996) as a precursor to the determination of cation exchange capacity (CEC). Procedurally, 5 g of air-dried soil sieved through a 2 mm mesh was weighed into a 50 ml centrifuge tube. 30 ml of 0.2 M NH₄Cl was added and tubes were shaken end-over-end for 5 minutes. Tubes were subsequently centrifuged at 3184 RCF for 10 minutes and the extractant was decanted into a 250 ml volumetric flask. This process was repeated four more times and the extractant was finally made to volume (250 ml) with 0.2 M NH₄Cl. Exchangeable cations were then determined by Atomic Absorption Spectroscopy on a Varian™® Spectra AA – 220 FS.

Cation exchange capacity was determined according to the method of Sumner and Miller, (1996) using a neutral un-buffered salt (NH₄Cl) based on the original method developed by Schofield (1949). Procedurally, 5 g of air-dried soil sieved through a 2 mm mesh was weighed into a 50 ml centrifuge tube. 30 ml of 0.2 M NH₄Cl was added and tubes were shaken end-over-end for 5 minutes. Tubes were subsequently centrifuged at 3184 RCF for 10 minutes and the extractant was decanted into a 250 ml volumetric flask. This process was repeated four more times and the extractant was finally made to volume (250 ml) with 0.2 M NH₄Cl. Furthermore, 30 ml portions of 0.04 M NH₄Cl were then added three times to the tubes containing soil samples. Tubes were re-suspended, shaken for 5 minutes, centrifuged and the supernatant discarded each time. After the supernatant was discarded at the end of the third and final addition of the 30 ml 0.04 M NH₄Cl, tubes were subsequently weighed to determine the volume of the entrained solution. Finally, 30 ml of 0.2 M KNO₃ was added, and tubes were re-suspended, shaken for 5 minutes, centrifuged and the supernatant collected in a 250 ml volumetric flask. This process was repeated a further four times with the supernatants being

combined and made up to volume. The collected solution was then analysed for NH_4^+ on a Biotek™® Powerwave XS microplate spectrophotometer according to the method of Mulvaney (1996) as well as for Cl^- on a Sherwood™® chloride analyser model 926, according to the method of Frankenberger et al., (1996).

Calculations:

$$CEC = 0.2775 \times \text{NH}_4^+ - 0.80 \times V_{en} \quad [3]$$

Where $\text{NH}_4^+ = \text{NH}_4^+$ in KNO_3 extract in ml L^{-1}
 $V_{en} =$ volume of entrained solution in ml.
 $CEC =$ Cation exchange capacity in $\text{cmol charge kg}^{-1}$

$$AEC = 0.14 \times \text{Cl}^- - 0.8 \times V_{en} \quad [4]$$

Where $\text{Cl}^- = \text{Cl}^-$ in KNO_3 extract in milligrams per liter
 $V_{en} =$ volume of entrained solution in millilitres
 $AEC =$ anion exchange capacity in centimoles of anion charge per kilogram

2.2 Calculation of bulk density, porosity, volumetric and gravimetric water content, millimetres of water per metre of soil, soil water pore space and effective saturation.

The calculation for the above soil properties was done following the procedures of the United States Department of Agriculture – Natural Resource Conservation Service, University of Nebraska Lincoln Extension Service (UNL, 2014):

$$2.2.1 \text{ Bulk Density } (g \text{ cm}^{-3}) = \frac{\text{oven dry soil (g)}}{\text{soil volume cm}^3} \quad [5]$$

$$2.2.2 \text{ Porosity } (cm^3 \text{ cm}^{-3}) = 1 - \frac{\text{Bulk Density}}{\text{Particle density (PD)}} \quad [6]$$

Where PD is a default value based on the average bulk density of rock with no pore space (2.65 g cm^{-3} constant).

$$2.2.3 \text{ Soil Gravimetric H}_2\text{O } (g \text{ g}^{-1}) = \frac{(\text{wt.of wet soil} - \text{wt.of dry soil})}{\text{wt.of dry soil}} \quad [7]$$

$$2.2.4 \text{ Soil Volumetric H}_2\text{O } (g \text{ cm}^{-3}) = \text{soil gravimetric H}_2\text{O} \times \text{BD} \quad [8]$$

$$2.2.5 \text{ mm of H}_2\text{O m}^{-1} \text{ soil} = \text{Volumetric H}_2\text{O} \times 1000 \quad [9]$$

$$2.2.6 \text{ Soil water filled pore space} = \frac{\text{Volumetric water content}}{\text{Soil porosity}} \times 100 \quad [10]$$

$$2.2.7 \text{ Effective Saturation} = \frac{\text{Volumetric water content}}{\text{porosity}} \quad [11]$$

2.3 Description of Study Site [refer to Chapter 3 for comprehensive details]

A comprehensive description of the study sites is provided in Chapter 3 entitled “Geophysical description of the Dominican environment and general characterization of study sites” and as such no further mention will be made.

2.4 Soil Sampling

Soil samples were first collected during the month of April 2013. Six sites were selected from which soil samples were taken from surface soil and sub-surface soil from different geographical locations representing different soil types according to the national soil survey (Lang, 1967). At each site, a soil auger (50.8 mm diameter) was used to take samples from the uppermost 0 - 0.2 m and 0.2 - 0.4 m layer at ten different points spaced at 30-m intervals on a zig-zag line transect.

Because the properties that might affect the rate of reaction were unknown, requests to those colleagues who collected the soils in April 2013 specified only that the soils be surface soils (0-0.2 m) and sub-surface soils (0.2-0.4 m), that they be either low in available phosphate and/or unfertilized with phosphate, and that the soils from each region be as diverse as possible. Soil were chosen to best represent important agricultural soils in the country, varying in drainage, soil type and soil chemical characteristics. Indeed the properties of available phosphate were unknown and subject to laboratory analysis.

2.5 Statistical Analysis

Sample analysis was done in triplicate with mean and standard error of the mean (SEM) calculated. Statistical analyses were performed using the SPSS version 20.0 for Windows program (SPSS Inc., Chicago, IL). A general linear model (ANOVA) was used to test for differences in means and generalized t-test to more than two groups. It was used to explain observations, and the observed variance in a particular variable could be portioned into components attributable to different sources of variation. The significance of differences among means was determined using Tukey's honest significant difference. Effect size was estimated as the proportion of the total variability that could be expressed by the treatment factor and was measured as a partial eta squared (PESq). The Pearson product-moment correlation coefficient was used as a measure of the degree of linear dependence between two variables. Mention of statistical significance refers to $\alpha = 0.05$ was used for type I errors, unless otherwise stated. All percentages are expressed on an air dry basis.

3. Results

3.1 Organic Matter

The analysis of variance (ANOVA) clearly demonstrate that the percentage organic matter (Fig. 4.1.1) in these volcanic soils was significantly different ($R^2 = 0.99$, $P < 0.001$) between the six contrasting sites ($F(5, 35) = 335.89$, $PESq = 0.99$). The difference was also significant between soil horizon ($F(1, 35) = 160.74$, $PESq = 0.88$), as well as the interaction between site and soil horizon ($F(5, 35) = 21.51$, $PESq = 0.83$). The overall mean was 10.6% (0.84) across all sites. The results tend to indicate that the organic matter content in these volcanic soils is apparently "high" and some authors have suggested that these Andosols have higher SOM levels than other soil types (Aguilera et al., 1997). However, changes in SOM has significant effect on the ratio of microbial biomass carbon to soil organic carbon (Sparling,

1992) which has implications for many soil processes such as mineralization and P acquisition (Robinson and Sharpley, 1995, 1996).

Post Hoc analysis detected four homogenous subsets and established that soils from Soufriere recorded the lowest SOM content with a mean of 5.28% (0.24), whilst soils from Pond Cassé, 16.94% (0.47) and Layou Valley, 16.81% (1.40) recorded the highest values (Fig. 4.1.1), which did not differ significantly from each other ($P = 0.999$). Similarly, the soils from Salisbury, 7.47% (0.20) and Castle Bruce, 7.36% (0.52) did not differ significantly from each other ($P = 1.000$). The soils from Morne Prosper had a mean value of 9.93% (1.38). These tropical volcanic soils in decreasing order (Pond Cassé, Layou Valley, Morne Prosper) showed a highly organic surface humus-accumulating horizon. These results are probably due in part to the high rainfall, abundance of flora and rapid decay of detritus material into humus, which is then retained.

In his field study, Lang (1967) reported that in these areas (i.e. Pond Cassé, Layou Valley, Morne Prosper) which are dominated by allophanoid clays, organic matter ranged between 20-30% and can even reach as high as 50%. On cultivating these soils, organic matter does not seem to be lost very quickly. It would seem that the organic matter of these soils is highly stable owing to the presence of Al-humus complexes and sorption of organic ligands onto amorphous minerals (Verde et al., 2005; Miyazawa et al., 2013). Thus, it appears that the accumulation of SOM in the topsoil of these allophanic soils is a key signature associated with their “andic” properties (Shoji et al., 1994; Neris et al., 2012).

3.2 Soil pH

Soil pH specifically affects plant nutrient availability by controlling the chemical forms of the various nutrients in the soil. The optimum pH range for most plants is between 5.5 and 7.0, however many plants have adapted to thrive at pH values outside this range.

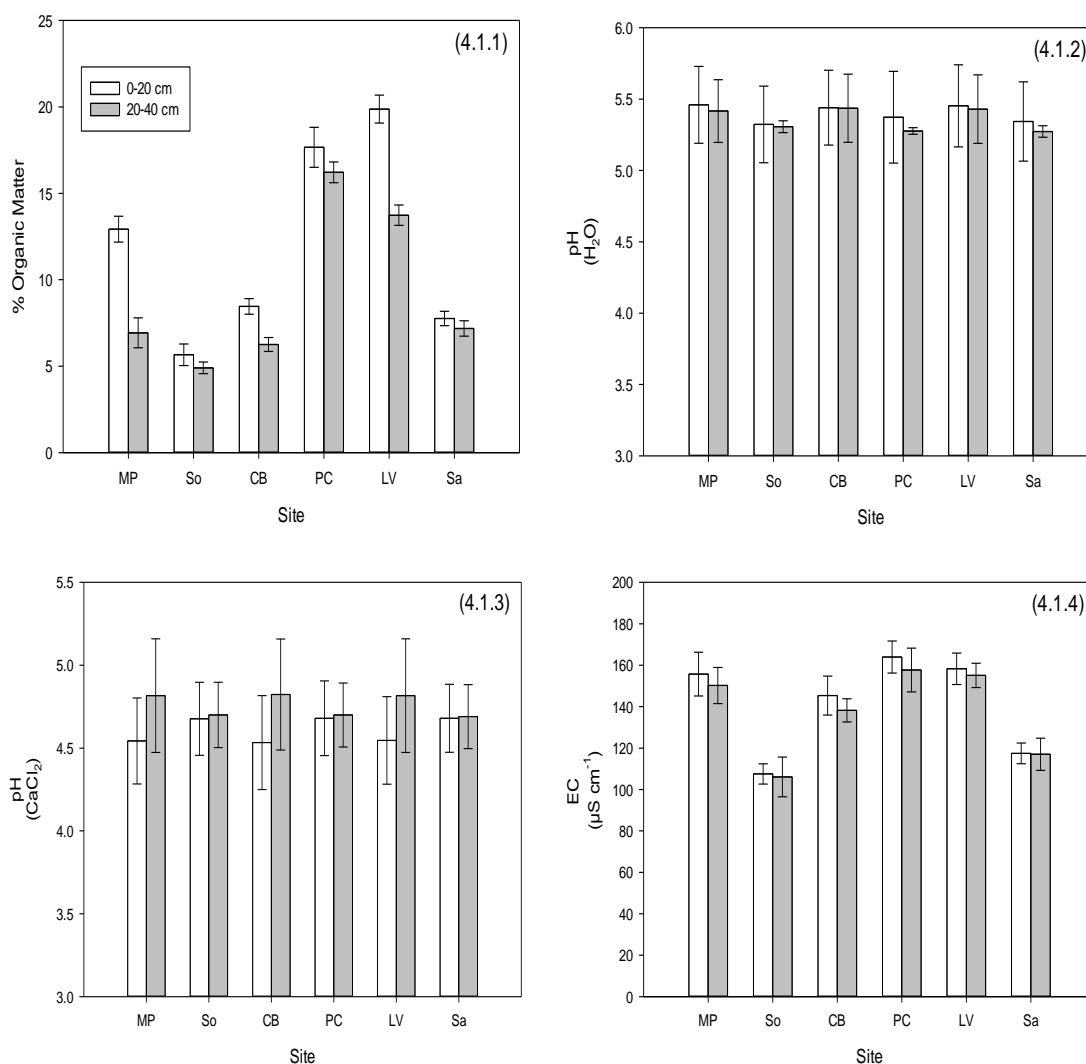


Fig. 4.1. Soil organic matter content, pH (H₂O), pH (CaCl₂), and electrical conductivity in six agricultural soils from the Commonwealth of Dominica. Values represent means and error bars indicate SEM. n = 36.

The results for pH both in H₂O (Fig. 4.1.2) and CaCl₂ (Fig. 4.1.3) indicate no significant difference between sites, soil horizon, and the interaction of sites with soil horizon. However values recorded for pH (CaCl₂) generally showed a tendency to be more acidic and lower but not by a constant factor. The overall mean pH (H₂O) and (CaCl₂) were 5.38 (0.03) and 4.68 (0.04) across all sites respectively. The difference in pH (0.7 pH units) may be due in part to both the displacement of Al³⁺ from the exchange complex and to increased hydrolysis of various kinds of Al species in the presence of CaCl₂ and as such displaces a higher percentage of the exchangeable H⁺ (Ragland and Coleman, 1960; Lierop and Mackenzie, 1977; McLean, 1982).

In essence, the lower soil pH associated with the salt solutions compared with water can be attributed to the increasing ionic strength of CaCl_2 and its effectiveness in compressing the electrical double layer and the activity of various cations in exchanging with these cations present on the soil exchange complex (Lierop and Mackenzie, 1977; Ross and Bartlett, 1996; Prado et al., 2007; Kissel et al., 2009). Hence, values for exchangeable hydrogen would normally tend to be lower for the less acidic soils and higher for the more acidic soils.

3.3 Electrical Conductivity

The ANOVA results for electrical conductivity (Fig. 4.1.4) showed significant differences ($P < 0.001$) between sites ($F(5, 35) = 44.38$, $R^2 = 0.91$, $\text{PESq} = 0.91$) but failed to detect significant differences between soil horizon as well as the interaction of site and soil horizon. The overall mean was $139 \mu\text{s cm}^{-1}$ (3.64) across all sites. Post Hoc analysis differentiated three homogeneous subsets and revealed that soils from Soufriere, $106 \mu\text{s cm}^{-1}$ (2.80) and Salisbury, $117 \mu\text{s cm}^{-1}$ (2.39) recorded the lowest EC values, not significantly differing from each other ($P = 0.280$). Contrarily, soils from Morne Prosper, $153 \mu\text{s cm}^{-1}$ (3.74), Layou Valley, $157 \mu\text{s cm}^{-1}$ (2.58), and Pond Cassé, $161 \mu\text{s cm}^{-1}$ (3.66) recorded the highest values which did not differ significantly from each other ($P = 0.57$). However, soils from Morne Prosper and Castle Bruce, $142 \mu\text{s cm}^{-1}$ (3.25) also did not differ from each other ($P = 0.215$) and constituted a separate subset.

The soil's electrical conductivity is a parameter of natural and artificially created electrical fields influenced by distribution of mobile electrical charges, mostly inorganic ions (Pozdnyakova, 1999). This parameter is of critical importance in terms of assessing the adequacy of leaching and drainage (Rhoades, 1996). Furthermore, the distribution of electrical charges is as a result of soil-forming processes and there are often significant relationships with other soil properties such as soil texture, bulk density, water content, cation exchange capacity,

humus content and base saturation (Pozdnyakova, 1999). Typically there is also good relationship between the permittivity of soil and its water content (Robinson et al., 2003).

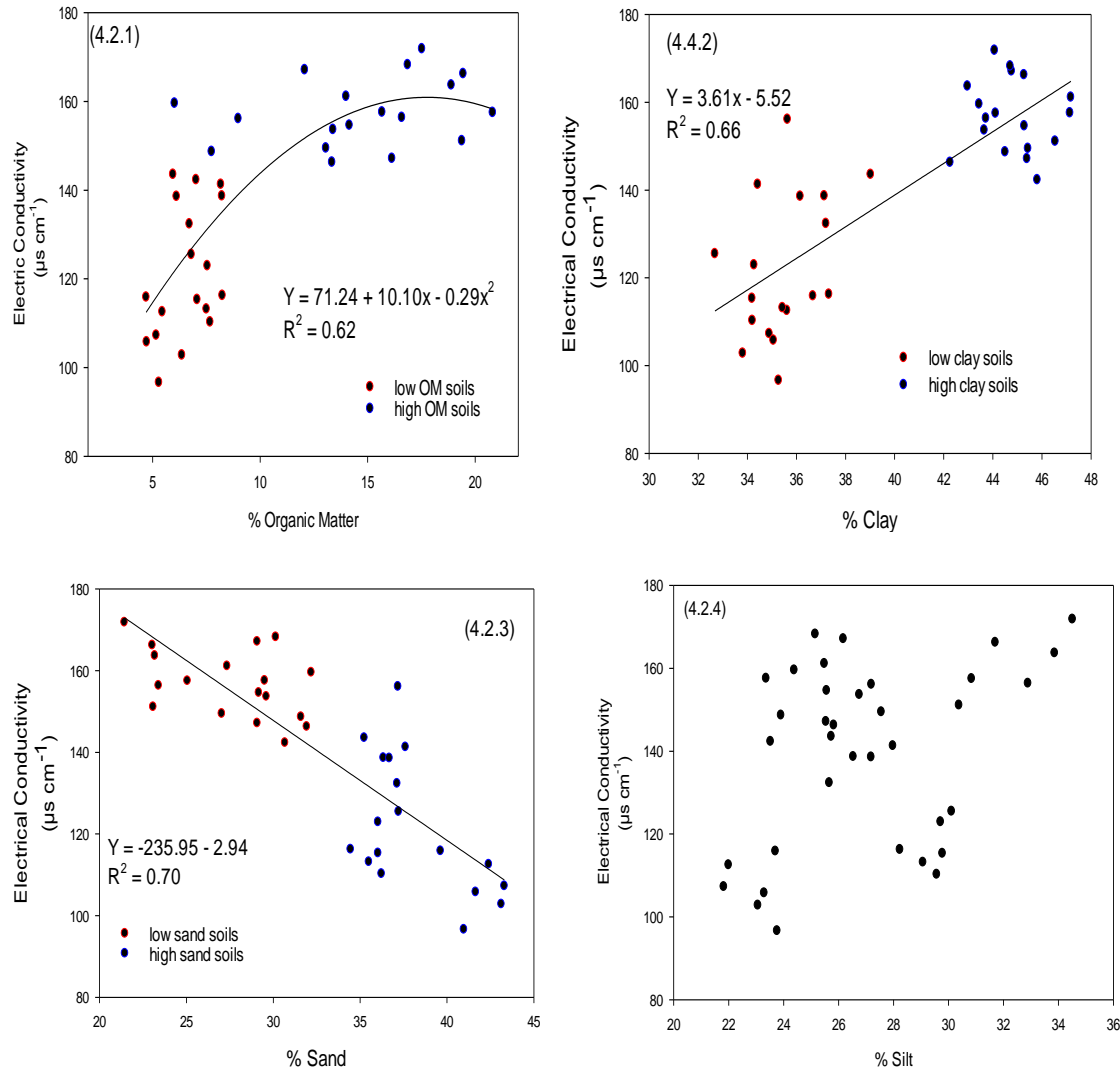


Fig. 4.2. Relationship between electrical conductivity and soil organic matter and soil clay, sand, and silt content in six agricultural soils from the Commonwealth of Dominica. n = 36, as grouped parameters.

The results (Fig. 4.2.1) also highlight significant ($P < 0.001$) positive relationships between electrical conductivity and organic matter, % clay, and % silt ($P < 0.05$). The results indicate a significant negative relationship with regards to percent sand content ($P < 0.001$). These results strongly suggest that the EC of these volcanic soils varies depending on the amount of moisture and cation exchange sites held by soil particles with clay particles having the highest conductivity, suggesting that EC correlates strongly to soil particle size and texture

(Rhoades et al., 1999, Noborio, 2001; Corwin and Lesch, 2003). However, Friedman (2005) was quick to point out that other factors such as bulk soil attributes, solid particle quantifiers, and soil solution attributes do not act independently and the combined effect of all influence soil EC and hence the ability of the soil to accommodate the transport of an electric charge.

3.4 Physical analysis

The ANOVA results (Fig. 4.3.1) of these volcanic soils revealed significant differences for sand content ($R^2 = 0.99$, $P < 0.001$) between sites ($F(5, 35) = 271.48$, $PESq = 0.98$); soil horizon ($F(1, 35) = 31.04$, $PESq = 0.59$), and the interaction between site and soil horizon ($F(5, 35) = 18.01$, $PESq = 0.80$). The overall mean sand content was 32.87% (1.04) across all sites. The Soufriere soils, 41.85% (0.57) recorded the highest sand content while soils from Layou Valley, 25.78% (1.01) and Pond Cassè, 26.12% (1.57) recorded the lowest values without significantly differing from each other ($P = 0.989$).

The silt content (Fig. 4.3.2) showed opposite trends with significant differences ($R^2 = 0.97$, $P < 0.001$) between sites ($F(5, 35) = 69.09$, $PESq = 0.94$); soil horizon ($F(1, 35) = 97.78$, $PESq = 0.816$), and the interaction between site and soil horizon ($F(5, 35) = 39.17$, $PESq = 0.90$). The overall mean silt content was 26.99% (0.55). Soils from Soufriere recorded the lowest value at 22.94% (0.34) whilst soils from Salisbury, 29.41% (0.27), Pond Cassè, 29.22% (2.06) and Layou Valley, 28.59% (1.12) recorded the highest values without significantly differing from each other ($P = 0.442$).

Opposing results were also obtained for the clay content (Fig. 4.3.3) in that there were significant differences ($R^2 = 0.97$, $P < 0.001$) between sites ($F(5, 35) = 122.31$, $PESq = 0.97$) but no statistical differences detected for soil horizon and the interaction between site and soil horizon. The overall mean clay content was 40.14% (0.82) across all sites. Soils from Layou Valley, 45.64% (0.44), Pond Cassè, 44.67% (0.60), and Morne Prosper, 44.07% (0.50) recorded the highest clay content without significantly differing from each other ($P = 0.209$),

whilst soils from Castle Bruce, 36.59% (0.64), Soufriere, 35.21% (0.38), and Salisbury, 34.68% (0.64) recorded the lowest clay content values at $P = 0.078$.

In relation to bulk density, there were significant differences ($R^2 = 0.92$, $P < 0.001$) between sites ($F_{95, 35} = 41.24$, $PESq = 0.904$) as well as between soil horizon ($F_{(1, 35)} = 27.70$, $PESq = 0.56$). There was no interaction between site and soil horizon. The overall mean bulk density was 0.61 g cm^{-3} (0.01) across all sites. Soils from Salisbury, 0.70 g cm^{-3} (0.01) and Soufriere, 0.67 g cm^{-3} (0.01) recorded the highest values without significantly differing from each other ($P = 0.333$), whilst soils from Pond Cassé, 0.57 g cm^{-3} (0.01), Morne Prosper, 0.56 g cm^{-3} (0.01), and Layou Valley, 0.55 g cm^{-3} (0.02) recorded the lowest bulk densities without significantly differing from each other ($P = 0.653$). Soils from the Castle Bruce site was in an independent subset with a mean of 0.63 g cm^{-3} (0.03).

Results for porosity were inversely related to bulk density and there was a strong negative relationship between these two soil parameters (Fig. 4.5.5). In relation to porosity, there were significant differences ($R^2 = 0.92$, $P < 0.001$) observed between sites ($F_{95, 35} = 41.24$, $PESq = 0.904$) and between soil horizon ($F_{(1, 35)} = 27.70$, $PESq = 0.557$). There was no interaction between site and soil horizon. Soils from Layou Valley, 0.79 (0.01), Morne Prosper, 0.79 (0.004), and Pond Cassé, 0.79 (0.004) recorded the highest porosity value at $P = 0.653$, whilst soils from Soufriere, 0.75 (0.003) and Salisbury, 0.74 (0.004) recorded the lowest porosity values at a $P = 0.333$.

The Castle Bruce soil type stood independently with a mean porosity of 0.77 (0.01). The overall mean was 0.77 (0.003) across all sites. The results indicate that bulk density of these Dominican volcanic soils (Fig. 4.3.4) is low ($0.55 - 0.72 \text{ g cm}^{-3}$) as is typical for Andosols (Shoji et al., 1994; Arnalds, 2004; Dahlgren et al., 2004a,b). There is a distinct inverse relationship between organic carbon and bulk density (Fig. 4.4.1). Hence it appears that the soil organic carbon content alters the soil's compressibility and thus affects its bulk density

(Buytaert et al., 2007; Ruehlmann and Körschens, 2009) in addition to isovolumetric weathering of parent material on bulk density (Jahn and Asio, 1998; Witanachchi, 2004).

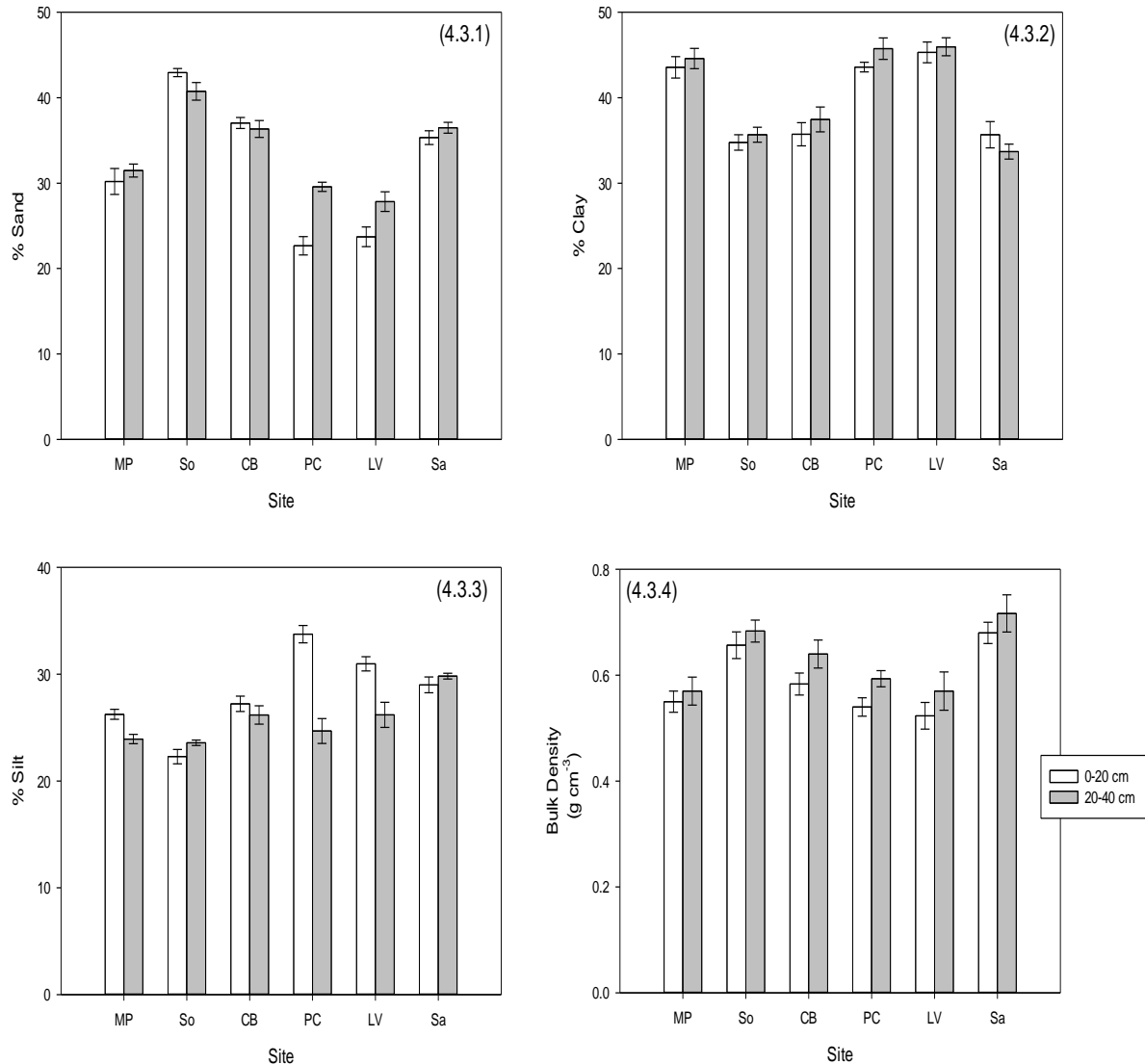


Fig. 4.3. Sand, clay, silt, and bulk density content in six agricultural soils from the Commonwealth of Dominica. Values represent means and error bars indicate SEM. n = 36.

A simple linear regression analysis showed that porosity was best explained by the influence of bulk density. $\text{Porosity} = 0.992 - (0.364 \text{ BD})$ ($R^2 = 0.99, P < 0.001$). Furthermore, multiple linear regression analysis revealed that soil bulk density was best predicted by a combination of OM content and clay content ($\text{BD} = 0.939 - (0.0042 \text{ OM}) - (0.00711 \text{ clay})$) ($R^2 = 0.66, P < 0.001$). However stepwise regression showed that ferrihydrite content (Chapter 5) was the most significant factor driving bulk density ($R^2 = 0.64, P < 0.001$).

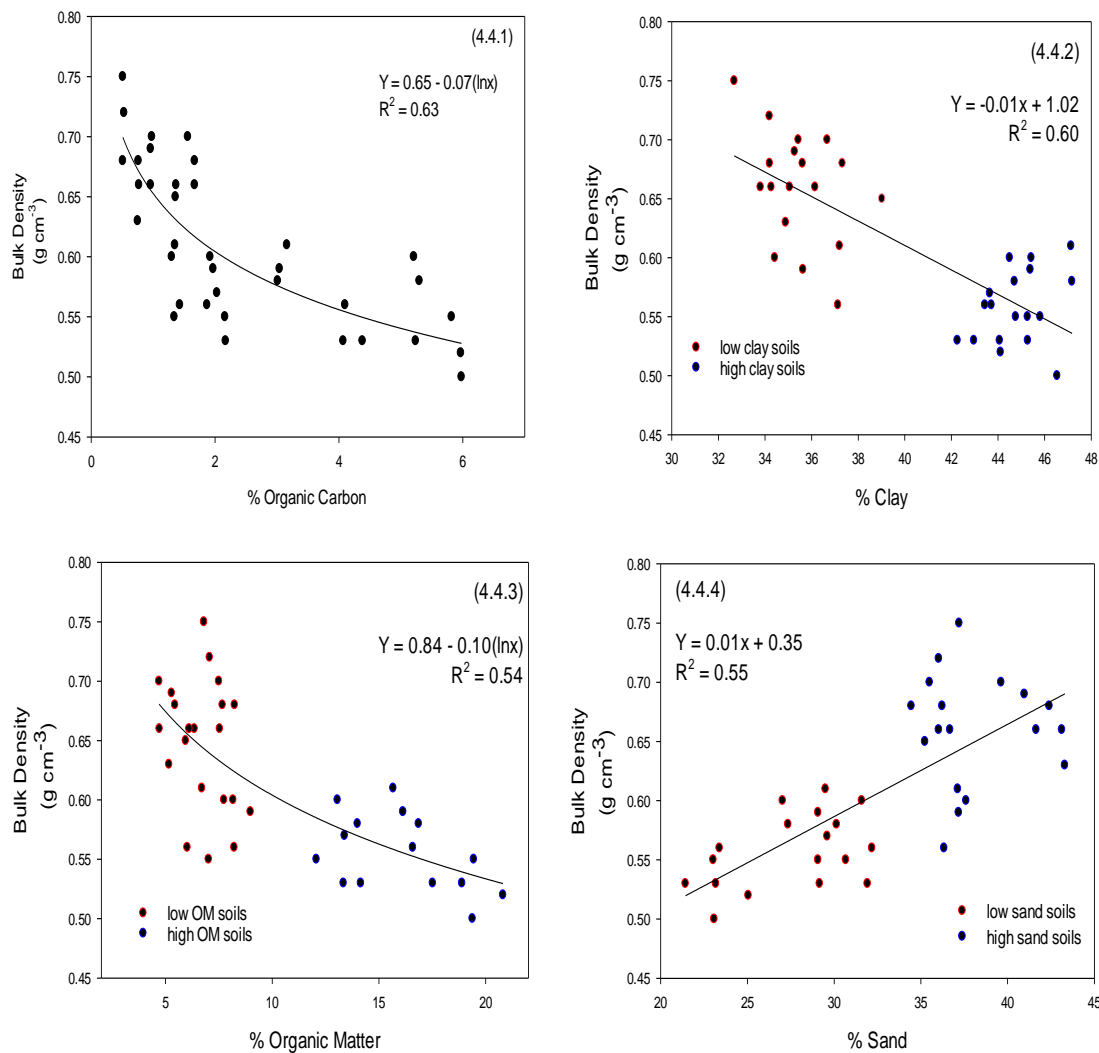


Fig. 4.4 Relationship between bulk density and organic carbon (4.4.1), % clay (4.4.2), % organic matter (4.4.3), and % sand (4.4.4) in six agricultural soils from the Commonwealth of Dominica. $n = 36$, $P < 0.001$. NB: Correlation analysis was done by grouping individual variables as a single unit of observation and does not account for differences between the 0-20 cm and 20-40 cm soil horizon.

The negative relationship between bulk density and organic matter was significant ($P < 0.001$) (Fig. 4.4.3), and was even stronger for clay content (Fig. 4.4.2). However there was a distinguishing significant positive relationship between bulk density and percent sand (Fig. 4.4.4). These results strongly suggest that although organic matter plays a critical role in determining bulk density properties of these volcanic soils, it appears that soil texture and in particular soil clay content, associated with non-crystalline materials and layered silicates, is a significant driver (Tisdall and Oades, 1982; Wada, 1985; Armas-Espinel et al., 2003; Yatno and Zaayah, 2008; Vacca et al., 2009).

There were significant ($P < 0.001$) negative relationships between bulk density and % allophane (Fig. 4.5.1) as well as % ferrihydrite (Fig. 4.5.2). There were also significant ($P < 0.001$) negative relationships between bulk density and oxalate extractable Si (Fig. 4.5.3) and bulk density and % ferrihydrite + allophane (Fig. 4.5.4). These results tend to suggest that the mineralogy of these soils had significant influence on the clay content and likewise bulk density. Hence the results tend to imply that the surface area of these secondary minerals has a marked influence on soil physical properties such as bulk density.

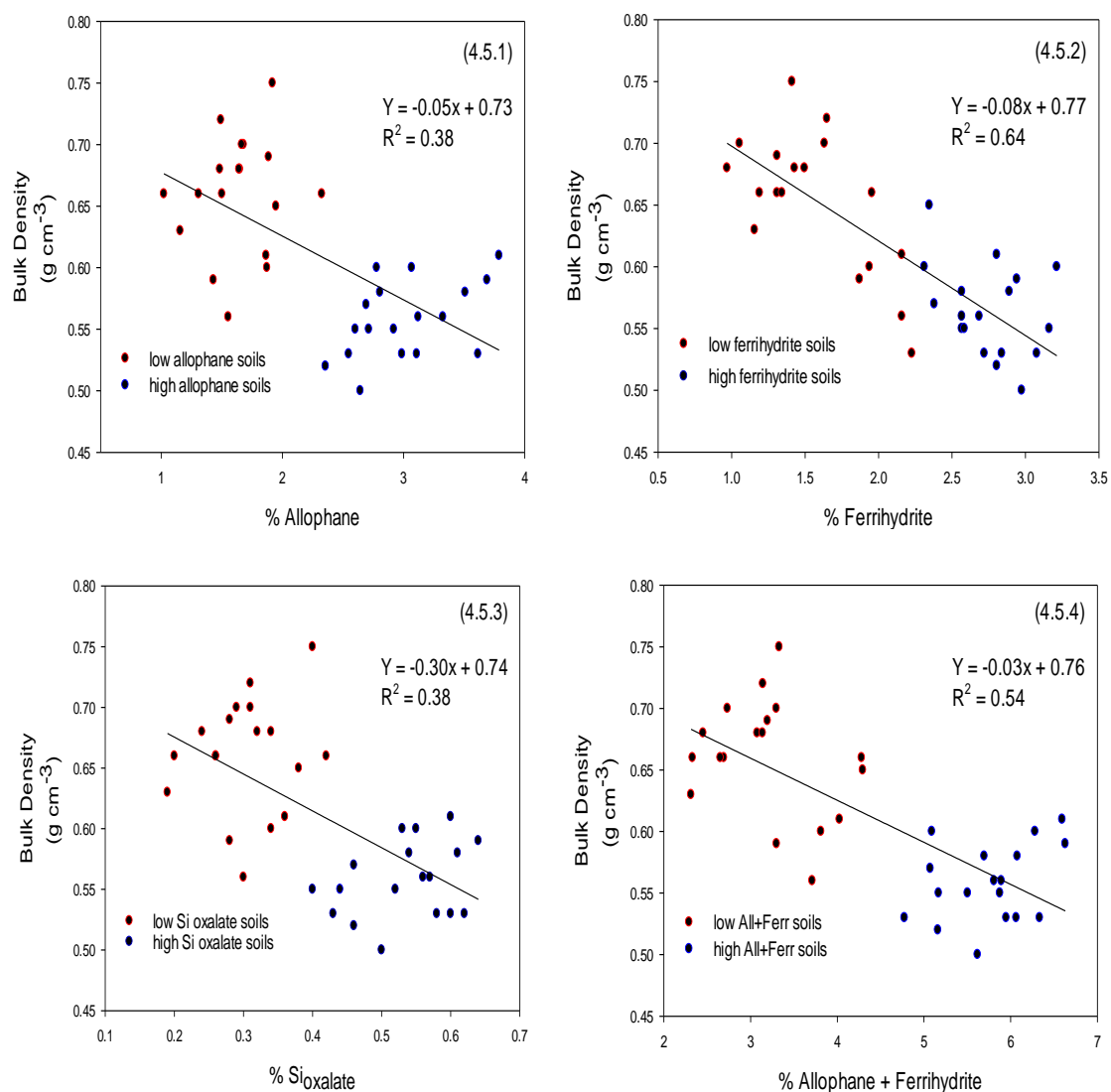


Fig. 4.5. Relationship between bulk density (BD) and allophane, and ferrihydrite and oxalate extractable Si content in six agricultural soils from the Commonwealth of Dominica. $n = 36$, $P < 0.001$. NB: Correlation analysis was done by grouping individual variables as a single unit of observation and does not account for differences between the 0-20 cm and 20-40 cm soil horizon.

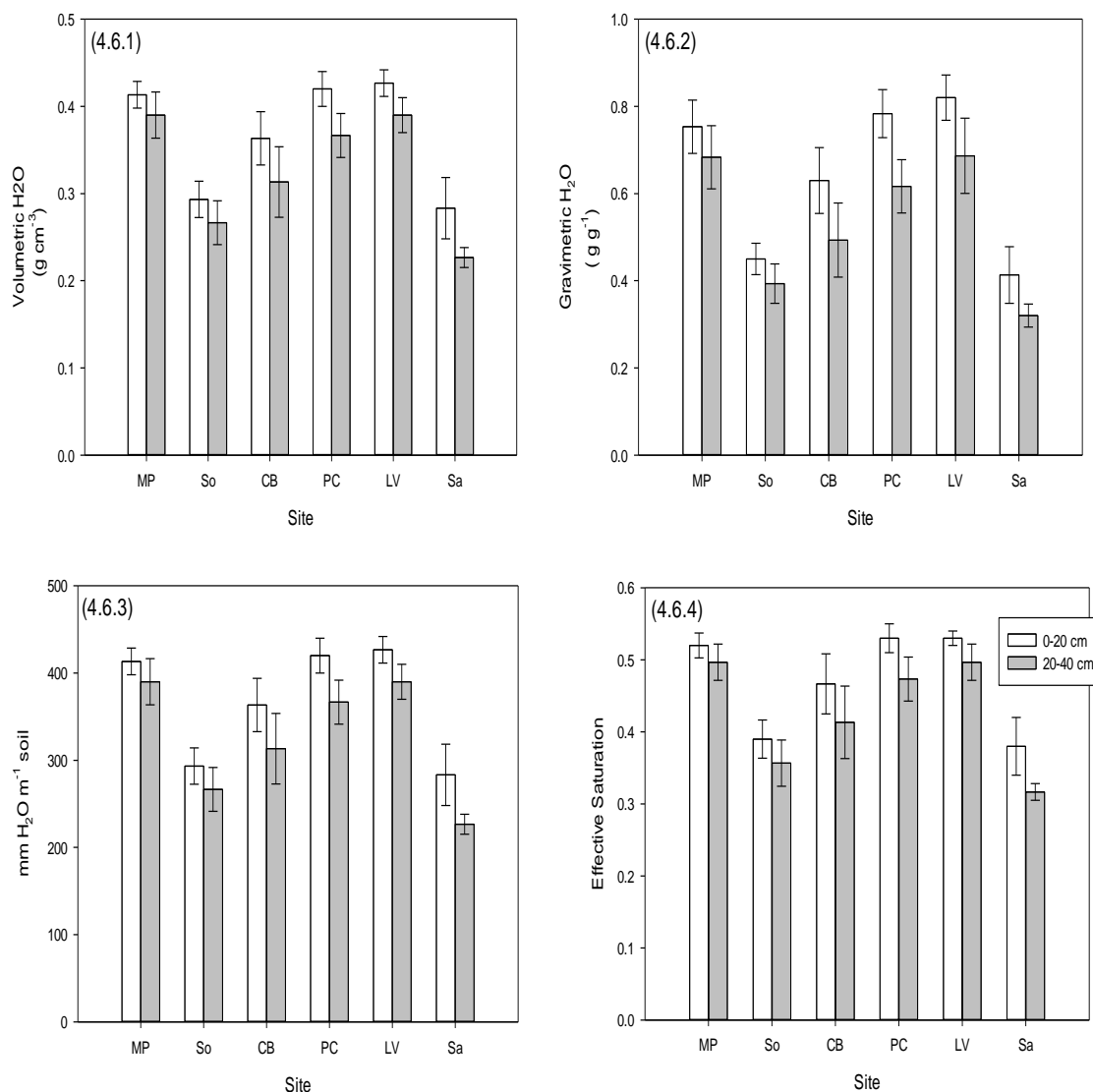


Fig. 4.6. Associated hydro-physical parameters of six agricultural soils from the Commonwealth of Dominica. Values represent means and error bars indicate SEM. n = 36.

The analysis of variance for the volumetric water content, which represents the fraction of the total volume of soil that is occupied by the water contained in the soil, showed significant differences ($R^2 = 0.91$, $P < 0.001$) between sites ($F(5, 35) = 39.69$, $PESq = 0.900$) and soil horizon ($F(1, 35) = 23.06$, $PESq = 0.512$) but failed to detect any significant interaction between site and soil horizon. The overall mean was 0.35 g cm^{-3} (0.01). Post Hoc analysis revealed that soils from Layou Valley, 0.41 g cm^{-3} (0.01), Morne Prosper, 0.40 g cm^{-3} (0.01) and Pond Cassé, 0.39 g cm^{-3} (0.01) recorded the highest value without significantly differing from each other ($P = 0.912$). On the contrary, soils from Soufriere, 0.28 g cm^{-3} (0.01) and

Salisbury, 0.26 g cm^{-3} (0.02) recorded the lowest values as a homogeneous subset ($P = 0.596$). Soils from Castle Bruce had a mean of 0.34 g cm^{-3} (0.02) and formed an independent subset.

Similar trends were observed for the gravimetric water content (Fig. 5.2) which showed significant differences between sites as well as soil horizon ($R^2 = 0.92$, $P < 0.001$), but failed to detect any significant interaction between site and soil horizon. The overall mean was 0.59 g g^{-1} (0.03). This tendency was also very evident in the results for millimetres of water per metre of soil ($R^2 = 0.91$, $P < 0.001$), also apparent for soil water pore space ($R^2 = 0.90$, $P < 0.001$), and noticeable for effective saturation ($R^2 = 0.90$, $P < 0.001$).

These results strongly suggest that parameters such as bulk density and porosity influences soil water content most significantly. However it should be noted that bulk density and porosity are influenced by organic matter and clay content and to this extent we would expect that soil water content to be strongly related to these parameters (Gupta and Larson, 1979; Tisdall and Oades, 1982). Hence we postulate that poor edaphic management of these soils will affect their physical properties such as porosity and in turn reduce their water holding capacity which has serious implication for nutrient mobilization and uptake (Robinson and Sharpley, 1995, 1996; Dugan et al., 2010).

The results for the hydrological characteristics of these volcanic soils evidently show that soil properties such as bulk density and mineralogical properties significantly affect the water holding properties of these soils (Allbrook, 1993; Yatno and Zauyah, 2008). In addition, the role of organic matter in the formation of macro-pores cannot be omitted. Furthermore, it has been reported that allophanic clays have a large affinity for water and soil water content has been used to differentiate Andosols from other type of soils (Dorel et al., 2000).

In this study the soil water content was significantly and negatively correlated with bulk density (Fig. 4.7.1). The data also highlights that soil water content is significantly and positively correlated to clay content (Fig. 4.7.2), soil organic matter (Fig. 4.7.3), organic carbon

(Fig. 4.7.4), as well as allophane (Fig. 4.7.5) and ferrihydrite content (Fig. 4.7.6) (Chapter 5). A logarithmic model involving percent organic matter (Fig. 4.7.3) gave a modest fit suggesting a key role of SOM in the formation of macro-pores. However, the relationship was stronger for clay content (Fig. 4.7.2) and was as strong as for the ferrihydrite content (Fig. 4.7.6).

Conversely, the data shows that the relationship of soil water content with allophane (Fig.4.7.5) was somewhat modest, whereby 58% of the variability could be accounted for by other factors. Nonetheless, the data tends to suggest that based on the irreversible volume change characteristic of allophane (Birrell and Fieldes, 1952; Maeda et al., 1977, Nanzyo et al., 1993a,b; Bishop et al., 2013) this could induce severe reduction in water storage attributed to less porosity and water retention.

On the contrary, the results suggest that ferrihydrite (Fig.4.7.6), which develops a net positive charge in acid soil environments leading to formation of bonds with negatively charged soil particles, had a positive effect in increasing water stable aggregation (Rhoton et al., 2003). Indeed a fair content of free iron oxides probably favours the formation of stable micro-aggregates made of ferrihydrite (Uehara and Gillman, 1981). Hence the stability of these micro-aggregates is probably enhanced by the high surface area of ferrihydrite with strong effects on the microstructure of clay particles (Waychunas et al., 1993).

Simple linear regression highlighted the influence of clay content ($-0.103 + 0.112 \text{ clay}$) ($R^2 = 0.65$, $P < 0.001$) but moreover the ferrihydrite content on volumetric water content ($0.173 + 0.0801 \text{ ferrihydrite}$) ($R^2 = 0.64$, $P < 0.001$). Porosity was also able to predict volumetric water content ($-1.790 + 2.775 \text{ porosity}$) ($R^2 = 0.95$, $P < 0.001$). However stepwise regression revealed soil volumetric water content was best predicted by ($0.966 - 1.017 \text{ BD}$) ($R^2 = 0.95$, $P < 0.001$) thus the inverse relationship and influence of BD on porosity.

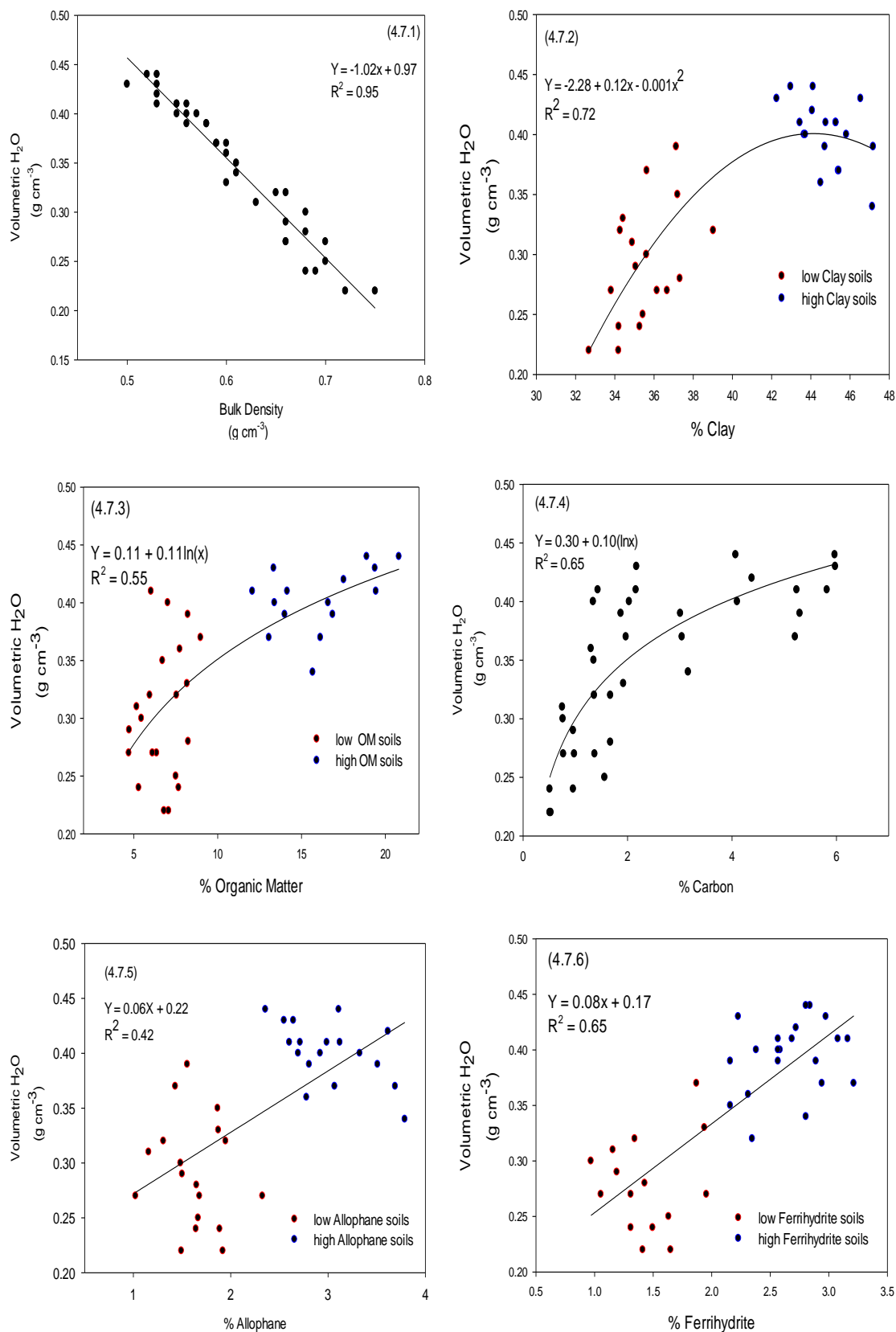


Fig. 4.7. Relationship between bulk density (BD) and various chemico-physical parameters of six agricultural soils from the Commonwealth of Dominica. n = 36, P<0.001. NB: Correlation analysis was done by grouping individual variables as a single unit of observation and does not account for differences between the 0-20 cm and 20-40 cm soil horizon.

3.5 Organic carbon and nitrogen

The results show that the mean soil organic carbon (Fig. 4.8.1) ranged from 0.75% to 5.98% which are quite variable but yet still typical for Andosols (Parfitt and Clayden, 1991). There were significant differences ($R^2 = 0.98$, $P < 0.001$) between sites ($F(5, 35) = 3545$, $PESq = 0.999$), as well as soil horizon ($F(1, 35) = 711.66$, $PESq = 0.970$). These values tend to suggest that these soils may either fall into the category of gleyic or brown Andosols as was suggested by Arnalds (2004) but by no means conclusive. A similar trend was observed for the percentage nitrogen content. The mean soil nitrogen percentage (Fig. 4.8.2) ranged from 0.11% to 0.47%. There were significant differences ($R^2 = 0.99$, $P < 0.001$) between sites ($F(5, 35) = 360.35$, $PESq = 0.988$), as well as between soil horizon ($F(1, 35) = 143.18$, $PESq = 0.867$). Notwithstanding, these values are in agreement with the findings of Lang (1967) who conducted over 200 soil profiles and found percent carbon to be in the range of 3.49%, and percent nitrogen in the range of 0.29% within the Dominican edaphic environment.

A simple linear regression between organic matter and carbon showed that OM was able to predict carbon content reasonably well ($\%C = -0.823 + 0.31 \text{ OM}$) ($R^2 = 0.79$, $P < 0.01$). Nonetheless, multiple regression analysis revealed that the combination of OM with ferrihydrite was still a better predictor at SOC content ($\%C = 11.383 - 0.743 \text{ allophane} + 1.373 \text{ ferrihydrite} + 0.242 \text{ OM}$) ($R^2 = 0.85$, $P < 0.001$). However, the best prediction of carbon content was explained by the N content and C:N ratios thus the strong influence of OM. ($\%C = -2.141 + (10.309 \text{ N}) + (0.226 \text{ C/N})$). ($R^2 = 0.97$, $P < 0.001$). OM content was able to predict N through simple linear regression by up to 83%. ($\%N = 0.0413 + (0.021 \text{ OM})$) and the inclusion of the C:N revealed ($\%N = 0.039 + (0.021 \text{ C/N}) + (0.01 \text{ OM})$) ($R^2 = 0.90$, $P < 0.001$).

From these relatively low and varied values across sites we postulate that in the case of carbon, volcanic activity may have influenced the accumulation of carbon probably caused by a rapid flux of tephra material during the late Pleistocene and Holocene period, (Óskarsson et

al., 2012), notwithstanding the influence of vegetation and current land use on carbon fluxes. In addition, the effect of eolian sediments cannot be ignored and is known to decrease the carbon content of soil (Arnalds, 2004; Óskarsson et al., 2012) and these events are known to occur within the wider Caribbean basin (Prospero and Carlson, 1972; Muhs et al., 2007).

It is fully understood that soil property variations can be ascribed to the accumulation of relatively high amounts of atmospheric mineral dust inputs during periods of land-surface stability (Reynolds et al., 2006); thus we postulate that these events may have influenced to a certain degree the carbon content of these volcanic soils and hence the possible rise in percent carbon with decreasing eolian input as is observed from the wetter tropical rain forest soils (Pond Cassè, Layou Valley, Morne Prosper, Castle Bruce) to the drier savannah and grassland semi-arid soil types (Soufriere, Salisbury). In the case of the nitrogen content we postulate that andic soil properties, low N mineralization rates and low atmospheric N deposition may have all contributed to these low values as was observed from the study.

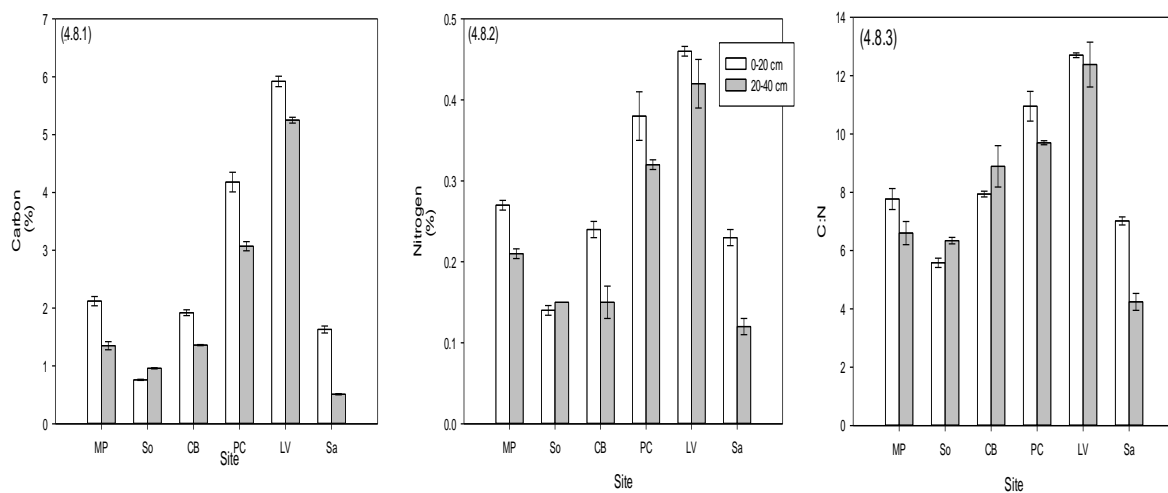


Fig. 4.8. Percent Carbon and Nitrogen, and C:N ratio of six agricultural soils from the Commonwealth of Dominica. Values represent means and error bars indicate SEM. n = 36

The results also highlight a significant ($P < 0.001$) positive relationship between percent carbon and allophane ($R^2 = 0.58$) but stronger between percent carbon and ferrihydrite ($R^2 = 0.72$) (Fig. 4.9). The results show that the allophane and ferrihydrite content (Chapter 5) increased rapidly with corresponding increases in percent carbon content. However, as was

observed by some researchers like Parfitt and Kimble (1989), Percival et al., (2000), Aran et al., (2001), Arnalds (2004), and Chevallier et al., (2010), with a carbon content of more than 10 percent, allophane formation tends to be inhibited and would progressively decrease with corresponding increases in % C values. In our study however the highest allophane content did not surpass 7% nonetheless there is a visible tendency towards a reduction in allophane content with increasing carbon (>4.0%) with ferrihydrite showing opposite trends.

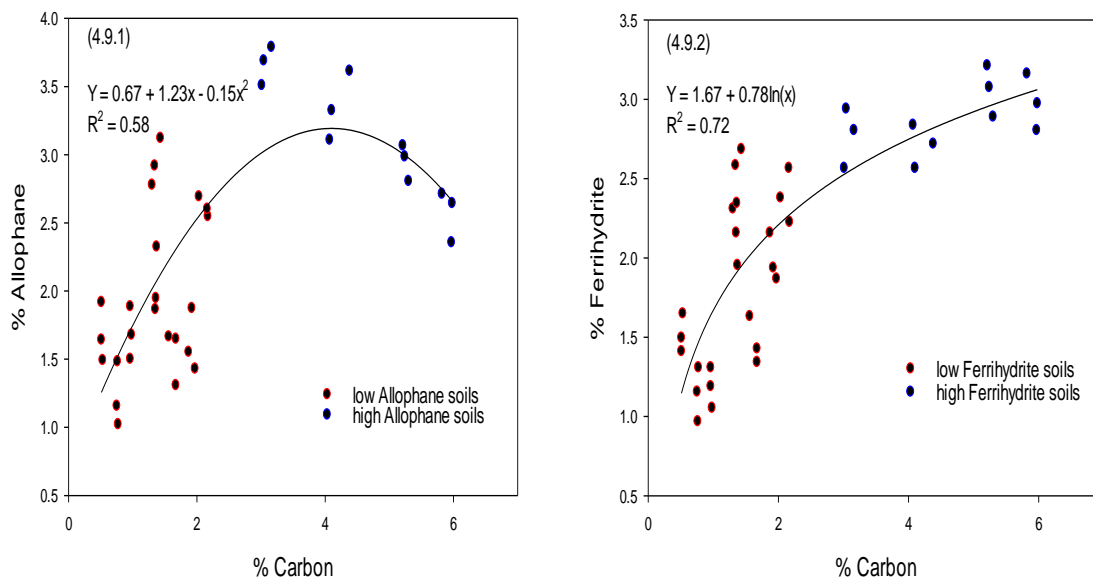


Fig. 4.9. Relationship between percent carbon and Allophane (a) and Ferrihydrite (b) contents of the soils calculated from Si_o and Fe_o values. $n = 36$, $P < 0.001$. Soils grouped as high and low allophane/ferrihydrite

These results tend to support some well documented characteristics of allophane chemistry and the mineralization of carbon and nitrogen in these soils. Soil organic matter (SOM) in allophanic soils is reported to accumulate due to protection caused by binding to allophane, aluminium and iron (Shoji, 1985; Shoji et al., 1993; Buurman et al., 2007). Furthermore, it would appear that the organic matter of these soils is highly stable owing of the presence of Al–humus complexes and sorption of organic ligands onto amorphous compounds (Verde et al., 2005; Miyazawa et al., 2013). Therefore we infer that the humification of the soil organic matter is strongly related to the stability of the soil carbon content as was highlighted by Miyazawa et al., (2013). Thus the high organic matter content can be attributed

to the stability of soil organic matter in organo-metallic complexes, their association with short-range-order minerals, and physical protection from microbial attack inside soil macro-aggregates and micro-aggregates (Oades, 1988; Yuan et al., 2000; Armas-Herrera et al., 2012). These results tend to suggest that chemical stabilization of organic matter is possibly the key process controlling soil C accumulation in these soils.

3.6 CEC and AEC analysis

The results for the cation exchange capacity ranged from 16.36 $\text{cmol}(+)\text{kg}^{-1}$ to 35.71 $\text{cmol}(+)\text{kg}^{-1}$ (Fig. 4.10). The overall mean was 25.51 $\text{cmol}(+)\text{kg}^{-1}$ (1.01). Generally, the CEC of these soils can be considered mid-high (Vacca et al., 2009; Churchman, 2010) and is typical for Andosols with corresponding low base saturation (Van Ranst et al., 2008). High organic matter content tends to account for some of the high CEC of many of these soils (Hart et al., 2003; Vacca et al., 2009). Organic matter content had a significant positive relationship with CEC ($R^2 = 0.67$, $P < 0.001$). More interestingly, the CEC of soils from Soufriere and Salisbury were high (18.57 $\text{cmol}(+)\text{kg}^{-1}$ and 18.90 $\text{cmol}(+)\text{kg}^{-1}$ respectively) even though organic matter was only 5.28% and 7.47% correspondingly. However, these two sites had levels of clay of 35.21% and 34.68% in turn. It seems that the constituents of the clay fraction was probably responsible for CEC values approximating 19.0 $\text{cmol}(+)\text{kg}^{-1}$. In addition, there was an increase in CEC with depth for the other sites which seems to suggest that the dissolution of SOM carboxyl groups contributes significantly to CEC for these soil with relatively high organic matter (Nanzyo et al., 1993b; Parfitt et al., 1995).

There was a significant positive relationship of CEC with allophane ($P < 0.001$, $R^2 = 0.79$) and CEC with ferrihydrite ($P < 0.001$, $R^2 = 0.82$). The relationship of CEC with extractable oxalate was also significant for Al_o ($P < 0.001$, $R^2 = 0.85$) and Fe_o ($P < 0.001$, $R^2 = 0.82$). Similar relationships were observed for extractable dithionite for Al_d ($P < 0.001$, $R^2 = 0.86$) and Fe_d ($P < 0.001$, $R^2 = 0.83$) (Fig. 4.11). However although significant, the

relationship of CEC with extractable pyrophosphate was particularly weaker for Al_p ($P < 0.001$, $R^2 = 0.79$) and somewhat higher for Fe_p ($P < 0.001$, $R^2 = 0.85$) in relation to Fe_p and Fe_o . The results tend to show that all extractable forms of iron as well as aluminium contributed significantly CEC values (Fig. 4.11) underscoring the effect of mineral charge on CEC.

Cation exchange capacity showed a tendency to be influenced by soil constituents such as pH (NaF), clay content, allophane and ferrihydrite content. Multiple regression gave a good fit for CEC with pH (NaF), clay content and OM ($R^2 = 0.84$, $P < 0.001$). However stepwise analysis revealed that CEC was best predicted by the combination of organic matter and oxalate extractable Al and Fe. $CEC = 7.137 + (0.226 OM) + (9.711 Al_o + 0.5 Fe_o)$ ($R^2 = 0.91$, $P < 0.01$) where the P value for OM was significant ($P = 0.032$) and for $Al_o + 0.5 Fe_o$ ($P < 0.001$). The results tend to suggest that the carbon content of the soil and high surface area of clay minerals give rise to the CEC, which is important for ion retention (Wada, 1985, 1989; Parfitt, 1990; Nanzyo et al., 1993a). These volcanic soils often tend to have CEC which is pH dependent (Barrow et al., 1980; Theng et al., 1982; Boland and Barrow, 1984). These properties are caused by the types of colloids that are formed in the soil, which constitute both clay minerals and metal-humus complexes.

These results tend to suggest that the association of allophane and ferrihydrite with Al- and Fe-oxides plays a critical role in determining CEC in these volcanic soils (Singh and Gilkes, 1992). It has been reported that there are only very few isomorphous substitutions in the aluminosilicate layers (Al-Ani and Sarapää, 2008) with the most common being Fe for Al. As a result the CEC of these soils containing allophane and ferrihydrite is most likely to be related to the surface area of these minerals (Okamura and Wada, 1983; Yatno and Zauyah, 2008; Churchman, 2010) which gives rise to surface charges (i.e. positive or negative) dependant on pH, hence the term variable charge.

Conversely, the ANOVA for AEC (Fig. 4.10.2) showed significant differences ($R^2 = 0.98$, $P < 0.001$) between sites ($PESq = 0.977$) as well as between soil horizon ($PESq = 0.571$). The mean was $3.95 \text{ cmol}(-)\text{kg}^{-1}$ (0.25). Soils from Pond Cassé, $5.91 \text{ cmol}(-)\text{kg}^{-1}$ (0.18) and Layou Valley, $6.03 \text{ cmol}(-)\text{kg}^{-1}$ (0.13) recorded the highest AEC values being equal ($P = 0.979$). Soils from Morne Prosper, $3.54 \text{ cmol}(-)\text{kg}^{-1}$ (0.18) formed an independent subset, whilst soils from Soufriere, $2.54 \text{ cmol}(-)\text{kg}^{-1}$ (0.14), Salisbury, $2.68 \text{ cmol}(-)\text{kg}^{-1}$ (0.12), and Castle Bruce, $3.03 \text{ cmol}(-)\text{kg}^{-1}$ recorded the lowest AEC values being equal at ($P = 0.063$).

The results for AEC tend to suggest that positive charges in the soil may have possibly originated either from the rupture of planes of the structural units and the resulting edge charges or of Al- and Fe-oxides that cover some crystalline clays or occupy an interlayer position in lattice layers (Uehara and Gillman, 1981; Zelazny et al., 1996). The effect is that these charges induce adsorption of anions (Rajan and Fox, 1975; Bowden et al., 1980; Parfitt and Henmi, 1980). However, AEC is concerned with ions that can be easily moved, and with P having low mobility, whose economic repercussions in agronomy is considerable, the AEC tends not to account for exchangeable forms (Barrow and Shaw, 1975a,b).

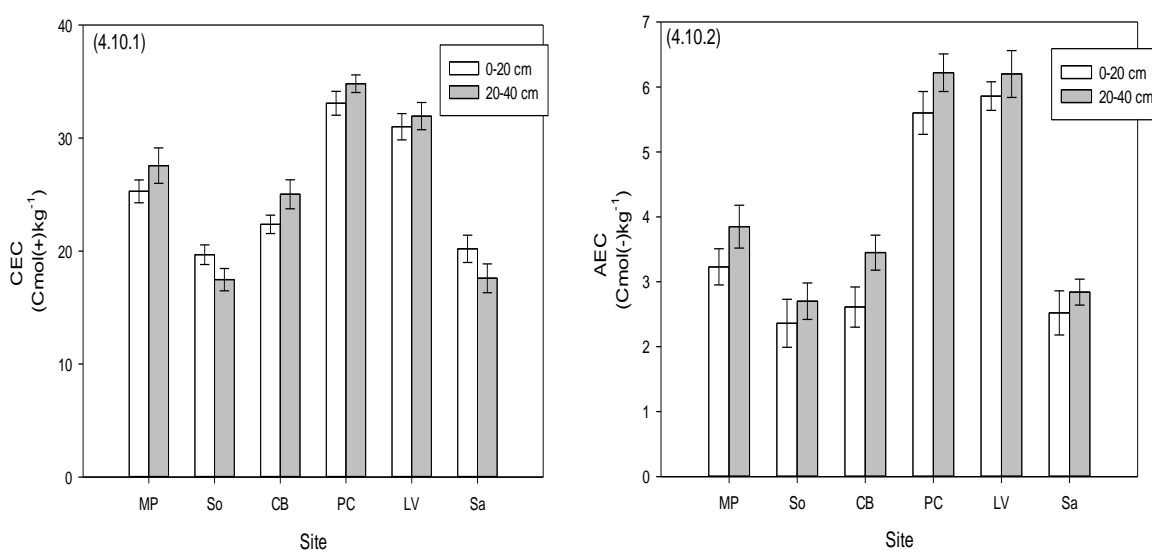


Fig. 4.10. Cation Exchange Capacity (NH₄Cl), Anion Exchange Capacity (AEC) of six agricultural soils from the Commonwealth of Dominica. Values represent means and error bars represent SEM. n = 36. NB: CEC did not include the determination of H⁺ and as such does not reflect effective CEC but reflects more of an estimate of the cation exchange capacity.

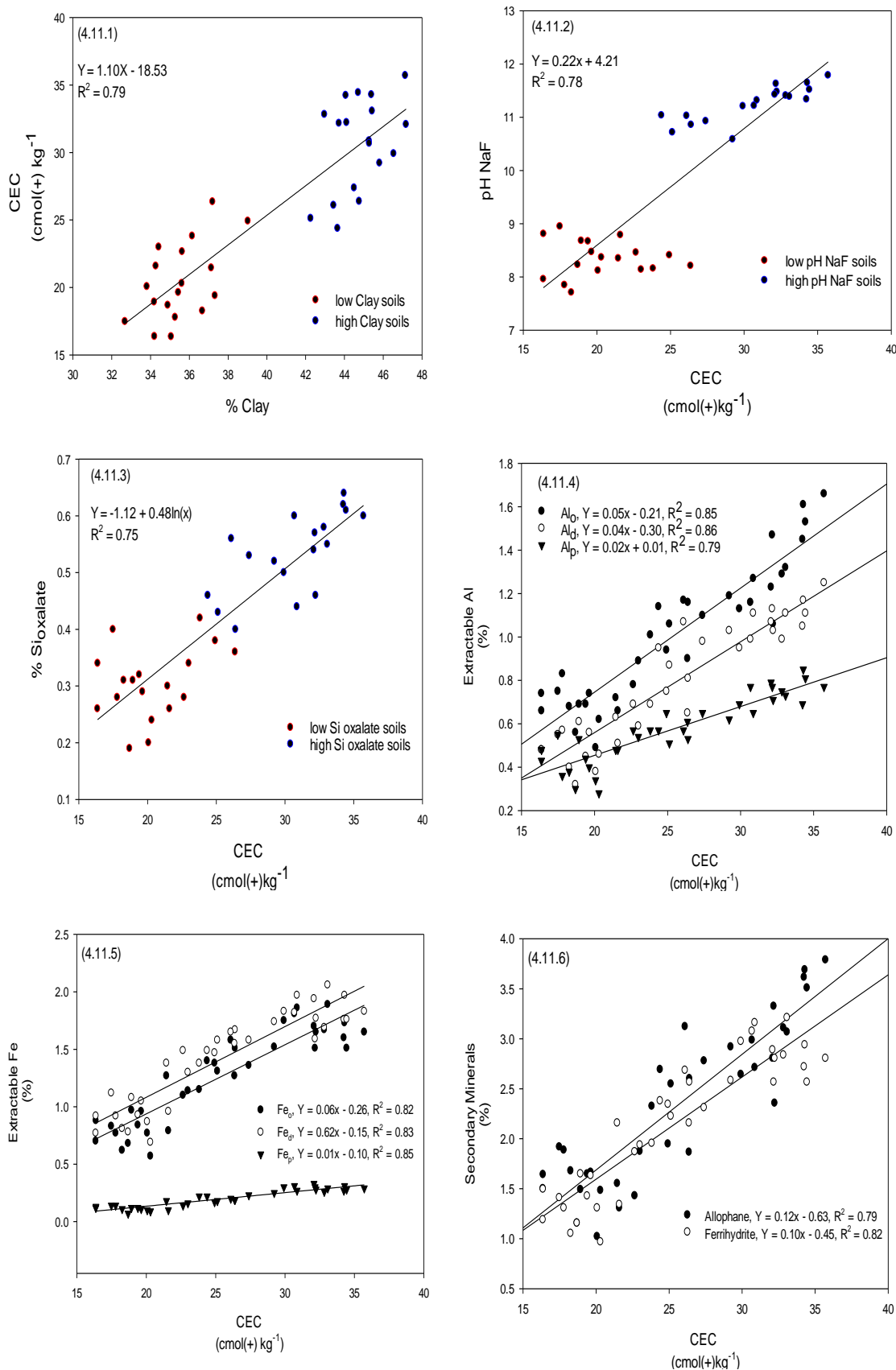


Fig. 4.11. Relationship between cation exchange capacity and various chemico-physical parameters studied in six volcanic soils from the Commonwealth of Dominica. $n = 36$, $P < 0.001$. Al_0 (Fe_o) = oxalate extractable Al (Fe); Al_p (Fe_p) = pyrophosphate extractable Al (Fe), Al_d (Fe_d) = dithionite extractable Al (Fe).

3.7 Exchangeable cations and base saturation

Exchangeable cations can be considered to be low with a corresponding very low base saturation (Vacca et al., 2009) with a minimum of 12.07% (0.20) in soils from Pond Cassé, and generally well below 60% which is considered ideal for optimum plant growth and development. Low values for exchangeable cations is a characteristic feature of young volcanic soils (Shoji et al., 1994; Navarrete et al., 2008). There is a corresponding decrease in base saturation with depth for all the soils with the exception of the Soufriere and Salisbury soil types (Table 4.1). The decrease with depth in the degree of base saturation probably reflects the depletion of soil nutrient cations, translocated and stored in the above ground biomass (Ugolini and Dahlgren, 2002). Conversely, the increase of base saturation with depth for soils from Soufriere and Salisbury tend to suggest that there is an accumulation of soil nutrient cations available in solution and accessible for plant uptake.

Table 4.1. Exchangeable cations (cmol(+)kg⁻¹) for six agricultural soils from the Commonwealth of Dominica. Values represents means with SEM indicated in parenthesis.

Site	Horizon (cm)	Exchangeable Cations (cmol(+)kg ⁻¹)					Base Saturation (%)
		Ca ²⁺	K ⁺	Mg ²⁺	Na ⁺	Al ³⁺	
Morne Prosper	0-20	0.95 (0.02)	0.43 (0.03)	0.86 (0.02)	0.30 (0.02)	1.09 (0.02)	14.39 (0.47)
	20-40	0.98 (0.01)	0.38 (0.04)	0.87 (0.02)	0.24 (0.02)	1.12 (0.03)	13.08 (0.35)
Soufriere	0-20	0.84 (0.02)	0.19 (0.03)	0.74 (0.02)	0.10 (0.01)	0.95 (0.02)	14.35 (0.58)
	20-40	0.88 (0.02)	0.17 (0.02)	0.78 (0.02)	0.07 (0.01)	0.98 (0.02)	16.58 (0.60)
Castle Bruce	0-20	0.91 (0.01)	0.25 (0.02)	0.85 (0.01)	0.18 (0.01)	1.02 (0.02)	14.38 (0.11)
	20-40	0.96 (0.02)	0.21 (0.02)	0.91 (0.02)	0.13 (0.01)	1.09 (0.03)	13.22 (0.38)
Pond Cassé	0-20	1.06 (0.02)	0.49 (0.03)	1.00 (0.02)	0.36 (0.01)	1.21 (0.03)	12.47 (0.19)
	20-40	1.11 (0.01)	0.42 (0.03)	1.11 (0.02)	0.33 (0.01)	1.24 (0.02)	12.07 (0.20)
Layou Valley	0-20	1.02 (0.02)	0.46 (0.03)	0.96 (0.02)	0.34 (0.01)	1.18 (0.02)	12.76 (0.20)
	20-40	1.04 (0.01)	0.41 (0.04)	0.99 (0.01)	0.32 (0.01)	1.22 (0.02)	12.47 (0.24)
Salisbury	0-20	0.89 (0.01)	0.21 (0.02)	0.79 (0.01)	0.11 (0.01)	0.96 (0.02)	14.77 (0.57)
	20-40	0.92 (0.01)	0.18 (0.02)	0.82 (0.01)	0.09 (0.01)	1.00 (0.02)	17.23 (0.81)

NB: Base saturation calculated from sum of total bases and CEC expressed as a percentage. H⁺ was not determined and hence not included and as such does not reflect effective CEC. In the absence of H⁺ base saturation tends to be underestimated.

Nonetheless, these low values generally tend to suggest that base saturation is related to the soil pH and/or with the absence of CaCO₃ (Beinroth, 1982; Yatno and Zauyah, 2008; Georgoulis and Moustakas, 2010) where it is known that some major elements, such as Ca, in

basaltic and andesitic rocks are easily mobilized during weathering and removed out of the system in the early stages of alteration (Fiantis et al., 2009). However, it should be noted that as soils weather and lose Al and Si, it leaves the soil colloid with a negative charge. The kind of parent material and the degree of weathering would ultimately determine the kinds of clays present in the soil and the amount of negative charge it will have.

These low values tend to suggest that exchangeable bases were almost totally depleted. The major exchangeable base cations at all sites are Ca^{2+} and Mg^{2+} . The ions in decreasing adsorption affinity were $\text{Al}^{3+} > \text{Ca}^{2+} \geq \text{Mg}^{2+} > \text{K}^+ > \text{Na}^+$. In addition, it is reported that a high content of exchangeable Na^+ raises the pH values of soils and thus from the results it can be noted that the contribution of exchangeable Na^+ to CEC is negligible attributed to the Na^+ content of the parent material and/or from sea deposits (Guicharnaud and Paton, 2006). Prado et al., (2007) highlighted that Ca^{2+} and Na^+ are usually the most abundant cations but also the most mobile ones and as such base saturation is closely linked to soil pH. In addition, Mekaruru and Uehara (1972) demonstrated that phosphate adsorption increased the CEC of highly weathered soils of Hawaii whereby specifically adsorbed anions render a surface more negative by displacing the zero point of charge to lower pH values.

Nonetheless, since soil particles are negatively charged and like charges repel and unlike charges attract there seems to be some form of antagonistic relationship between elements or conversely some elements tend to enhance the utilization of others. An example is that of Ryan and Kochian (1993) who showed that exposure to Al^{3+} can inhibit the uptake of many cations including Ca^{2+} , Mg^{2+} , K^+ , and NH_4^+ . The discrepancy between CEC, as determined with unbuffered NH_4Cl salt, and the sum of exchangeable cations, including extractable Al, can be attributed to pH-dependent negative charges which may develop as the pH of an acid soil is increased to near 7 by the NH_4Cl salt (Wada and Ataka, 1958) and that pH-dependent charge may be predominantly a function of organic matter.

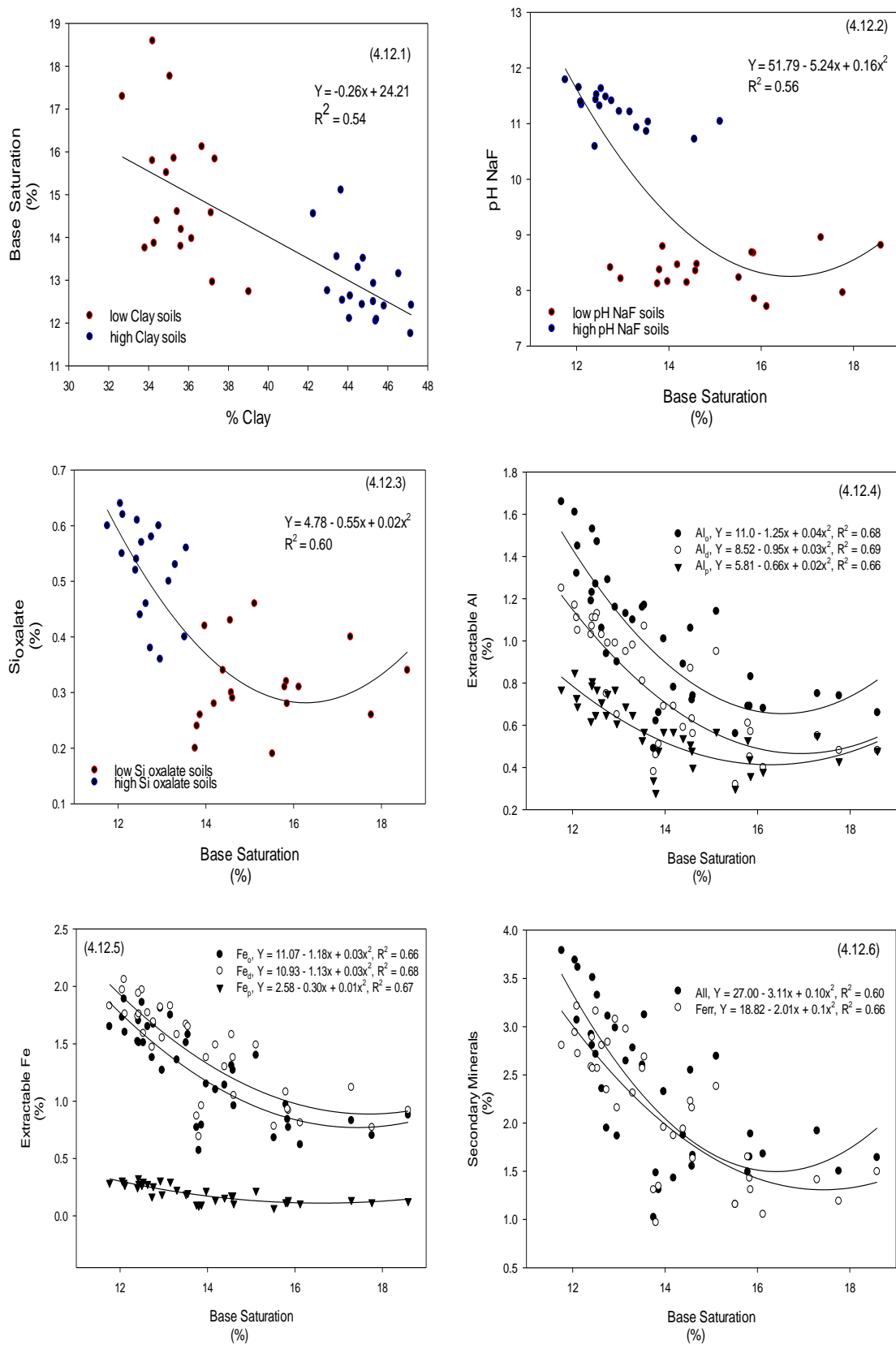


Fig. 4.12. Relationship between percent Base Saturation and various chemico-physical parameters studied in volcanic soils from the Commonwealth of Dominica. $n = 36, P < 0.001$. Al_o (Fe_o) = oxalate extractable Al (Fe), Al_p (Fe_p) = pyrophosphate extractable Al (Fe), Al_d (Fe_d) = dithionite extractable Al (Fe), All = Allophane, $Ferr$ = Ferrihydrite. Soils grouped as low and high clay, pH NaF and oxalate extractable Si.

A number of soil parameters had significant relationships with base saturation (Fig. 4.12). Parameters such as pH NaF, clay content, CEC, OM, allophane, ferrihydrite and silica as well as the oxalate, dithionite and pyrophosphate extractable forms of Al and Fe were correlated to base saturation, with CEC accounting for 78% of the variance solely. However stepwise regression revealed that base saturation was incomparably predicted by a combination of CEC, Si_o, and OM, which accounted for 92% of the variance. The multiple regression equation was significant ($R^2 = 0.92$, $P < 0.001$) and base saturation was explained by the regression equation $(21.999 - (0.511 \text{ CEC}) + 0.149 \text{ OM}) + (8.195 \text{ Si}_o)$. These results tend to suggest that the number of basic cations occupying cation exchange sites in comparison to the total number of sites is low. The suggestion is at low pH some H⁺ and Al³⁺ might be finding their way onto the surface of the soil mineral and organic particles and might be related to secondary forms of P (Tiessen et al., 1984). Hence the results tend to infer that these soils will most likely need be limed in order to increase the amount of soil particle exchange sites occupied with bases.

Table 4.2. Total reflection X-ray fluorescence (TXRF) analysis of some major elements from six agricultural soils from the Commonwealth of Dominica. Values represent means with SEM indicated in parenthesis. n = 36.

Site	Horizon	g kg ⁻¹		mg kg ⁻¹	
		Al	Ca	P	K
Morne Prosper	0-20 cm	22.96 (0.32)	2.02 (0.05)	269.87 (6.22)	615.56 (42.01)
	20-40 cm	27.66 (0.77)	2.04 (0.09)	244.30 (7.27)	664.70 (28.84)
Soufriere	0-20 cm	12.19 (0.36)	1.17 (0.06)	136.52 (5.41)	441.84 (19.06)
	20-40 cm	13.90 (0.55)	1.09 (0.04)	125.72 (3.42)	393.90 (30.90)
Castle Bruce	0-20 cm	13.67 (0.26)	2.33 (0.07)	188.44 (5.43)	1,585.57 (42.62)
	20-40 cm	16.89 (0.49)	1.61 (0.05)	165.21 (5.31)	2,099.12 (84.92)
Pond Cassè	0-20 cm	24.92 (0.96)	2.58 (0.08)	277.36 (10.02)	1,150.51 (75.28)
	20-40 cm	26.11 (0.66)	1.77 (0.08)	251.13 (8.31)	1,113.07 (47.98)
Layou Valley	0-20 cm	23.09 (0.37)	2.71 (0.10)	270.33 (8.15)	1,739.89 (49.58)
	20-40 cm	28.96 (0.74)	2.36 (0.06)	247.81 (9.83)	1,712.56 (38.57)
Salisbury	0-20 cm	14.94 (0.45)	3.34 (0.04)	145.03 (6.67)	926.00 (48.94)
	20-40 cm	16.50 (0.68)	3.67 (0.06)	146.81 (8.99)	788.59 (30.13)

NB: An under estimation of P using the method of total reflection x-ray fluorescence (TXRF) has been reported by Stosnach (2005, 2006) and Towett et al., (2013).

Chemical differences with depth are observed as a varied matrix for most sites. Nonetheless, there is a generalized trend displayed by P, K, and Ca towards decreasing contents with depth relative to the upper horizons. The concentrations of bulk soil Al content by and large increased with depth and was most evident in the Morne Prosper, Pond Cassé and Layou Valley sites. These results strongly suggest that Al was least mobile at these sites and displayed levels of enrichment within the lower soil horizon. Given climatic conditions at Pond Cassé in particular, we speculate some level of podsolization taking place at this site (Anderson et al., 1982; Farmer et al., 1983; Buurman and Van Reeuwijk, 1984). However as was noted by Óskarsson et al., (2012), Al may also be mobilized and transferred from the surface with organic colloids to precipitate in deeper levels where the colloids decompose and are less able to transport Al. Given the nature of the parent material (Lang, 1967) and the rate of dissolution of the same in comparison crystalline rocks (Shoji et al., 1975; Le Bas et al., 1986) suggest that the end product results in high dissolution rates of base cations and oversaturation of Al, Fe and Si in soil solutions which group into colloids (Ugolini and Dahlgren, 2002; Georgoulis and Moustakas, 2010).

Bulk soil Ca concentrations in soils from Salisbury also showed levels of enrichment in the 20-40 cm soil horizon as opposed to the 0-20 cm surface soil horizon (Table 4.2). Additionally, in soils from Morne Prosper and Castle Bruce, the bulk soil content of K also displayed levels of enrichment in the 20-40 cm in comparison to the 0-20 cm surficial soil horizon. These results tend to suggest that these elements are mobile, most likely shortly after deposition, but would be followed by a reduction in the rate of mobilization upon burial. On the other hand, the bulk soil content of P was consistently lower in the 20-40 cm at all sites suggesting the importance of organic versus inorganic P dynamics, as well as secondary P minerals in terms of dissolution and precipitation processes affecting P availability.

The bulk soil content of some of the major elements such as Al with a mean value of 20.15 g kg⁻¹ (0.99) and Fe with a mean value of 9.53 g kg⁻¹ (0.36) are particularly high. There were significant differences (P<0.001) for both elements between sites, soil horizon, and the interaction of site with soil horizon. On the contrary, the bulk soil P content show low values with a mean of 205.7 mg kg⁻¹ (9.80). There were significant differences (R² = 0.97, P<0.001) between sites and soil horizon but the ANOVA failed to detect any significant difference in the interaction of site with soil horizon.

The bulk soil Ca content with a mean of 2.22 g kg⁻¹ (0.12) also show significant differences (R² = 0.99, P<0.001) between sites, soil horizon, and the interaction of site with soil horizon. Likewise, the bulk soil K content with a mean value of 1.10 g kg⁻¹ (0.09) show significant differences between sites and the interaction of site and soil horizon (P<0.001) but failed to detect any significant difference between soil horizon (P = 0.09).

The mobilization trends of these alkaline metals alludes to the intensity of weathering (Navarrete et al., 2008; Fiantis et al., 2009, 2010) and with favourable conditions for weathering, mobilization should to take place following the incipient near-surface weathering stage. Elements, such as Ca, in basaltic and andesitic/dacitic rocks are easily mobilized during weathering, and Ca and Na are more mobile elements and easily displaced than Al, Fe and even Si and Ti (Fiantis et al., 2010). The effect normally results in a depletion of these elements in more mature and deeper soil horizons as a result of chemical weathering during pedogenesis. The role of vegetation is critical whereby plant uptake at the surface, especially of base cations, increases acidification which contributes to elemental mobilization (Óskarsson et al., 2012).

The data tends to indicate that these soils can generally be separated into two distinct groups, primarily allophanic versus non-allophanic Andosols. Furthermore, soil properties such as allophane and ferrihydrite content, oxalate extractable Si, clay and OM differ much more between these two groups of soils rather than within them (Fig. 4.5.1-4.5.3; 4.7.2, 4.7.3).

Table 4.3. Mean values for Total X-ray Fluorescence (TXRF) analysis of some minor elements of the Dominican soils under study. n = 36.

Site	Horizon	Fe	Mn	Cu	Zn
		g kg ⁻¹		mg kg ⁻¹	
Mome Prosper	0-20 cm	8.99 (0.19)	184.33 (7.07)	29.96 (0.73)	14.49 (0.43)
	20-40 cm	10.29 (0.35)	277.10 (4.59)	36.73 (0.82)	17.27 (0.68)
Soufriere	0-20 cm	6.35 (0.27)	181.37 (6.45)	26.66 (0.95)	13.13 (0.11)
	20-40 cm	6.74 (0.23)	179.74 (4.18)	22.61 (0.41)	11.06 (0.18)
Castle Bruce	0-20 cm	7.61 (0.21)	317.96 (11.0)	24.97 (0.67)	20.11 (0.53)
	20-40 cm	12.82 (0.27)	276.31 (5.23)	22.10 (0.17)	17.67 (0.50)
Pond Cassè	0-20 cm	10.82 (0.48)	163.92 (6.35)	18.24 (0.66)	17.48 (0.40)
	20-40 cm	12.17 (0.43)	120.02 (6.29)	23.23 (1.18)	14.32 (0.48)
Layou Valley	0-20 cm	10.15 (0.27)	281.26 (7.21)	29.23 (1.13)	14.77 (0.20)
	20-40 cm	12.02 (0.38)	317.89 (5.95)	22.91 (0.72)	14.63 (0.25)
Salisbury	0-20 cm	7.85 (0.28)	264.29 (12.96)	21.00 (0.80)	16.70 (0.41)
	20-40 cm	8.57 (0.21)	181.39 (6.52)	21.83 (0.81)	10.50 (0.26)

On the contrary, elements such as Al, Fe, and Mn are deemed to be the least mobile species and generally should be found enriched within more mature and deeper soil horizons as the desilication of the glass is concomitant with relative Al and Fe enrichment (Gérard et al., 2007). In addition, given that the weak granular structure of the surface is more permeable, and cause higher rates of denudation (Rao, 1996), will result in large surface areas reacting with circulating runoff waters (Rouse, 1990; Rad et al., 2007, Prado et al., 2007; Rad et al., 2013) and accelerate solute movement to the ground water. Thus the uppermost part of the soils will tend to weather more quickly whereas the lower horizons are more compacted and less mechanically exposed to the weathering elements. However it should be taken into account that lower pH leads to higher electron activity, and hence species such as Fe and Mn with several oxidation states tend to undergo reduction and resultantly may become more mobile (Óskarsson et al., 2012).

Undoubtedly, the geochemical tendencies are somewhat inconsistent and somehow lean towards some level of asymmetric variation between sites. However when the major element variation of the soil samples are looked as a whole the trend becomes more apparent. The concentrations of Fe generally displayed levels of enrichment in the lower 20-40 cm soil

horizon as opposed to the upper 0-20 cm. The concentration of Mn also showed levels of enrichment in the lower 20-40 cm soil horizon at two sites namely the Morne Prosper and Layou Valley. Likewise, the concentration of Cu was higher in the 20-40 cm soil horizon at the Morne Prosper and Pond Cassé sites while the concentration of Zn only showed levels of enrichment in the 20-40 cm soil horizon at the Morne Prosper site. Hence although the behaviour varies, the overall trend was mostly towards nutrient depletion which has serious agronomic implication for soil fertility management.

4. Discussion

The mineral fraction of soils has a profound effect on the quantity and quality of organic matter (Parfitt et al., 1997). This effect is partly due to the adsorption on clay surfaces by which a large part of the organic matter is protected from microbial decomposition (Oades, 1988; Yuan et al., 2000; Armas-Herrera et al., 2012) and owed partly to physical inaccessibility of OM within pores of micro-aggregates (Tisdall and Oades, 1982). As explained by Perrott (1977), Parfitt (1980), and Sollins et al., (1988), these volcanic soils with variable charge contain relatively large amounts of organic matter (Fig. 4.1.1) because the organic matter is stabilized by iron oxides and allophane, both of which have a small particle size and a large specific surface area (Theng et al., 1982; Parfitt, 1990; Creton et al., 2008). In addition, the formation of complexes between allophane and organic matter in soil would also enhance the retention of heavy metals and non-ionic organic contaminants, so reducing their mobility in the soil column (Yuan et al., 2000; Bolan et al., 2003; Krull et al., 2004, Bruce et al., 2009).

From an agronomic standpoint this is extremely important because Cu, Zn and Mn which are available primarily as divalent cations are likely to show antagonism or synergism in their uptake with P (Dolar and Keeney, 1971) and under humid weathering conditions, such as the conditions prevalent in the Commonwealth of Dominica, allophane would tend to have a strong affinity for trace metals such as Cu and Zn (Latrille et al., 2003). It has been reported that the

availability of P decreases as the availability of Zn, Cu, and Mn increases (Dolar and Keeney, 1971; El-Kherbawy and Sanders, 1984) probably owing to the formation of complex phosphate salts (Misra et al., 1964 cited by Dolar and Keeney, 1971; Kumpiene, 2010). On the other hand, contrary reports were highlighted by Murphy et al., (1981) and Zhu et al., (2002) showing increase availability of P with increasing availability of Zn, Cu and Mn. However Dolar and Keeney (1971) went on to suggest that the formation of hydroxides of Zn and Mn, and of phosphate salts of Cu and Mn is a primary cause of reduce availability of these elements in soils. Soil pH has been reported to markedly alter the distribution (i.e. mobilization and exchangeability) of Mn and Zn but has little effect on Cu (El-Kherbawy and Sanders, 1984; Sims, 1986; Macfie and Taylor, 1989; Graham et al., 2012). More importantly it has been shown that pH alters the rate at which the precipitation of Mn on to root surfaces occurs (Macfie and Taylor, 1989) and in Mn-sensitive plants may lead to reduce growth rates and photosynthetic activity. Furthermore, it has also been reported that in Mn-sensitive crops such as wheat, increases in organic acid content more likely reflect responses to Mn toxicity (Macfie et al., 1994).

In this exploratory study the pH-effect does not give much clarity because there were significant differences observed between sites for Mn concentrations ($P < 0.001$, $R^2 = 0.97$), for Cu concentrations ($P < 0.001$, $R^2 = 0.95$), and Zn concentrations ($P < 0.001$, $R^2 = 0.96$) even though there was no significant difference observed between the various sites in relation to pH. Seemingly, exchangeable Mn and Zn are generally the dominant species of the elements below pH 5.2, while at higher pH values organically complexed and Fe-oxide bound forms are dominant (Sims, 1986). Soil pH is one of the main factors controlling the solubility and bioavailability of heavy metals and these generally increase when the pH falls below 6.0 (Ross, 1994). These soils are generally separated into two distinct groups (e.g.) high pH NaF versus low pH NaF soils (Fig. 4.11.2), but SOC showed no relationship with goethite (Chapter 5).

The C:N ratio from these volcanic soils (Fig. 4.8.3) were in the range of 4:1 -13:1 and this may be related to the presence of allophane and ferrihydrite (Parfitt et al., 1997; Woignier et al., 2007). However the data tends to suggest that the higher C:N ratios observed could be partly associated with some less decomposed or partially decomposed organic matter (Yatno and Zaayah, 2008). The results tend to strongly suggest that a large part of the organic matter is likely to be present as an organo-mineral complex (Shoji et al., 1993; Ildefonse et al., 1994; Ugolini and Dahlgren, 2002; Verde et al., 2005; Creton et al., 2008; Tsai et al., 2010; Miyazawa et al., 2013) most probably containing a large number of aliphatic groups which may be resistant to decomposition. This would account for relatively low C:N ratios at most sites and a relatively small decline in the soil C content with cropping (Parfitt et al., 1997).

Although not within the scope of this study, consideration has to be given to the pool of passive organic matter and the role that aliphatic groups play in the enrichment of SOM. For soils with variable charge, of which these volcanic soils are examples, modifying factors such as the presence of allophane and/or ferrihydrite and their specific surface area may be required in order to give stability of organic matter (Sollins et al., 1996; Parfitt et al., 1997). The results from this present study show that the C:N ratio was relatively lower in soils from Soufriere (C:N = 6:1), a site which has been predominantly under natural pasture as well as in soils from Salisbury (C:N = 5.6:1), a site with dry grassland characteristics but semi-intensively cultivated. These low C:N ratios are suspected to be partly resulting from the inputs of nitrogen, most probably arising from symbiotic fixation occurring in these Dominican natural and semi-cultivated pastures and grasslands (Day et al., 1975; Neyra and Dobereiner, 1977).

The accumulation of organic carbon (Fig. 4.8.1) or humus in these volcanic soils has significant effect on the CEC and based on the soil moisture regime (Fig. 4.6) they show very low contents of exchangeable bases and very low base saturation (Table 4.1). According to Wada and Ataka (1958), the smaller contribution of 2:1 layer silicates to CEC is considered to

be due to the Al-layering of these minerals and the acidity reflects the low base saturation. The mean pH in H₂O was generally low and there was evidence of high Al and Fe saturation. However, speciation of Al forms should be considered to give more insights as to Al activity. In this study, soil acidity is moderate. Evidently extractable Al, which may be toxic to plant roots at high concentrations as extracted with KCl, is indisputably predominant. Furthermore it has been reported that high concentrations of KCl extractable Al can cause serious Al toxicity to plant roots (Delhaize and Ryan, 1995; Shoji and Takahashi, 2002; Kochian et al., 2005; Takahashi et al., 2008; Silva, 2012) thus limiting their uptake of nutrients.

In Andosols, allophane-imogolite and SOM content can drastically modify exchange properties (Wada and Okamura, 1980; Okamura and Wada 1983). On the other hand, these soils contain Al-humus complexes and as such the positive charges are weak, making it possible to differentiate Al-OH complexes in humus and in the mineral fraction. In addition, the specific fixation of anions such as fluoride can also result in considerable release of OH⁻ which makes it possible to test the soils containing active aluminium forms using the NaF test (Fieldes and Perrott, 1966; Perrott et al., 1976a,b).

The mean native P content in the bulk soil (205.71 mg kg⁻¹ (9.80)) suggest that this nutrient is low. Coupled with the high P fixation capacity by Al- and Fe-oxide (Hedley et al., 1994; Solomon et al., 2002; Takahashi and Anwar, 2007) it is evident that P would have severe limitations for agricultural development in these Dominican soils. According to Vacca et al., (2009), the moderate acidity of these soils may be partially explained by the progressive removal of alkali and alkali-earth cations from igneous rocks, lost both by leaching during rock weathering, and by plant uptake. As a consequence these processes probably result in a subsequent relative enrichment in Al and Fe, therefore promoting an acidic environment by hydrolysis reactions. This has great implications on nutrient management since buffering capacity determines the amount of resources, such as lime, that must be added to correct soil

acidity (Wada and Ataka, 1958). More importantly from an edaphic economic perspective, soils that have high buffering capacities require larger amounts of liming resources to raise the pH to a target value than soils with low buffering capacities, properties which differ strongly.

These volcanic soils show many characteristic physical and chemical properties such as low bulk density, high water retention, a large capacity for available water, accumulation of organic carbon, high CEC dominated by variable charges, and low base saturation generally associated with “andic” properties. However, these results start to raise the very important question of the classification of allophane versus non-allophane Andosol. This is of utmost importance with regards to soil management because allophane and non-allophane soils have a number of physical and chemical properties in common (Dahlgren and Saigusa, 1994; Shoji et al., 1996; Saigusa and Matsuyama, 1998; Takahashi et al., 2003; Poulénard et al., 2003; Matsuyama et al., 2005; Yatno and Zauyah, 2008) which are extremely difficult to differentiate the two in the field (Shoji, 1985) but with tendencies expressed in a number of parameters.

There are significant differences between non-allophanic and allophanic Andosols which must be given due attention especially with regards to Al activity and the possible effects of Al toxicity. The differentiation of allophane and non-allophane also becomes important in terms of their porous features and the relevance of understanding such features in relation to the mechanism of C and N sequestration (Woignier et al., 2007). Saigusa and Matsuyama (1998) differentiated them based on their exchange acidity (y_1) where $y_1 < 6$ was designated for allophanic and $y_1 \geq 6$ designated for non-allophanic soils. On the contrary, Poulénard et al., (2003) looked at their hydric properties which have been generally reported for Andosols characterized by advanced stages of weathering and unambitiously showed that non-allophanic soils exhibit these characteristics in horizons rich in volcanic glass. However, Shoji (1985) eloquently showed that non-allophanic Andosols have an Al-humus complex as the main active Al and show mostly thick, very dark humus horizons, reflecting repetition of intermittent ash

deposition and humus accumulation whereas in allophanic Andosols the active Al comes primarily from allophane and imogolite.

From these observation it becomes clearer that more information on Andosols is necessary for the exact characterization, rational classification and management of these soils. Lang (1967) reported that these Dominican Andosols originate from mainly andesitic/dacitic parent material and are mostly dominated by non-coloured volcanic glass (Shoji et al., 1975, Shoji, 1985). The absence or virtual absence of allophane and imogolite is closely related to the soil acidity and supply of organic matter (Shoji and Fujiwara, 1984) and several distinctive characteristics of non-allophanic Andosols are attributed to 2:1 layer silicates. Furthermore, it is important to differentiate between allophanic Andosols versus non-allophanic Andosols in terms of understanding their ion uptake mechanism which has further importance for soil fertility (Wada and Ataka, 1958) which tend to differ much more between groups of soils.

The question of geographic location and topography becomes extremely important in the characterization of allophanic versus non-allophanic Andosols. This observation is supported by the marked differentiation between two groups of soils with regards to clay content, pH NaF, % extractable Si-oxalate, % allophane as well as organic matter content. According to Vacca et al., (2009), non-allophanic soils tend to occur in areas where the increase in surface run-off, erosion phenomena and colluvial movements may have decreased soil depth and the degree of weathering. According to these authors, under the environmental conditions, the temporary drying of the soil promotes a transformation of amorphous materials into better organized minerals. Within the Dominican context, constant high temperatures, abundant moisture, the youthfulness of the landscape, parent material, and the high rates of slope erosion has meant that there has been limited time for soil development and the relative uniform and recent andesitic-dacitic eruptive history has led to variations in rainfall as being the dominant determination for soil types (Lang, 1967; Goldsmith et al., 2010). In addition, Reading (1991)

alluded to the effect of clay mineral composition and the influence the distribution of these minerals have on the higher expression of native Al content as opposed to Fe.

However, Vacca et al., (2009) went on to clarify that allophanic soils would normally be located in areas where the decrease in surface runoff, the high water infiltration rate, the absence of significant erosion and colluvial movements may have increased the extent of weathering processes. In these conditions, although allophanes are rarely found in soils under xeric moisture regime, due to the restricted leaching of silica (Parfitt and Kimble, 1989), soil remains moist for a period long enough to protect the short-range-order components against transformation into more organized materials.

The chemical and physical properties of these soils in turn dictates the behaviour of Al and Fe which are mainly active forms (Vacca et al., 2009). Although the soils under study had low bulk density and in turn high porosity, Shoji (1985) showed that a close negative correlation between total carbon and bulk density and concluded that humus greatly contributes to the lowering of bulk density through the formation of porous soil structures and as such more accumulation of organic carbon or humus takes place in non-allophanic Andisols. In addition, in weathered tropical soils, it should be expected that silicate will be lost with progressing pedogenesis while Fe- and Al-oxides accumulate over time (Rajan and Perrott, 1975; Parfitt et al., 1980; Doucet et al., 2001). This is of importance because adsorbed silicate could block active Al-OH sites where phosphate would otherwise adsorb and where a positive charge would develop.

5. Conclusion

The presence of large amount of organic matter in these volcanic soils is partly responsible in the formation of large pore space because soils with high organic matter content tend to be well aggregated and consequently have better porosity. These properties provide a conducive

soil environment for deeper rooting activity and therefore supply more nutrients and water for vigorous plant growth (Balwin, 1975). In addition, low bulk density and good internal drainage contribute to more favourable soil tilth leading to easy tillage, seedling emergence, and root development. Aggregates of these volcanic soils are highly stable, being cemented by non-crystalline materials and soil organic matter (Ugolini and Dahlgren, 2002, Creton et al., 2008; Tsai et al., 2010). Stable aggregate and high porosity of these soils could minimize water erosion and these properties significantly contribute to maintaining their high productivity.

The apparent high bulk soil concentration of Al and Fe is most probably as a result of the replacement of Si, Ca and other cations by hydrogen cations (Wada, 1967; Parfitt and Kimble, 1989; Woignier et al., 2007). In addition, owing to textural differences in geomorphic position and precipitation, the pedogenetic conditions would not be uniform over the island and as a consequence the soils exhibit some dissimilar features. Such contrasting features would lead to the dissolution of some elements from the soil system while re-precipitating other elements as poorly crystallized material (Shoji et al., 1993) and/or even “lateritic” material (Beinroth, 1982). On the other hand, clay layers also appear to withhold elements from leaching, acting as capillary barriers by impeding water percolation where leached elements may be complexed with organic substances or bound to clay surface (Óskarsson et al., 2012).

From a soil management perspective, it is becomes even more important to determine whether these cultivated Andosols are allophanic or non-allophanic. Al toxicity is often observed in non-allophanic Andosols attributed to the presence of high concentrations of KCl extractable Al whereas this condition rarely occurs in allophanic Andosols (Dahlgren et al., 2004a,b; Takahashi et al., 2008; Yatno and Zauyah, 2008). The primary manifestation of Al toxicity is impaired root development resulting in the formation of a shallow rooting systems (Delhaize and Ryan, 1995; Kochian et al., 2005). This effect results in reduced uptake of water and nitrogen and based on the shallow rooting system, leaching of nutrients, especially nitrate,

is another serious consequence (Kochian et al., 2005). Based on these andic properties, the avoidance of heavy application of ammonium fertilizers will become critical in retarding exchange acidity in relation to soil productivity.

As positive cations are applied to the soil, the negatively charged clay colloids adsorb these cations and for every cation that it adsorbs it releases one of the same into soil solution making it available for plant uptake (Okamura and Wada, 1983). As the soil reaches equilibrium however cations are held tightly to the clay colloid until another application of nutrients is made and thus offsetting the balance until the soil reaches optimum level of saturation (Wada, 1985). Thus in order to make sure that nutrients are available for plant utilization in soil solution all the soil exchange sites must be occupied or cations should be at optimum saturation.

The presence of allophane or amorphous minerals in the soils developed on volcanic materials influences soil bulk density values, available water contents, CEC, and P retention. The weathering stage probably influences nutrient availability through basic cation flow from primary minerals to soil solution and finally exchange complex through soil-solution and root-solution equilibria (Delvaux et al., 1989). The higher the CEC the higher the optimum level of nutrients, the more exchange sites that needs to be satisfied because as CEC increases so does the efficiency of the exchange sites and root interception (Parfitt, 1980). The higher the clay content in soil the greater the CEC and the greater the negative charge on that colloid. This means the greater is that soil's ability to hold nutrients at a given soil depth, and the greater that soils buffering capacity. On the contrary, the lower the CEC, the lower the clay content and thus these soils cannot hold nutrients as readily and as such are easily leached. In effect, the release of cations from the soil colloid is how the soil feeds the plant. Therefore it is important to build soils up and balance the nutrients so that the plant has a readily available supply during the growing season and hence the slogan "feed the plant and not the soil".

In a nutshell, the results starts to highlight the possible co-existence of both allophanic and non-allophanic Andosols developed from the same volcanic material, but under varying climatic and topographic conditions. These results begins to suggest that andic soil properties are not merely classified according to mineral parent material, but rather according to chemical, physical and mineralogical properties acquired as a whole during weathering and evolution which is expressed holistically from a pedogenetic and edaphic point of view. Hence given the clear distinction between primarily two groups of soils with regards to organic matter content, electrical conductivity, clay content and the presence of aluminosilicates material among other variables, this adds to the assemblage of data which supports the co-existence of both allophanic and non-allophanic Andosols within the edaphic environment of Dominica.

Given the finite and fragile nature of this resource, high erosion risk should discourage clean cultivation unless planting follows the contour and cover strips alternate with crops therefore any significant change to land use will have irreversible negative effects, however grass-tree crop systems is probably best for most of these soils (Schroth and Sinclair, 2003; Schroth and McNeely, 2011). The chemistry of these soils suggest that nearly all the nutrients are concentrated in the organic matter and to the extent loss of the humic horizon would leave only a very efficiently leached subsoil with loss of fertility. Experiments on minimal cultivation-minimal compaction techniques thus becomes increasingly significant, although it is obvious that a continuous crop cover will be of importance. Undeniably, soil conservation certainly becomes the most essential aspect of good husbandry for preserving the Dominica heritage of productive soils. Crop trials are required with regards to fertilizer type (chemistry and speed of nutrient release); placement and frequency of application need investigation, coupled with the effect of micro-climate variations and conservation practises. The development of these activities coupled with soil testing and analysis will only expand and strengthen management strategies.

CHAPTER 5

ESTIMATION OF Fe AND Al FORMS IN TROPICAL VOLCANIC SOILS: IMPLICATIONS FOR P FERTILITY MANAGEMENT IN THE COMMONWEALTH OF DOMINICA

Abstract Given the complex nature of rain fed cropping systems in Dominican agriculture and the dynamic nature of phosphorus (P) in tropical volcanic soils, agronomic assessment of P availability is an essential exercise in order to better understand the chemistry of soil phosphorus and by extension soil fertility management. The distribution of the various forms of inorganic phosphorus in the soil is largely controlled by the activities of the various ions (Al and Fe), in turn reflecting soil pH, age, drainage, and mineralogical nature. This research investigates the estimation of Al and Fe forms on six volcanic soils using three different extracting reagents (oxalate, pyrophosphate, dithionite). The research also investigates the use of the sodium fluoride pH test (pH NaF), the toluidine blue metachromasis test (TB test), as well as the Chang and Jackson sequential phosphorus fractionation in order to better comprehend P activity in these volcanic soils.

The results show that the soil pH (pH NaF) is a reasonable predictor for estimating P sorption with soils from three sites having pH values above 9.5 after 2 minutes. The results also indicate that the estimated forms of Al and Fe followed the order of $Al_o > Al_d > Al_p$ and $Fe_d > Fe_o > Fe_p$ respectively for all sites. The TB test gave a fair assessment of the spatial variation of allophane but should be used with caution in interpreting results as they are by no means conclusive. The diversity of P forms as revealed by P sequential fractionation was typical for tropical volcanic soils with high P immobilization and by no surprise low P status. Total P from the four extractable fractions ranged from $106.35 \mu\text{g g}^{-1}$ to $60.23 \mu\text{g g}^{-1}$ with inorganic P predominantly being non-occluded.

Key Words: Andosols. Allophane. Phosphate adsorption. Oxalate, Dominica

1. Introduction

The chemical weathering of soil minerals is a continuous reactive geochemical process which enriches the magnitude of base cations in soil solution and in effect determines the long-term availability of plant nutrients and the chemical status of the soil (Bascomb, 1968; Arshad et al., 1972; Fox, 1982; Duan et al., 2002). In this regard, the determination of the inorganic forms of soil phosphorus (P) provides a means of quantitatively measuring soil chemical weathering (Chang and Jackson, 1958). Hydrous oxides of aluminium (Al) and iron (Fe) are substantial components of weathered tropical volcanic soils and they are usually exceedingly reactive owing to large specific areas with an extraordinary high ratio of reactive sites (Imai et al., 1981; Okamura and Wada, 1983; Wada and Kakuto, 1985a; Parfitt et al., 1997; Van Ranst et al., 2004).

Volcanic soils are found under a variety of environmental conditions, and have been studied in various regions of the world (Birrell and Fieldes, 1952; Beinroth, 1982; Arnalds, 2004; Broquen et al., 2005; Madeira et al., 2007a,b; Yatno and Zauyah, 2008; Fiantis et al., 2010). Notwithstanding, not much information is currently available about the properties of weathered volcanic soils of the Lesser Antilles, far less for the Commonwealth of Dominica in particular; and the few studies conducted on soil and land use are limited in scope (Lang, 1967; Shillingford, 1972, Evans, 1986).

On the contrary, a number of on-island studies have been undertaken with regards to volcanism and gas and water geochemistry of geothermal systems (Roobol et al., 1983; Gurenko et al., 2005; Samper et al., 2008; Joseph et al., 2011; Felicite et al., 2013), the volcanically most buoyant island in the Lesser Antilles volcanic arc, with 9 epicentres classified as potentially active (Lindsay et al., 2005a,b; Joseph et al., 2011). There has also been studies on geological engineering which has shed some added information of the soil physical and chemical properties (Reading, 1991; Rao, 1996; Goldsmith et al., 2010).

The Lesser Antilles arc includes 21 potentially active volcanoes spread across 11 volcanically active islands (Joseph et al., 2011). The Commonwealth of Dominica, with abundant amount of pyroclastic deposits is centrally located in this very active and dynamic Lesser Antilles Island Volcanic Arc (Le Friant et al., 2002; Rad et al., 2007) and to this extent parent material and associated minerals in soil formation processes has significantly influenced nutrient status and in particular phosphorus availability. It is an island where explosive silicic eruptions have been especially prominent (Gurenko et al., 2005; Halama et al., 2006). Consequently, studying the expression of Al and Fe forms of these volcanic soils is extremely important in getting a wide-ranging and improved outlook with regards to fertility and nutrient management as well as understanding the limiting factors associated with nutrient availability for crop uptake.

It is generally accepted that soils which have developed on the deposits of volcanic ash usually have a predominance of non-crystalline alumino-silicates such as allophane, imogolite, and allophane-like constituents in the clay fraction and as such the sorption capacity is significantly affected by the presence of these minerals (Yoshinaga and Aomine, 1962; Follett et al., 1965; Wada, 1967; Wada and Higashi, 1976; Ross, 1980; Gérard et al., 2007; Churchman, 2010). Nonetheless these soils are considered to be the most productive soil types on a global scale (Ugolini and Dahlgren, 2002; Shoji and Takahashi, 2002; Navarrete et al., 2008), although phosphorus is usually a limiting nutrient for most crops grown on these soils. The reactivity often expresses itself in terms of the adsorption of phosphate and other anions, and in terms of variable charge (Hingston et al., 1972; Parfitt and Childs, 1988; Pardo and Guadalix, 1990; Fontes and Weed, 1996).

Phosphate sorption in acidic soils has been reported to be more closely related to the content of oxalate-extractable aluminium than to any other soil constituent (Mizota and Van Reeuwijk, 1989; Gilkes and Hughes, 1994). Furthermore, the rapid weathering of parent material releases

elements such as Fe, Al and Si faster than crystalline minerals can form (Mizota and Van Reeuwijk, 1989; Ugolini and Dahlgren, 2002; Buurman et al., 2007; Georgiadis et al., 2013), resulting in the soil solution becoming over-saturated with respect to metal stable, non-crystalline materials. More importantly, it has been reported that the allophane content has a profound effect on the soil's chemical behaviour most notably P-sorption (Van Ranst et al., 2004), and it is reported that phosphate rapidly and strongly adsorbs on to allophane via ligand exchange with Al-OH (Parfitt, 1979, Shoji et al., 1993; Van Ranst et al., 2004) making it sparingly available for plant uptake.

In light of the aforementioned, the objective of this study is carried out with the aim of testing three dissolution methods on six contrasting Dominican soils to see how successful they are in extracting various forms of Fe and Al. The immediate purpose of the present study is to investigate the chemical properties [%Fe_p, %Al_p, %Fe_o, %Al_o, %Si_o, %Fe_d, %Al_d, Al/Si, pH (NaF)] of these same weathered soils in comprehending P-sorption. The investigation has three components: (1) determine the spatial variability of these soils regarding pH sodium fluoride (NaF), extractable sodium pyrophosphate (p), extractable acid ammonium oxalate (o), and extractable citrate bicarbonate dithionite (d), (2) determine the relationship between plant available P and Al and Fe forms, and (3) produce a statistical examination of the soil chemical properties related to the expression of Al and Fe forms.

The ultimate goal is to understand the mechanisms of Al and Fe dissolution and apply the principles to land use and management exercises with emphasis on phosphorus nutrition in agriculture. Thus the study attempts to obtain an improved comprehension of Dominican soils by assembling new data and methodologies to be merged into national databases. To this extent, incorporating measurable parameters of allophane chemistry such as pH NaF in routine soil testing exercises is a starting point, especially in tropical areas where P-fixation is problematic coupled with limited resources in conducting more in-depth soil analysis locally.

2. Materials and Methods

2.1 Sodium Fluoride pH

The test selected was performed as described by Fieldes and Perrott (1966), Brydon and Day (1970), and Perrott et al., (1976a) all who recommended that 50 ml of 1.0 M sodium fluoride (NaF) buffered at pH 8.2 be added to 1.0 g of soil, previously grounded, and passed through a 100-mesh sieve. Soils were stirred immediately and the pH of the soil solution was subsequently measured after 2 minutes on a Hanna™® model 209 pH and again at 30, 45, 60, and 90 minutes after being intermittently stirred in between.

2.2 Toluidine Blue Test

The test for allophane and imogolite was performed by taking 30 mg of air-dried soil sample sieved to 2 mm and placing it on a white spot plate with 0.4 ml of 0.02% toluidine blue ($C_{15}H_{15}N_3SCl$) in an aqueous solution and by stirring the mixture with a spatula for 15 seconds (Wada and Kakuto, 1985a,b). The test instructs that if the colour of the solution remains blue (absence or scant TB metachromasis), it was considered that allophane and imogolite predominated whereas if the solution became colourless and the colour of the soil turned purple or purplish red, it was considered that there was a substantial amount of layer silicates. Wada and Kakuto (1985a,b) also noted that intermediate situations could occur depending on the relative amounts of the two groups of minerals.

2.3 Acid Ammonium Oxalate Reagent

The determination of Al, Fe and Si (Al_o , Fe_o , and Si_o) was done according to the method described by Blakemore et al., (1987). Procedurally, 0.25 g of soil (<2 mm sieved air-dried samples) was placed in a 50 ml centrifuge tube and 25 ml of 0.2 M $(NH_4)_2C_2O_4$ (ammonium oxalate) added which was buffered to **pH 3.0**. Samples were immediately shaken in the dark (tubes covered with tin foil) for 4 hours on an Edmund Bühler GmbH SM-30™® shaker with 10 drops of 0.2% of “superfloc” (organic flocculating agent) added. Darkness is required,

since light reduces the dissolution of the crystalline forms of the Fe oxides (del Campillo and Torrent, 1992). Samples were allowed to settle overnight and then centrifuged at 448 RCF for 15 minutes on an Eppendorf™® 5810 R centrifuge and the supernatant subsequently analysed by atomic absorption spectroscopy (AAS) on a Varian™® Spectra AA – 220 FS. The acid ammonium oxalate reagent is reported to extract amorphous inorganic Al and Fe oxides and organic complexed Fe and Al from soils (Parfitt and Childs, 1988; Dahlgren, 1994). It attacks most silicate minerals only slightly, but dissolves easily-weathered silicates considerably. In relation to Fe oxides it is fairly specific to ferrihydrite and used to estimate the presence.

2.4 Sodium Pyrophosphate Reagent

Pyrophosphate is generally used to assess the amounts in organic forms of Al, Fe, and Si (McKeague, 1967; Arshad et al., 1972; Sheldrick and McKeague, 1975; Farmer et al., 1983; Childs et al., 1983; Loveland and Digby, 1984; Cornell and Schwertmann, 2006), representing the organically complexed extractable Al, Fe and Si (Al_p , Fe_p , Si_p). Si_p values are usually low since little allophane is dissolved by pyrophosphate (Parfitt and Childs, 1988). The determination was done according to the method describe by Bascomb (1968), McKeague et al., (1971) and Wada and Higashi (1976). Procedurally, 0.5 g soil was weighed into centrifuge tubes and 50 ml of 0.1 M $Na_4P_2O_7 \cdot 10H_2O$ (sodium pyrophosphate) buffered at **pH 10.0** added. Samples were capped and placed on a shaker (Edmund Bühler GmbH SM-30™®) overnight (16 hrs) with 10 drops of “superfloc” added. Samples were then centrifuge for 15 minutes at 448 RCF on an Eppendorf™® 5810 R centrifuge and the supernatant analysed by AAS on a Varian™® Spectra AA – 220 FS.

2.5 Dithionite-citrate-bicarbonate Reagent

Dithionite–citrate–bicarbonate extractable Al (Al_d) and Fe (Fe_d) were determined following the procedures of Mehra and Jackson (1960). Procedurally, 0.5 g soil was weighed into centrifuge tubes and 45 ml 0.3 M $C_6H_5Na_3O_4 \cdot 2H_2O$ (sodium citrate) and 5 ml 1.0 M

NaHCO₃ (sodium bicarbonate) added to buffer the solution to **pH 7.3**. Tubes were then placed in a water bath (Clifton™® DU-4 Ultrasonic bath) at 80°C and allowed to stand until samples reached the desired temperature. One (1.0) g of Na₂S₂O₄ (sodium dithionite) powder was added and stirred constantly for 1 minute and intermittently every 5 minutes for 15 minutes. A second 1.0 g portion of Na₂S₂O₄ was added and occasional stirring continued for another 10 minutes. Samples were then removed from the water bath and allowed to cool. Samples were centrifuge (Eppendorf™® 5810 R) for 15 minutes at 448 RCF and analysed by AAS on a Varian™® Spectra AA – 220 FS. The procedure is reported to remove amorphous coatings and crystals of free iron oxides and some coatings of alumina thereby assisting in the dissolution of free silica (Mehra and Jackson, 1960). It also removes amorphous inorganic Fe and Al oxides and organic-complexed Fe and Al. It results in an almost complete solution of Fe oxides without differentiation between various crystalline forms (Parfitt and Childs, 1988).

2.6 Chang and Jackson Extraction

The Chang and Jackson (1957) procedure, as described by Olsen and Sommers (1982), was utilized to fractionate P into NaOH (P_{NaOH}), citrate–bicarbonate (P_{CB}), citrate–bicarbonate–dithionite (P_{CBD}), and HCl (P_{HCl}) extractable forms. This procedure was chosen primarily because some of the extractants of the Chang and Jackson procedure parallels those used for Al and Fe, allowing P fractions to be related to Fe and Al forms (Cade-Menun et al., 2000). Procedurally, the method involved sequentially extracting 0.5 g soil with (1) 30 ml 0.1 M NaOH (sodium hydroxide); (2) 30 ml (27 ml 0.3 M C₆H₅Na₃O₄.2H₂O (sodium citrate) + (3 ml 1.0 M NaHCO₃ (sodium bicarbonate); (3) 30 ml Citrate-Bicarbonate-Dithionite (27 ml 0.3 M C₆H₅Na₃O₄.2H₂O (sodium citrate) + (3 ml 1.0 M NaHCO₃ (sodium bicarbonate) + 2 g of Na₂S₂O₄; and finally (4) 30 ml 1.0 M HCl. The concentration of P in each fraction was determined colorimetrically by the Murphy and Riley (1962) molybdate blue method using a Biotek™® Powerwave XS microplate spectrophotometer.

2.7 Calculation of allophane, ferrihydrite, goethite, and Al and Fe amorphous and crystalline forms.

The allophane content was determined according to the calculations by Parfitt and Wilson (1985) which was further developed by Mizota and Van Reeuwijk (1989):

$$\% \text{ Allophane} = \frac{100}{Y} \times \% \text{SiO} \quad [15]$$

Y = % Si in allophane

$$\text{where: } Y = -5.1x + 23.4 \text{ and } x = \frac{\% \text{AlO} - \% \text{Alp}}{\% \text{SiO}}$$

The ferrihydrite content was estimated by the formula (Childs et al., 1991):

$$\% \text{ Ferrihydrite} = \text{Fe}_o \times 1.7 \quad [16]$$

where Fe_o = acid ammonium oxalate extractable Fe

The % goethite content was calculated by the formula as was proposed by Jahn and Asio (1998):

$$\% \text{ Goethite} = (\text{Fe}_d - \text{Fe}_o) \times 1.6 \quad [17]$$

The Al and Fe crystalline forms were calculated by (dithionite – oxalate) respectively and the amorphous forms of Al and Fe calculated by (Oxalate – Pyrophosphate) respectively.

2.8 Description of Study Site [refer to Chapter 3 for comprehensive details]

A mountainous Caribbean island nation distinguished by geothermal hot springs, with the most famous spring being the volcanically heated, steam-covered Boiling Lake, which falls within the Morne Trois Pitons National Park, a UNESCO world heritage site since 1997.

A comprehensive description of the study sites has been elaborated in Chapter 3 entitled “Geophysical description of the Dominican environment and general characterization of study sites” and as such no further mention will be made.

2.9 Soil Sampling

Soil samples were collected during the month of April 2013. Six sites were selected at which soil samples were taken from surface soil (0-20 cm) and sub-surface soil (20-40 cm) representing different soil types according to the local classification of Lang (1967). Because the properties affecting phosphorus availability were unknown, requests to those colleagues who collected the soils specified only that the soils from each region be as diverse as possible and preferably unfertilized and amended with compost. Indeed the properties of available phosphate were unknown and subject to laboratory analysis. Soil samples from the different soil horizons were thoroughly mixed then taken for air-drying and preparation for shipment.

2.10 Statistical Analysis

Sample analysis was done in triplicate with mean and standard error of the mean (SEM) calculated. Statistical analyses were performed using the SPSS version 20.0 for Windows program (SPSS Inc., Chicago, IL). A general linear model (ANOVA) was used to test for differences in means and generalized t-test to more than two groups. It was used to explain observations, and the observed variance in a particular variable could be portioned into components attributable to different sources of variation.

The significance of differences among means was determined using Tukey's honest significant difference. Effect size was estimated as the proportion of the total variability that could be expressed by the treatment factor and was measured as a partial eta squared (PESq). The Pearson product-moment correlation coefficient was used as a measure of the degree of linear dependence between two variables. Mention of statistical significance refers to alpha = 0.05 was used for type I errors, unless otherwise stated.

Data from soil chemical, selective dissolution, and estimated Al and Fe forms were correlated to other soil constituents to gain better understanding of the dynamics of phosphorus behaviour. All percentages are expressed on air-dried soil basis.

3. Results

3.1 Soil pH measured in Sodium Fluoride (NaF)

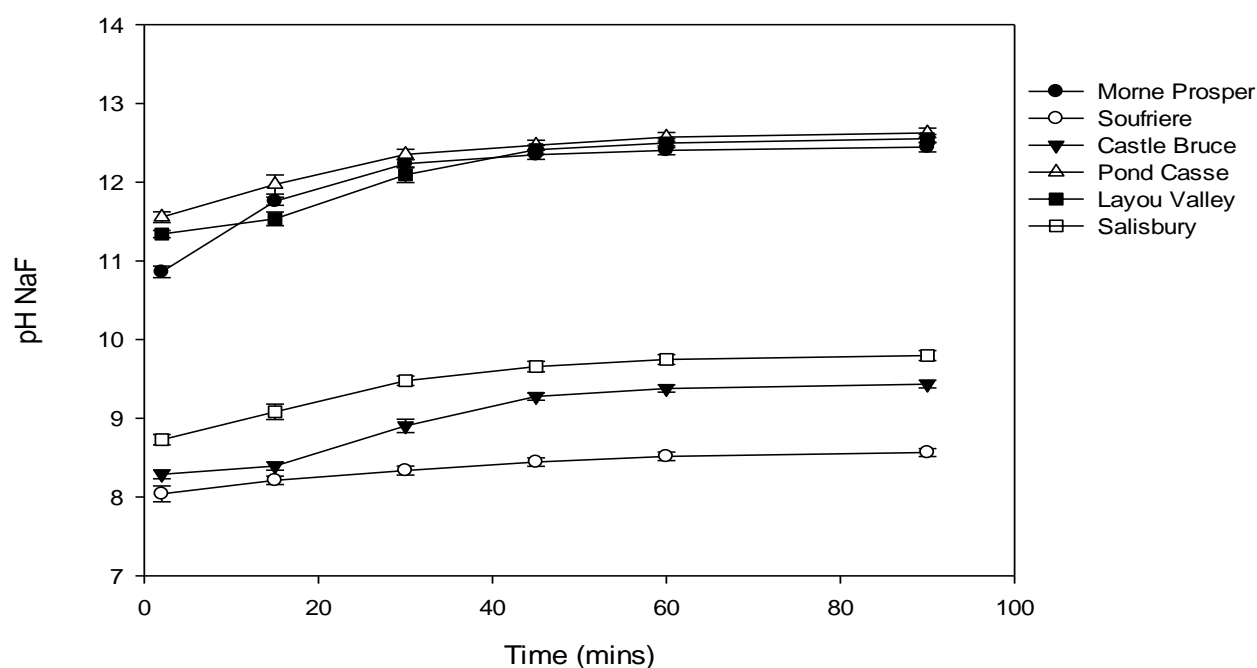


Fig. 5.1. Soil pH (NaF) measured in sodium fluoride at six time intervals for six major agricultural soils from the Commonwealth of Dominica. $n = 36$. Differentiation between 0-20 cm and 20-40 cm soil horizon were not made and soils were grouped according to local soil classification as distinct observational units.

After 2 minutes of submersion, the soil pH as measured in NaF varied from 8.04 (0.10) to 11.56 (0.07). There were significant differences ($R^2 = 0.99$; $P < 0.001$) between the six contrasting sites, which were separated into four homogeneous groups. Soils from Layou Valley, 11.35 (0.05) and Pond Cassé, 11.56 (0.07) were not statistically different from each other ($P = 0.160$) and recorded the highest pH values. Conversely soils from Soufriere, 8.04 (0.10) and Castle Bruce, 8.28 (0.05) were not statistically different from each other ($P = 0.075$) but recorded the lowest pH values (Fig. 5.1). Soils from Salisbury also recorded a low pH with a value of 8.73 (0.07). There was a noticeable significant interaction between site and soil horizon ($F(5, 35) = 3.147$, $P < 0.05$, $PESq = 0.417$). ANOVA failed to detect any significant difference between soil horizon ($P = 0.721$). The overall mean was 9.80 (0.25).

Subsequently at 90 minutes submersion, the soil pH had significantly increased in soils from all sites, ranging from 8.57 (0.05) to 12.62 (0.06) (Fig. 5.1). In that respect, there were

marked significant differences ($R^2 = 0.99$, $P < 0.001$) between the six contrasting sites ($F(5, 35) = 958.113$, $PESq = 0.995$), which were separated into four homogeneous groups. The data showed that soils from Morne Prosper, 12.45 (0.06), Layou Valley, 12.55 (0.05), and Pond Cassé, 12.62 (0.06) were not significantly different from each other ($P = 0.304$) recording the highest pH values, whereas soils from Soufriere, 8.57 (0.05) recorded the lowest pH value. There was no observed significant difference between soil horizon as well as the interaction between site and soil horizon. The overall mean was 10.90 (0.28).

The results show that the pH curve for soils from Soufriere has little slope with the curve being relatively flat in comparison with the other sites under study. The probable explanation for the relatively flat curve is that the soil contains low amounts of oxalate-extractable Al and little amount of reactive $Al(OH)_3$ which would catalyse the release of hydroxyl ions and cause a rise in pH. In addition the slope also gives information about the potential of phosphate buffering capacities of these soils with the curves having a steeper slope showing tendencies of possessing a relatively high buffering capacity and vice versa.

According to Perrott et al., (1976a) the release of hydroxyl ions on treatment with sodium fluoride solution is initially very small but hydroxyl released from alumina gel and poorly ordered aluminosilicates is appreciable with the progress of time and varies little with pH, but that from crystalline forms of alumina decreases. The pH values gives an indication of the anion adsorption capabilities of clay minerals superficial layer. Based on the study performed, our results generally tend to be in agreement with the findings of Fieldes and Perrott (1966), Brydon and Day (1970), Perrott et al., (1976a), and Gilkes and Hughes (1994) regarding the reaction of fluoride with allophanic material.

The results (Fig. 5.2) also highlight a significant positive linear correlation ($P < 0.001$) between the percentage of oxalate extractable Al ($\%Al_o$) and pH (NaF), as well as the percentage of oxalate extractable Fe ($\%Fe_o$) and pH (NaF) ($P < 0.001$). These results

demonstrate that across all sites, as the percentage of oxalate extractable Al and Fe increased there was a corresponding increase in pH (NaF) values. In this regard it should be expected that the P-sorption potential would be highly correlated to pH (NaF) and P retention would increase with increasing oxalate extractable Al and allophane (Yatno and Zauyah, 2008). Similar results (Fig. 5.2) were obtained for pyrophosphate extractable Al ($P < 0.001$, $R^2 = 0.66$) and Fe ($P < 0.001$, $R^2 = 0.76$) with pH NaF. However the relationship of dithionite extractable Al (Al_d) with pH NaF was stronger ($P < 0.001$, $R^2 = 0.87$) when compared to the relationship of dithionite extractable Fe (Fe_d) with pH NaF ($P < 0.001$, $R^2 = 0.72$). In addition, the results showed that the relationship between oxalate extractable Si and pH NaF was significant ($P < 0.001$) with a linear relationship of ($Y = 10.04x + 5.60$, $R^2 = 0.80$).

More interestingly when one examines the data with regards to pH NaF values for 60 and 90 minutes respectively, the data tends to suggest some level of podsolization may be potentially be taking place in the lower soil horizons as was perceived by Lang (1967) and suggested by Chang and Jackson (1958) and Brydon and Day (1970). The latter authors contend that podsollic B horizons generally have pH NaF values greater than 10.2 and distinguishes reasonable well the Bf from the Bm and the Bg horizons, distinction that are sometimes impossible to make in the field, as was reported by Lang (1967). Thus the test can be a valuable guide between morphologically similar soils. Hence, these results on soil chemistry tend to support the argument of the signature characteristics of soils which exhibit “andic” properties. To that extent some authors have suggested that P retention is a suitable indicator of the extent to which non-crystalline minerals influence soil C quality (Hernández et al., 2012). The data clearly indicates that these soils can generally be separated into two distinct groups, primarily allophanic versus non-allophanic Andosols. Furthermore, soil properties such as oxalate, dithionite and pyrophosphate extractable Si, Al and Fe differ much more between these two groups of soils rather than within them (Fig. 5.2).

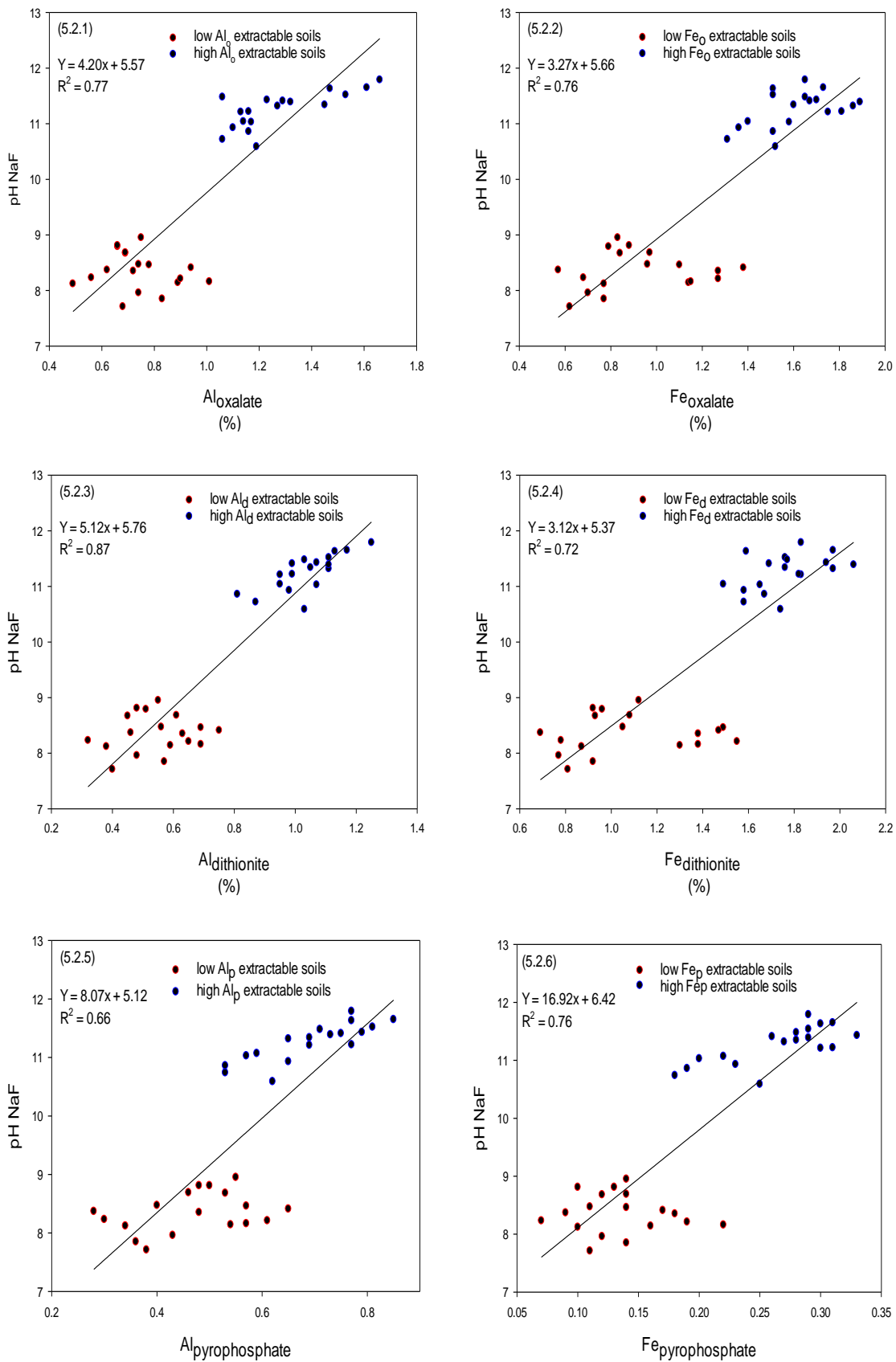


Fig. 5.2. Relationship between oxalate, dithionite, and pyrophosphate extractable Al and Fe forms and pH (NaF). $n = 36$, $P < 0.001$ level. Soils grouped according to high and low extractable Al/Fe. The visible trend is two distinct group of soils with potentially distinct P retention capacities based on sodium fluoride pH.

3.2 Toluidine Blue Test (TB test)

The test for allophane and imogolite using TB blue (Wada and Kakuto, 1985a, b) revealed a matrix of mixed results with regards to metachromasis (Table 5.1). The results highlight that soils from Morne Prosper did not or hardly displayed metachromasis with TB, unlike soils from Soufriere, Castle Bruce and Salisbury which exhibited a positive TB metachromasis, and soils from Pond Cassé and Layou Valley which had a negative TB metachromasis.

The results for the TB test strongly suggest that allophane and imogolite did not predominate across all sites and on the contrary, a substantial amount of layered silicates might be present at sites such as Soufriere, Castle Bruce and Salisbury. However, the Pond Cassé and Layou Valley sites contained allophane indicating that the absence of TB metachromasis is a result of the presence of net positive charges with possibly low $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios. In addition, the absence of TB metachromasis suggests that most of the cation exchange sites including those arising from variable negative charges had no access to TB in the solution.

In the case of soils from Castle Bruce, Salisbury and Morne Prosper, which displayed a negative-positive metachromasis, this difference in reaction with TB may have been related to the presence of negatively charged colloids. It is possible that the negative charge sites in these soils had access to TB as a result of the interaction between humus and layered silicates possibly through hydroxyl-Al and Fe cations (Hingston et al., 1972; Uehara and Gillman, 1980). This condition may have resulted in a display of positive metachromasis whereby the colour of soil samples changed from blue → pale blue → purplish red. These results tend to be in agreement with earlier observations (Okamura and Wada, 1983; Wada and Tange, 1984). These authors showed that allophanes with varying (high and low) $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios have different negative charge characteristics and selectiveness for organic cations and as such can display a positive TB metachromasis.

Table 5.1. Estimation of the presence of allophane and or imogolite by the toluidine blue test on six major agricultural soils from the Commonwealth of Dominica.

Site	Horizon	Im and/or All ^a	TB Test ^b
Morne Prosper	0-20 cm	✓	-(+)
	20-40 cm	✓	-
Soufriere	0-20 cm	✗	+
	20-40 cm	✗	+
Castle Bruce	0-20 cm	✗	+
	20-40 cm	✓	-(+)
Pond Cassé	0-20 cm	✓	-
	20-40 cm	✓	-
Layou Valley	0-20 cm	✓	-
	20-40 cm	✓	-
Salisbury	0-20 cm	✗	+
	20-40 cm	✓	-(+)

^a Im, Imogolite, All, allophane; ^b (-), supernatant = blue; -(+), supernatant = pale blue; (+), supernatant = colourless with sediment soil being purple or purplish red; ✗ = absent, ✓ = present.

The positive TB result for soils from Soufriere as an example might be in part related to TB being adsorbed on negatively charge sites in addition to low carbon content (Uehara and Gillman, 1980) showing the characteristic colour change from blue to purplish red. These negative charges could possibly arise from isomorphic substitution on the surface of layered silicates (Al-Ani and Sarapää, 2008), ionization of hydroxyl groups, presence of surface and broken-edge-OH groups or even a combination of constant and variable charge (Perrott, 1977; Barber, 1995). The results tend to suggest that these soils reacted with TB in conformity with their mineralogy and with pH (NaF) hence would reacted in a similar way in conformity to phosphate retention.

3.3 Extractable Al and Fe using oxalate, pyrophosphate, and dithionite

The results from the extraction with ammonium oxalate, citrate-bicarbonate-dithionite, and sodium pyrophosphate for Al and Fe are presented in Tables 5.2 and 5.3 respectively. The results indicate that the estimated forms of Al and Fe followed the order of Al_o>Al_d>Al_p and Fe_d>Fe_o>Fe_p respectively for all sites. The amount of Al and Fe extracted by the various reagents was generally higher in the 20-40 cm and significantly different to the concentrations

in the 0-20 cm soil horizon ($P < 0.001$), indicating that a relatively higher concentration of non-crystalline alumino-silicate material to be present in the sub-soil horizon. Interestingly, it has been reported that the accumulation of Al and Fe species in the subsoil (20-40 cm) gives a good indication of the process of podsolization taking place as has been suggested by Chang and Jackson (1958) and Brydon and Day (1970).

Table 5.2: Estimation of Al forms extracted with Ammonium Oxalate (o), Citrate-Bicarbonate-Dithionite (d), and Sodium Pyrophosphate (p). Values represent means of three replicates with SEM in parenthesis.

Site	Horizon	Si _o (%)	Al _o (%)	Al _d (%)	Al _p (%)
Morne Prosper	0-20 cm	0.43 (0.02)	1.12 (0.03)	0.88 (0.04)	0.54 (0.02)
	20-40 cm	0.54 (0.01)	1.15 (0.03)	1.03 (0.03)	0.61 (0.02)
Soufriere	0-20 cm	0.21 (0.02)	0.56 (0.04)	0.39 (0.04)	0.31 (0.02)
	20-40 cm	0.28 (0.01)	0.75 (0.04)	0.48 (0.05)	0.39 (0.02)
Castle Bruce	0-20 cm	0.31 (0.02)	0.80 (0.05)	0.64 (0.03)	0.53 (0.03)
	20-40 cm	0.39 (0.02)	0.95 (0.03)	0.70 (0.03)	0.61 (0.02)
Pond Casse	0-20 cm	0.59 (0.02)	1.40 (0.06)	1.06 (0.04)	0.74 (0.02)
	20-40 cm	0.62 (0.01)	1.60 (0.04)	1.18 (0.04)	0.81 (0.02)
Layou Valley	0-20 cm	0.47 (0.02)	1.15 (0.06)	1.03 (0.05)	0.68 (0.02)
	20-40 cm	0.56 (0.02)	1.24 (0.05)	1.057 (0.04)	0.76 (0.02)
Salisbury	0-20 cm	0.29 (0.02)	0.70 (0.02)	0.51 (0.03)	0.44 (0.02)
	20-40 cm	0.35 (0.03)	0.70 (0.03)	0.55 (0.04)	0.52 (0.02)

Si, Silicate; *Al_o*, oxalate extractable Al; *Al_d*, dithionite extractable Al, *Al_p*, pyrophosphate extractable Al.

Al oxalate was significantly different ($R^2 = 0.97$, $P < 0.001$) between sites ($F(5, 35) = 128.123$, $PESq = 0.967$) as well as between soil horizon ($F(1, 35) = 21.952$, $PESq = 0.499$). In the 20-40 cm soil horizon, *Al_o* decreased substantially from 1.60% in the case of the Pond Cassé site to 0.75% in the case of the Soufriere site (Table 5.2), which infers a decrease in weathering from udic to xeric moisture regime. In these volcanic Dominican soils, oxalate-extractable aluminium (*Al_o*) significantly increased within the soil horizon implying a higher weathering of sub-superficial horizons. An increase proportion of acid ammonium oxalate extractable Al gives rise to a process Taylor et al., (2012) referred to as “dealunimation”, used to describe an increase in the concentration of acid extractable Al as a result of accelerated weathering or chemical attack of primary crystalline and short-range order aluminosilicates.

With regards to Al_p , there were significant differences ($R^2 = 0.96$, $P < 0.001$) between sites ($F(5, 35) = 106.445$, $PESq = 0.96$) and soil horizon ($F(1, 35) = 40.825$, $PESq = 0.65$). Pyrophosphate-extractable aluminium was on average lower in the 0-20 cm soil horizon, with a mean value of 0.54 (0.04), with the 20-40 cm horizon having a mean of 0.61 (0.04).

Table 5.3: Estimation of Fe forms extracted with Ammonium Oxalate (o), Citrate-Bicarbonate-Dithionite (d), and Sodium Pyrophosphate (p). Values represent means of three replicates with SEM in parenthesis.

Site	Horizon	Fe _o (%)	Fe _d (%)	Fe _p (%)
Morne Prosper	0-20 cm	1.41 (0.06)	1.58 (0.05)	0.20 (0.01)
	20-40 cm	1.49 (0.07)	1.66 (0.05)	0.23 (0.01)
Soufriere	0-20 cm	0.67 (0.06)	0.78 (0.05)	0.09 (0.01)
	20-40 cm	0.70 (0.04)	0.83 (0.04)	0.12 (0.01)
Castle Bruce	0-20 cm	1.17 (0.05)	1.39 (0.06)	0.16 (0.01)
	20-40 cm	1.27 (0.07)	1.47 (0.05)	0.19 (0.01)
Pond Casse	0-20 cm	1.59 (0.05)	1.68 (0.05)	0.28 (0.01)
	20-40 cm	1.63 (0.06)	1.85 (0.06)	0.29 (0.01)
Layout Valley	0-20 cm	1.75 (0.06)	1.86 (0.06)	0.28 (0.01)
	20-40 cm	1.80 (0.06)	1.94 (0.07)	0.31 (0.01)
Salisbury	0-20 cm	0.87 (0.05)	0.98 (0.04)	0.11 (0.01)
	20-40 cm	0.89 (0.04)	1.04 (0.06)	0.13 (0.01)

Fe_o, oxalate extractable Fe; Fe_d, dithionite extractable Fe; Fe_p, pyrophosphate extractable Fe.

The outcomes of the estimated forms of Al and Fe revealed some very interesting trends. Throughout the 0-20 cm and 20-40 cm horizons of the investigated sites, there are noticeable quantities of iron. This is apparently related with the nature of the parent material, containing easily weathered, iron-rich minerals as was observed by Lang (1967) who reported a yellow-brown colour of the subsoil, consistent to free iron oxides in a hydrated form such as limonite. The proportional large quantities of iron forms decreased as $Fe_d > Fe_o > Fe_p$ for each Fe-form (Table 5.3) with significant differences ($P < 0.001$) between sites. However, with regards to soil horizon, Fe_o showed no significant difference, while Fe_d showed a significant difference between horizon ($P < 0.01$) as well as Fe_p ($P < 0.001$).

The corresponding percentages vary by site, most probably on account of the variation in both physico-chemical properties as well as climatic conditions (Tsai et al., 2010; Taylor et

al., 2012). To this extent, the Fe_d percentages greater than Fe_o and Fe_p tend to suggest that high amounts of Fe, released from the weathering of Fe-bearing minerals are transformed into more or less crystalline Fe-oxides. Quite a contrasting tendency can be appreciated for the various Al forms (Table 5.2). The relative abundance of aluminium forms decreases as $Al_o > Al_d > Al_p$. Different from iron, all the Al forms showed significant differences ($P < 0.001$) between soil horizon and between site ($P < 0.001$).

Soil samples in this present study, had low levels of Si_o ranging from 0.21% to 0.62% (Table 5.2). From this data analysis the results tend to suggest that the soils examined are most definitely in an early stage of development (Shoji et al., 1975; Le Bas et al., 1986). These arguments have been put forward by Lang (1967) whereby based on volcanic activity concluded that from a geological standpoint the island is relatively young, with soil maturity dependent on the duration and intensity of the weathering process. The Si_o values tend to indicate a low rate of weathering, although higher in soils from Pond Cassé than in soils from Soufriere. This may in part be attributed to annual precipitation and potential evaporation which undoubtedly affects the leaching potential. In addition, soil cultivation and management practices with a certain dependence to soil moisture regime may also influence leaching.

Table 5.4: Calculated percentages of crystalline (Cry) and amorphous (Amph) forms of Fe and Al. Values represent means of three replicates with SEM in parenthesis. n = 36.

Site	Horizon	$Al_o + 0.5Fe_o$ (%)	Al_{Cry} (%)	$Al_o - Al_p / Si_o$ (%)	Al_{Amph} (%)	Fe_{Cry} (%)	Fe_{Amph} (%)
Morne Prosper	0-20 cm	1.82 (0.06)	0.24 (0.05)	1.36 (0.10)	0.58 (0.02)	0.17 (0.05)	1.21 (0.06)
	20-40 cm	1.90 (0.06)	0.13 (0.02)	1.00 (0.07)	0.54 (0.05)	0.17 (0.05)	1.26 (0.07)
Soufriere	0-20 cm	0.89 (0.01)	0.17 (0.04)	1.18 (0.21)	0.25 (0.06)	0.11 (0.01)	0.59 (0.06)
	20-40 cm	1.098 (0.07)	0.27 (0.01)	1.28 (0.21)	0.36 (0.06)	0.14 (0.03)	0.57 (0.03)
Castle Bruce	0-20 cm	1.38 (0.04)	0.16 (0.07)	0.86 (0.09)	0.27 (0.04)	0.22 (0.09)	1.01 (0.04)
	20-40 cm	1.58 (0.03)	0.25 (0.04)	0.87 (0.09)	0.34 (0.05)	0.20 (0.06)	1.07 (0.08)
Pond Casse	0-20 cm	2.20 (0.04)	0.35 (0.03)	1.13 (0.10)	0.67 (0.07)	0.09 (0.04)	1.32 (0.06)
	20-40 cm	2.42 (0.07)	0.42 (0.01)	1.28 (0.10)	0.79 (0.05)	0.22 (0.02)	1.34 (0.06)
Layou Valley	0-20 cm	2.03 (0.09)	0.12 (0.05)	1.02 (0.20)	0.47 (0.08)	0.10 (0.01)	1.47 (0.06)
	20-40 cm	2.14 (0.06)	0.18 (0.02)	0.85 (0.10)	0.47 (0.06)	0.14 (0.07)	1.49 (0.07)
Salisbury	0-20 cm	1.13 (0.04)	0.19 (0.03)	0.88 (0.15)	0.26 (0.05)	0.12 (0.02)	0.75 (0.05)
	20-40 cm	1.15 (0.02)	0.15 (0.04)	0.52 (0.01)	0.18 (0.01)	0.15 (0.07)	0.76 (0.05)

The results for the calculated percentages of crystalline and amorphous forms of Al and Fe are presented in table 5.4 and results for the calculated percentages of allophane, ferrihydrite, and goethite are presented in table 5.5. The results indicate that the calculated percentages of allophane and ferrihydrite were highest in the soils which had corresponding higher values of pH (NaF), as well as oxalate extractable Al and Fe respectively. There were significant differences between sites ($P < 0.001$). Thus it is being suggested that an increase in amorphous forms of Al may result in increased availability of both Al and a range of trace elements usually associated with crystalline aluminosilicates.

There were significant differences ($P < 0.001$) between sites for both the amorphous forms of Fe ($F(5, 35) = 68.201$, $PESq = 0.939$, $R^2 = 0.94$, overall mean = 1.07 (0.06); as well as Al ($F(5, 35) = 27.152$, $P < 0.001$, $PESq = 0.861$, $R^2 = 0.87$, overall mean = 0.43 (0.03) (Table 5.4). There were no significant differences between soil horizon as well as the interaction of soil horizon with site for both amorphous Al and Fe. Evidently it can be observed that the dithionite procedure extracted more amorphous Fe than Al which tends to suggest that Al was strongly bonded to clay particles and apparently less available in soil solution (Holmgren, 1967). These results also tend to strongly suggest that iron associated with organic matter dominated both the 0-20 cm and 20-40 cm soil horizon, and the amorphous forms of Al tends to indicate that Al associated with organic matter being significantly different across sites was most probably influenced by site specific differences in SOM.

The crystalline forms of both Fe and Al in the 0-20 cm were not significantly different ($P = 0.255$; $P = 0.198$ respectively) from the crystalline forms in the 20-40 cm (Table 5.4), with relatively equal percentages. In addition, there was no statistical difference between sites for Fe_{cry} however Al_{cry} showed significant differences ($R^2 = 0.76$, $P < 0.001$) between sites. The amorphous forms of Al and Fe were significantly different ($P < 0.001$) from the crystalline concentration indicating that organic Al and Fe were dominant in both horizons.

Table 5.5: Calculated percentages of Allophane (All), Ferrihydrite (Ferr), and Goethite (Gt). Values represent means of three replicates with SEM in parenthesis. n = 36.

Site	Horizon	%All ¹	%All ²	%Ferr	%Gt ³	%Ferr+All
Morne Prosper	0-20 cm	2.61 (0.04)	2.61 (0.04)	2.39 (0.10)	0.28 (0.08)	5.00 (0.12)
	20-40 cm	2.94 (0.10)	2.94 (0.10)	2.53 (0.11)	0.27 (0.08)	5.47 (0.21)
Soufriere	0-20 cm	1.22 (0.14)	1.22 (0.14)	1.14 (0.10)	0.17 (0.01)	2.37 (0.04)
	20-40 cm	1.69 (0.11)	1.69 (0.11)	1.18 (0.07)	0.22 (0.06)	2.87 (0.16)
Castle Bruce	0-20 cm	1.62 (0.13)	1.62 (0.13)	1.99 (0.09)	0.35 (0.14)	3.61 (0.16)
	20-40 cm	2.05 (0.14)	2.05 (0.14)	2.15 (0.11)	0.32 (0.09)	4.20 (0.09)
Pond Casse	0-20 cm	3.35 (0.15)	3.35 (0.15)	2.71 (0.08)	0.14 (0.06)	6.06 (0.14)
	20-40 cm	3.66 (0.08)	3.66 (0.08)	2.77 (0.10)	0.36 (0.03)	6.43 (0.18)
Layout Valley	0-20 cm	2.57 (0.11)	2.57 (0.11)	2.98 (0.10)	0.17 (0.02)	5.55 (0.21)
	20-40 cm	2.95 (0.08)	2.95 (0.08)	3.06 (0.09)	0.22 (0.10)	6.01 (0.17)
Salisbury	0-20 cm	1.54 (0.12)	1.54 (0.12)	1.47 (0.09)	0.19 (0.04)	3.00 (0.19)
	20-40 cm	1.68 (0.12)	1.68 (0.12)	1.52 (0.07)	0.23 (0.12)	3.20 (0.06)

All¹, Calculated Allophane (Parfitt and Wilson, 1985), All², calculated Allophane (Mizota and Van Reeuwijk, 1989), %Ferr, ferrihydrite, Gt³, Goethite.

The results also highlight that the calculated percentages of allophane and ferrihydrite were highest in the 20-40 cm soil horizon indicating the higher values of non-crystalline aluminosilicate material in the sub-soil horizon as opposed to the top-soil (Table 5.5). The estimated percentage of allophane was highest in soils from Pond Cassé (3.66%), decreased in soils from Morne Prosper (2.94%), and was lowest in soils from Soufriere (1.69%). However, the results tend to suggest that the precipitation of hydroxyl-Al orthosilicate complexes, which gives way to the formation of allophane, was presumable perturbed by the action of organic acids derived from organic matter (Inoue and Huang, 1986), and thus a low expression of allophane even in soils such as Pond Cassé. In addition, a certain influence of anthropogenic activity on land use may be inferred, being probably higher under semi-intensely/intensively cultivated soils (Pond Cassé, Layout Valley, Morne Prosper) than under natural grasslands and pasture as in the case of soils from Soufriere.

This condition may be attributed to the differences in type and quantity of organic matter input, with probably a higher organic matter content and lower humic acid/ fulvic acid (HAc/FAc) ratio under the semi-intensive/intensive cultivated soils (Donisa et al., 2003;

Broquen et al., 2005). In this regard, Broquen et al., (2005) have suggested that lower HAC/FAC values indicate a more reactive organic matter due to the higher content of functional groups of FAC which may be somewhat responsible for the weathering degree (Senesi et al., 1977). Arguably, there may be intermediate cases in which the effect of soil moisture regime and vegetation/land use are superimposed and thus contributing to the degree of weathering.

The calculated percentages of goethite did not show that clear pattern as reported for allophane and ferrihydrite (Table 5.5). It has been suggested in the literature that with the dissolution of ferrihydrite, goethite crystals form in solution from dissolved monovalent Fe(III) ions $[\text{Fe}(\text{OH})_2^+$ and $\text{Fe}(\text{OH})_4^-]$ and as such the formation of these Fe-oxides is intrinsically influenced by pH (Hingston et al., 1972; Schwertmann and Murad, 1983; Cornell and Schwertmann, 2006). In addition, the formation of goethite usually increases with a corresponding decrease in pH (~ 4.0-5.6). Therefore, goethite should be favoured as the concentration of Fe(III) ions in equilibrium with ferrihydrite increases (Cornell et al., 1974; Schwertmann and Murad, 1983; Cornell et al., 1987).

Interestingly, it can be observed that goethite was generally higher in the sub-soil (20-40 cm) horizon as compared to the top-soil (0-20 cm) horizon and was particularly noticeable in soils from Pond Cassé. Moreover the data shows that the percentage of goethite in the 0-20 cm soil horizon in soils from Castle Bruce was equal to the percentage in the 20-40 cm soil horizon in soils from Pond Cassé, but with a higher standard error of the mean. These results appear non-conclusive and interpretation of these should be pursued with caution. However, across all sites, the percentage of goethite did not surpass 1.0% and this can be partly attributed to the low concentrations of ferrihydrite but more so the silica content which is known to influence the dissolution-reprecipitation leading to goethite (Cornell et al., 1974, 1987) by modifying the solubility, surface area, and dehydroxylation behaviour of ferrihydrite especially when co-precipitated with Fe^{3+} (ferric) thus retarding goethite transformation.

Table 5.6: Results of selective dissolution analysis of the various Al and Fe forms. Values represent means of three replicates with SEM in parenthesis. n = 36.

Site	Horizon	Al _p /Al _o	Al _o - Al _p	Al _d -Al _p	Al _o /Si _o	Al _p /Al _d	SOC/Al _p
Morne Prosper	0-20 cm	0.48 (0.01)	0.58 (0.02)	0.34 (0.03)	2.61 (0.14)	0.61 (0.02)	3.47 (0.19)
	20-40 cm	0.53 (0.03)	0.54 (0.05)	0.41 (0.05)	2.15 (0.07)	0.60 (0.04)	2.54 (0.13)
Soufriere	0-20 cm	0.56 (0.07)	0.25 (0.06)	0.08 (0.05)	2.66 (0.15)	0.81 (0.10)	1.96 (0.12)
	20-40 cm	0.52 (0.05)	0.36 (0.06)	0.09 (0.06)	2.67 (0.24)	0.83 (0.10)	3.17 (0.20)
Castle Bruce	0-20 cm	0.67 (0.04)	0.27 (0.04)	0.11 (0.03)	2.60 (0.11)	0.83 (0.04)	3.15 (0.11)
	20-40 cm	0.64 (0.04)	0.34 (0.05)	0.09 (0.02)	2.46 (0.03)	0.88 (0.03)	2.58 (0.12)
Pond Casse	0-20 cm	0.53 (0.03)	0.67 (0.07)	0.32 (0.04)	2.38 (0.10)	0.70 (0.03)	5.17 (0.18)
	20-40 cm	0.51 (0.02)	0.79 (0.05)	0.36 (0.06)	2.60 (0.08)	0.69 (0.04)	4.17 (0.12)
Layou Valley	0-20 cm	0.60 (0.04)	0.47 (0.08)	0.34 (0.06)	2.48 (0.20)	0.67 (0.04)	7.76 (0.12)
	20-40 cm	0.62 (0.03)	0.47 (0.06)	0.29 (0.05)	2.20 (0.14)	0.72 (0.04)	7.69 (0.17)
Salisbury	0-20 cm	0.64 (0.05)	0.26 (0.05)	0.07 (0.05)	2.42 (0.13)	0.88 (0.08)	3.15 (0.18)
	20-40 cm	0.74 (0.01)	0.18 (0.01)	0.02 (0.03)	2.01 (0.10)	0.96 (0.04)	1.18 (0.06)

Site	Horizon	Fe _p /Fe _o	Fe _o /Fe _d	Fe _d -Fe _p	Fe _o -Fe _p
Morne Prosper	0-20 cm	0.14 (0.01)	0.89 (0.03)	1.38 (0.06)	1.21 (0.06)
	20-40 cm	0.15 (0.01)	0.90 (0.03)	1.43 (0.04)	1.26 (0.07)
Soufriere	0-20 cm	0.13 (0.02)	0.86 (0.02)	0.69 (0.05)	0.59 (0.06)
	20-40 cm	0.18 (0.00)	0.84 (0.04)	0.71 (0.04)	0.57 (0.03)
Castle Bruce	0-20 cm	0.14 (0.01)	0.85 (0.05)	1.23 (0.06)	1.01 (0.04)
	20-40 cm	0.15 (0.02)	0.86 (0.04)	1.27 (0.06)	1.07 (0.08)
Pond Casse	0-20 cm	0.17 (0.01)	0.95 (0.02)	1.40 (0.06)	1.32 (0.06)
	20-40 cm	0.18 (0.00)	0.88 (0.01)	1.56 (0.05)	1.33 (0.06)
Layou Valley	0-20 cm	0.16 (0.01)	0.94 (0.01)	1.57 (0.06)	1.47 (0.06)
	20-40 cm	0.17 (0.01)	0.93 (0.03)	1.63 (0.08)	1.49 (0.07)
Salisbury	0-20 cm	0.13 (0.01)	0.88 (0.03)	0.87 (0.04)	0.75 (0.05)
	20-40 cm	0.15 (0.01)	0.87 (0.06)	0.91 (0.06)	0.76 (0.05)

The results from the dissolution analysis (Table 5.6) give further indication that most soils exhibit “andic” properties. Using the mean figures of the sum of Al_o+ 0.5Fe_o (Table 5.4) it was found that andic features decreased in soils from udic moisture regimes (Pond Cassé, Layou Valley, Morne Prosper) to xeric moisture regimes (Castle Bruce, Soufriere, Salisbury).

Al_p/Al_o yielded information about the relative composition of colloidal fraction (Table 5.6), being 0.5 the ratio value used to separate Al-humus complexes (<0.5) from allophanic materials (>0.5) (Shoji et al., 1988; Mizota and Van Reeuwijk, 1989; Aran et al., 2001; Vacca et al., 2003). The observation that these mean values were ≥0.5 in the 0-20 cm and 20-40 cm

horizons of all sites strongly suggest that much of the extractable Al was present in Al-humus complexes rather than being incorporated mainly into short-range-order alumino silicate material, thus possibly producing an anti-allophanic effect as suggested by (Shoji et al., 1993; Prado et al., 2007). The Al_p/Al_o ratio has also been used by several authors (Shoji et al., 1993; Aran et al., 2001; Ndayiragije and Delvaux, 2003; Vacca et al., 2003; Tsai et al., 2010) to estimate the presence of allophanic material. In the studied soils, the mean Al_p/Al_o ratio ranged from 0.48 (0.01) - 0.53 (0.03) in soils from Morne Prosper to 0.64 (0.05) - 0.74 (0.01) in soils from Salisbury (Table 5.6). To this end the result tends to strongly suggest that some of the soils were bordering on the range for allophanic properties (0.1 – 0.4) whilst others bordered on the range for non-allophanic properties (0.8 – 1.0) hence the tendency of two distinct groups.

The results for the relationship between soil organic carbon (SOC) and the calculated concentration of allophane and ferrihydrite were previously presented (Chapter 4) and showed significant relationships ($P < 0.001$) but with the content of allophane tending to decrease with increasing content of SOC ($> 4.0\%$), suggesting an anti-allophanic affect. However with regards to the relationship between SOC and goethite, no significant relationship was detected (Fig. 5.3) with no clear relationship detected within each identified group.

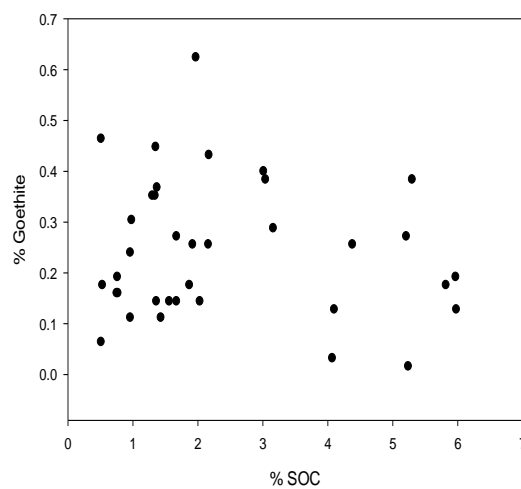


Fig. 5.3. Relationship between % soil organic carbon (SOC) and % goethite from six major agricultural soils from the Commonwealth of Dominica. Relationship not significant ($P > 0.05$). $n = 36$. No clear differentiation between soils groups. No clear relationship observed within each soil group.

The apparent non-relationship of goethite with SOC might be partly related to the low content of goethite brought about by a reduce oxidation state change of Fe^{2+} to Fe^{3+} associated with the oxalate reagent and as such the estimated calculation proposed by Jahn and Asio (1998) might probably be underestimated. This also possibly explains the reduced presence at surface conditions not withstanding that the Castle Bruce showed higher content in the 0-20 cm soil horizon. On the contrary there were significant relationships ($P < 0.001$) between the various extractable forms of Al and Fe and their dissolution relationships (Fig. 5.4).

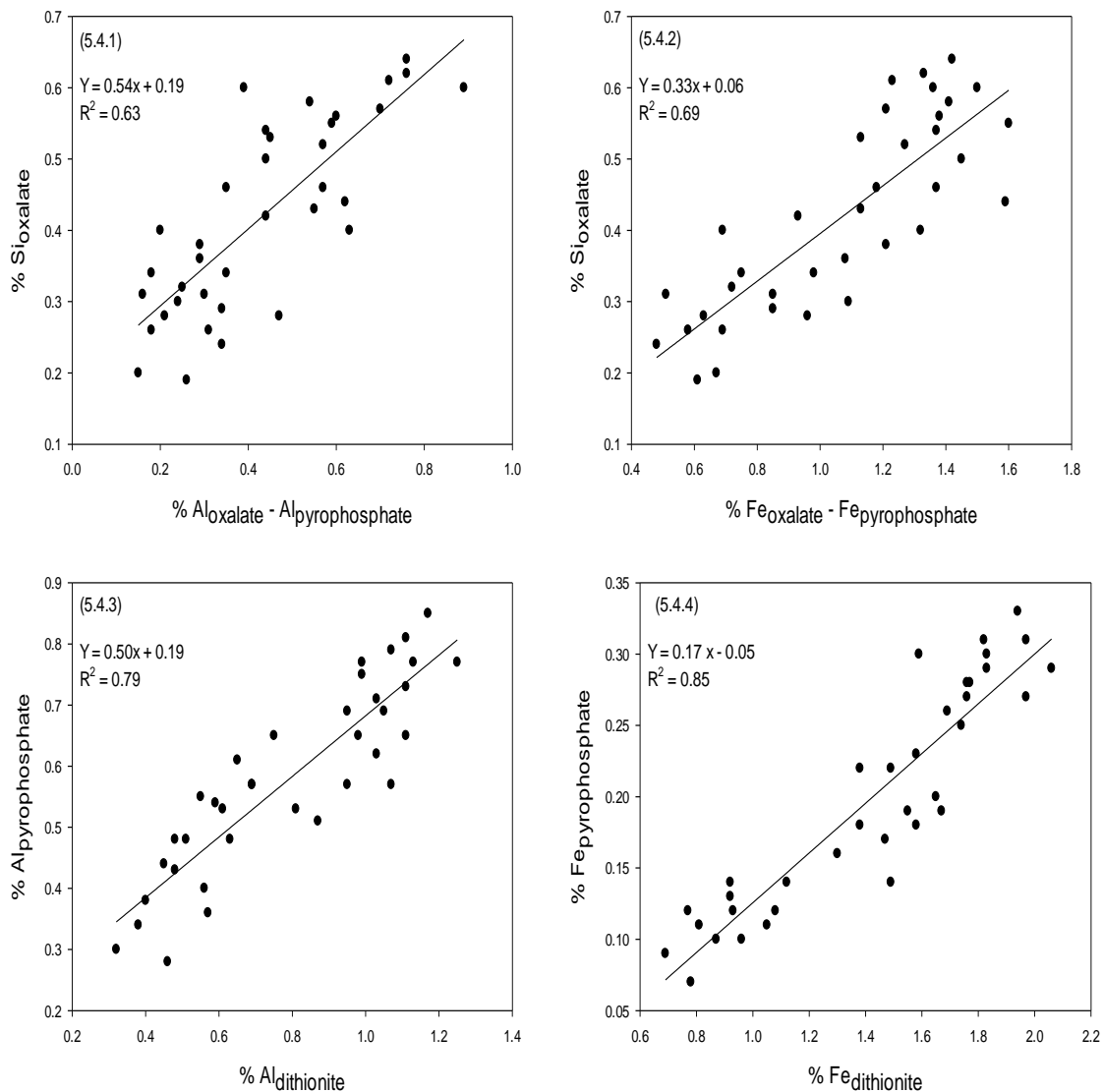


Fig. 5.4. Relationship between oxalate extractable Al (Fe) - pyrophosphate extractable Al (Fe) (%Al_o-Al_p; %Fe_o-Fe_p) and %Si_o; and Dithionite extractable Al (Fe) (%Al_d; %Fe_d) and pyrophosphate extractable Al (Fe) (%Al_p; %Fe_p). $P < 0.001$, $n = 36$.

The application of the Si_o method (Parfitt and Wilson, 1985) yielded very low values across all sites with an estimated 1.22 - 1.69% allophane content in soils from Soufriere, and an estimated 3.35 - 3.66% in soils from Pond Cassé. The Al_o-Al_p/Si_o ratio (Table 5.4) has been used by several authors to determine the ratio of allophane and imogolite (Parfitt and Wilson, 1985). Ratios between 1 and 2 are generally considered the range of ratios expected for allophane. The results (Table 5.4) generally highlight that all sites with the exception of the Castle Bruce, 0.86 (0.09) - 0.87 (0.09) and Salisbury, 0.88 (0.15) - 0.52 (0.01) had values within that range. Additionally, the $Al_o + 0.5 Fe_o$ data obtained for soils from Pond Cassé, 2.20 (0.04) - 2.42 (0.07) and Layou Valley, 2.03 (0.09) - 2.14 (0.06) tend to strongly suggest that active forms of Al and Fe may be accumulating in these soils. On the other hand, the interpretation of the data for the other sites is not as evident. However, the results tend to be in agreement with the hypothesis of Vacca et al., (2009). According to these authors, values for $Al_o + 0.5 Fe_o$ less than 1 percent (<1%) tend to suggest that active Al and Fe may have changed to more crystalline forms which can be associated to warmer and less moist environments.

The soil OC/Al_p ratio has been shown to be greatly dependent on the degree of humification and on the chemistry of soil organic matter, providing a measure of the degree of Al-saturation of humus (García-Rodeja et al., 2007). The values of this ratio (Table 5.6) ranged from 1.18 (0.06) to 7.76 (0.12). These values do not clearly show high Al saturation probably due to the significant complexing power of the decomposing organic matter, in relation to rapid drainage and warm conditions (Vacca et al., 2003). Nonetheless, for all sites with the noticeable exception of the Soufriere site, the soil OC/Al_p ratio is relatively higher in the organic matter-rich surface horizon (0-20 cm) and decreased with depth (20-40 cm).

Some authors have reported that when using the sodium pyrophosphate extraction however, it is inevitable that any other water-soluble material present in the soils when collected will also be re-dissolved and co-extracted and likely to exchange a considerable

fraction of the base cations from the cation exchange complex (Parfitt and Childs, 1988; Donisa et al., 2003). It has also been suggested that sodium pyrophosphate may dissolve some of the Fe oxide fraction (McKeague, 1967; Sheldrick and McKeague, 1975; Farmer et al., 1983; Childs et al., 1983; Parfitt and Childs, 1988; Cornell and Schwertmann, 2006). Consequently, the total pyrophosphate extractable fraction of these elements could probably represent an overestimate of the amount complexed with humic matter (Donisa et al., 2003). However, an increase in Al_p content with depth, despite the decrease of SOC content, has been reported in other research worldwide (Vacca et al., 2003; Delvaux et al., 2004).

In contrast, the Fe_o showed only a slight decrease with values of $(Fe_o - Fe_p)$ which indicates that Fe is present as amorphous Fe-oxyhydroxides (Table 5.6). Fe_d values greater than Fe_o and Fe_p suggest that high amounts of Fe, released from the weathering of Fe-bearing minerals, are transformed into more or less crystalline Fe-oxides (Vacca et al., 2009). Fe_o values were higher than Fe_p , but the Fe_p/Fe_o ratios were generally low across all sites, with Soufriere, 0.13 (0.02) - 0.18 (0.00) whilst slightly increasing in Morne Prosper and Castle Bruce, 0.14 (0.01) - 0.15 (0.01) and reaches its maxima in soils from Pond Cassé and Layou Valley, 0.17 (0.01) - 0.18 (0.00) and 0.16 (0.01) - 0.17 (0.01) respectively. The data strongly suggests that non-crystalline, or poorly crystalline forms of iron, are prevalently ferrihydrite rather than organically bound iron, although the relative abundance of Fe-humus complexes increased at the Morne Prosper, Layou Valley and Pond Cassé sites as reflected in the C:N ratios (Chapter 4). This increase in Fe-humus complexes has thus been attributed to an increase abundance of organic matter and a better humification and stabilization of organic matter (Zech et al., 1997; Vacca et al., 2009).

The Fe_o/Fe_d ratio has been used as a geochemical index and is related to the degree of Fe oxides crystallinity (Schwertmann, 1985; Buondonno and Coppola, 2005). In the investigated soils, the Fe_o/Fe_d ratio averaged 0.89 (0.02) in soils from Morne Prosper, 0.84

(0.02) in soils from Soufriere, 0.91 (0.02) in soils from Pond Cassé, 0.93 (0.02) in soils from Layou Valley, and 0.87 (0.03) in soils from Salisbury and 0.86 (0.03) in soils from Castle Bruce. It has been reported that these values are generally higher in more evolved soils, thus tends to reflect the degree of soil development from volcanic materials (Malucelli et al., 1999).

3.4 Chang and Jackson P fractionation

The results from the Chang and Jackson fractionation indicate the occurrence of P in the inorganic forms: $P_{NaOH} \gg P_{CBD} \gg P_{HCl} \gg P_{CB}$ (Fig. 5.6). Very little P was extracted by citrate–bicarbonate (P_{CB}) and across all sites P_{CB} extracted an average of 2.42% (0.13). To this extent, some authors have suggested that P_{CB} is largely or wholly derived from P resorbed during the preceding NaOH extraction (Cade-Menun et al., 2000). On the contrary, P_{NaOH} is thought to be the non-occluded phosphate bound to the surfaces of Al or Fe hydrous oxides as was reported by Olsen and Sommers (1982).

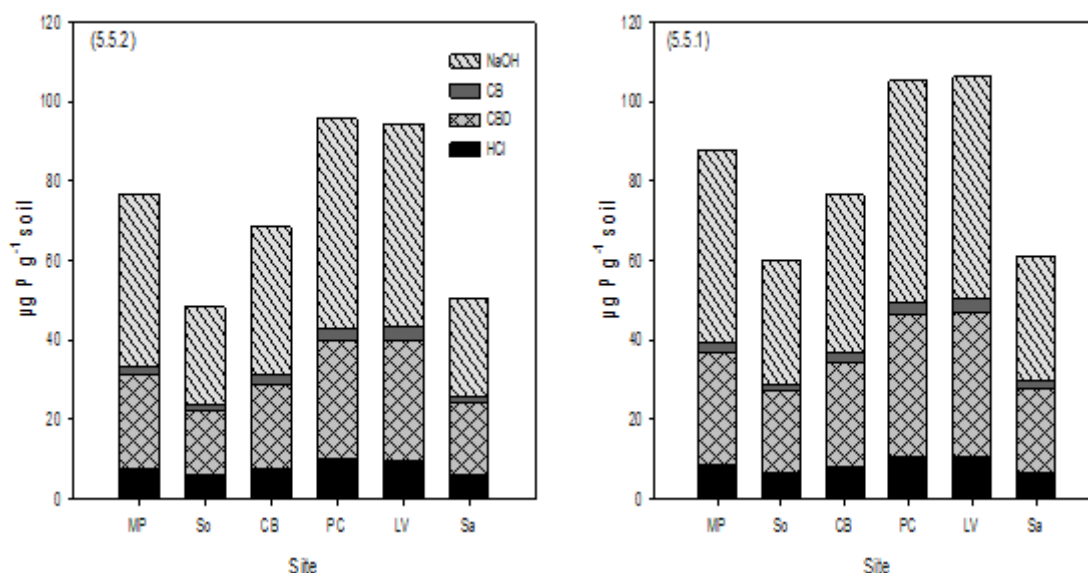


Fig 5.5. Values for P ($\mu\text{g g}^{-1}$) extracted in the 0-20 cm strata (5.5.1) and the 20-40 cm strata (5.5.2) by the Chang and Jackson P fractionation. Values represent means of three replicates. $n = 36$. MP = Morne Prosper, So = Soufriere, CB = Castle Bruce, PC = Pond Cassé, LV = Layou Valley, Sa = Salisbury. NB: Across all sites, the residual inorganic P fraction was not determined (by Na_2CO_3 fusion) and thus values represent an underestimation of total available inorganic P. In addition, residual organic P which is removed prior to the determination of residual inorganic P (by ignition at 550°C for 1 hour) was not determined and as such the total organic P fraction could not be established. However, the fractions give a fair assessment of the easily and reductant soluble P forms as well as acid extractable Ca-P complexes.

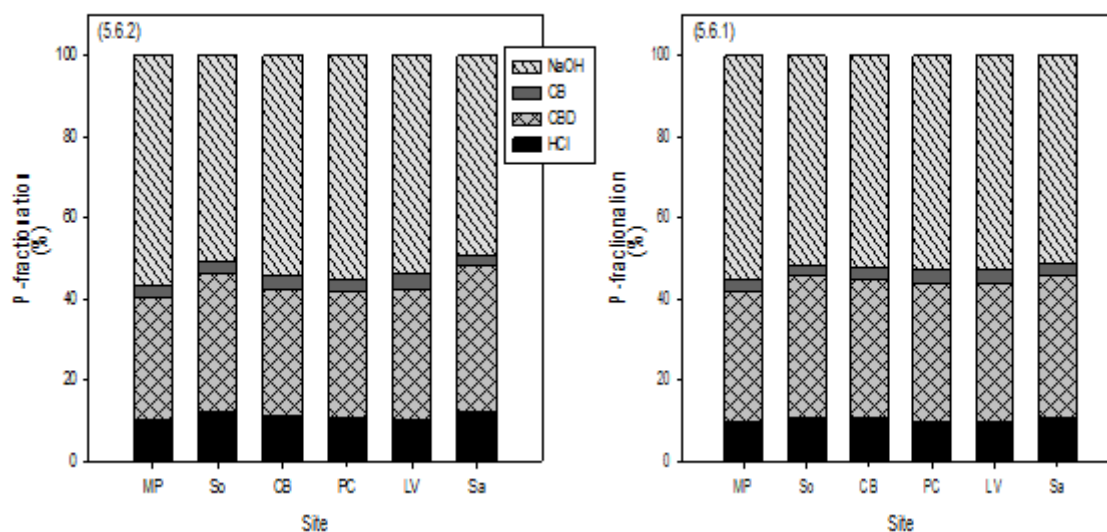


Fig 5.6. Percentage P extracted by NaOH, Citrate–Bicarbonate (CB), Citrate–Bicarbonate–Dithionite (CBD), and HCl in the 0-20 cm strata (5.6.1) and the 20-40 cm strata (5.6.2). Values represent means of three replicates. n = 36.

The P_{CBD} fraction is thought to be comprised of P occluded within the matrices of Fe and Al oxides and hydrous oxides, while the P_{HCl} is thought to be the extracted calcium phosphates of the non-occluded apatite fraction (Williams et al., 1971; Olsen and Sommers, 1982). The P_{HCl} concentrations were much lower than those for P_{NaOH} and P_{CBD} . The sum of all the fractions highlighted that the P content was higher and significantly different in the 0-20 cm as compared to the 20-40 cm (Fig. 5.5) and the corresponding percentages of the various fractions also reflect such (Fig. 5.6).

The ANOVA for the P_{CB} fraction showed significant differences ($R^2 = 0.97$, $P < 0.001$) between site ($F(5, 35) = 157.52$, $\text{PESq} = 0.973$) and soil horizon ($F(1, 35) = 22.65$, $\text{PESq} = 0.507$). There was no significant interaction between site and soil horizon. Sites were divided into 3 homogeneous subsets with soils from Layou Valley, $3.46 \mu\text{g g}^{-1}$ (0.07) and Pond Cassé, $3.27 \mu\text{g g}^{-1}$ (0.09) recording the highest values with no significant difference ($P = 0.342$). Soils from Soufriere, $1.40 \mu\text{g g}^{-1}$ (0.07) and Salisbury, $1.55 \mu\text{g g}^{-1}$ (0.09) recorded the lowest values with no significant difference ($P = 0.624$). Soils from Castle Bruce, $2.39 \mu\text{g g}^{-1}$ (0.06) and Morne Prosper, $2.46 \mu\text{g g}^{-1}$ (0.11) constituted the third homogeneous subset ($P = 0.975$). These results

strongly suggest that non-occluded phosphate bound to the surfaces of Al or Fe hydrous oxides was significantly different between sites and between the soil horizons.

The P_{NaOH} fraction showed a significant difference ($R^2 = 0.97$, $P < 0.001$) between site ($F(5, 35) = 155.72$, $\text{PESq} = 0.973$), as well as between soil horizon ($F(1, 35) = 39.39$, $\text{PESq} = 0.643$). There was no significant interaction between site and soil horizon. The sites were divided into 4 homogeneous subsets with soils from Layou Valley, $53.51 \mu\text{g g}^{-1}$ (1.44) and Pond Cassé, $54.22 \mu\text{g g}^{-1}$ (1.10) recording the highest values with no significant difference ($P = 0.995$) whilst soils from Soufriere, $27.93 \mu\text{g g}^{-1}$ (1.67) and soils from Salisbury, $28.11 \mu\text{g g}^{-1}$ (1.79) recorded the lowest values with no significant difference ($P = 1.000$). Soils from Morne Prosper, $46.05 \mu\text{g g}^{-1}$ (1.32) and soils from Castle Bruce, $38.51 \mu\text{g g}^{-1}$ (1.10) not significantly differing from each other constituted independent subset.

Similar trends were observed for the P_{HCl} fraction (Fig. 5.6) which showed significant differences ($R^2 = 0.97$, $P < 0.001$) between site ($F(5, 35) = 128.16$, $\text{PESq} = 0.967$), as well as between soil horizon ($F(1, 35) = 17.199$, $\text{PESq} = 0.439$). The sites were divided into 3 homogeneous subsets with soils from Layou Valley, $10.04 \mu\text{g g}^{-1}$ (0.21) and Pond Cassé, $10.23 \mu\text{g g}^{-1}$ (0.19) recording the highest values with no significant difference ($P = 0.951$) whilst soils from Soufriere, $6.15 \mu\text{g g}^{-1}$ (0.13) and Salisbury, $6.40 \mu\text{g g}^{-1}$ (0.17) recorded the lowest values with no significant difference ($P = 0.852$). Soils from Morne Prosper, $8.08 \mu\text{g g}^{-1}$ (0.18) and Castle Bruce, $7.83 \mu\text{g g}^{-1}$ (0.18) did not significantly differ from each other ($P = 0.827$).

This trend was also observed for the P_{CBD} which showed significant differences between site and soil horizon ($R^2 = 0.97$, $P < 0.001$). Sites were divided into 3 homogenous subsets as was the case for the P_{HCl} fraction. Although some authors have suggested that P_{CB} is largely or wholly derived from P resorbed during the preceding NaOH extraction (Cade-Menun et al., 2000), there were significant differences between site ($F(5, 35) = 167.52$, $\text{PESq} = 0.973$), as well as between soil horizon ($F(1, 35) = 22.65$, $\text{PESq} = 0.507$).

The total combined quantity of P extracted by the four individual extractants showed that soils from Layou Valley and Pond Cassé extracting the most P with average values of 106.35 $\mu\text{g P g}^{-1}$ soil and 105.36 $\mu\text{g P g}^{-1}$ soil respectively. Soils from Soufriere (60.23 $\mu\text{g P g}^{-1}$ soil) and Salisbury (61.20 $\mu\text{g P g}^{-1}$ soil) recorded the lowest values respectively. As a total percentage of P extracted, NaOH had an average of 52.7% of total P extracted across all sites. Citrate-Bicarbonate-Dithionite (CBD) accounted for 34.10% across all sites whilst HCl accounted for 10.2% across all sites (Fig. 5.6). Citrate-Bicarbonate (CB) represented a mere 2.42% across all sites, with 1.40% in soils from Soufriere to 3.46% in soils from Layou Valley.

With regards to P_{CB} , the difference between soil horizons was highest in soils from Layou Valley with a recorded difference of 0.24%, followed by soils from Soufriere with a difference of 0.21%. Soils from Morne Prosper had a difference of 0.12%, followed by Salisbury (0.04%), and finally Pond Casse (0.03%). However P_{CB} showed a significant ($P < 0.001$) relationship with Al_p ($R^2 = 0.87$) as well as with Fe_p ($R^2 = 0.91$) (Fig. 5.7).

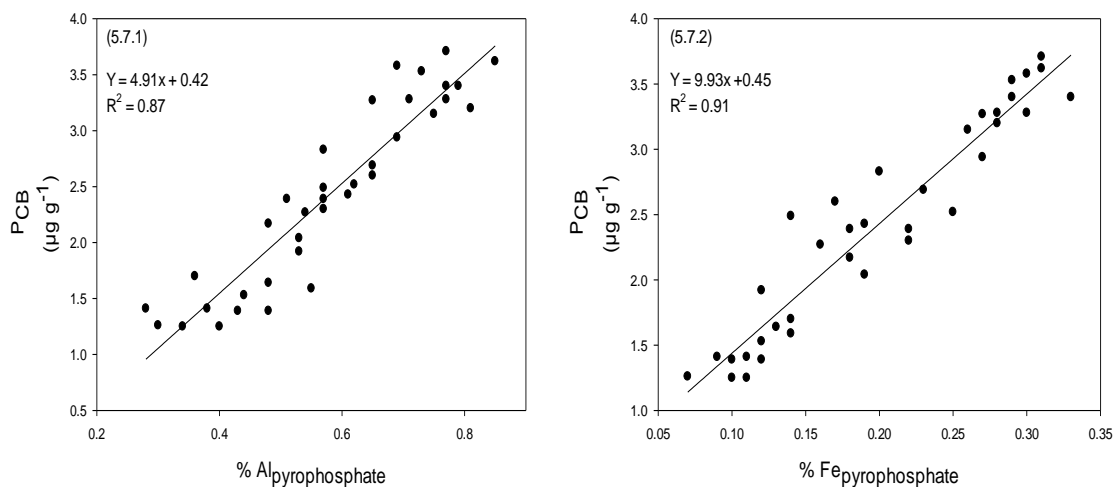


Fig. 5.7. Relationship between pyrophosphate extractable Al ($\%Al_p$), and pyrophosphate extractable Fe ($\%Fe_p$) with phosphate extractable citrate-bicarbonate (P_{CB}). $n = 36$, $P < 0.001$.

The P_{CBD} fraction showed that for soils from Morne Prosper, the difference was 1.92%. Soils from Soufriere had a difference of 0.96% and soils from Castle Bruce had a difference of 2.63%. Soils from Pond Cassé had the highest difference, 2.87% but surprisingly, soils from

Layout Valley only showed a difference of 1.95%. Soils from Salisbury recorded a difference of 0.81%. For the P_{HCl} fraction the differences were 0.52% for Morne Prosper, 1.79% for Soufriere, 0.33% for Castle Bruce, 0.65% for Pond Casse, 0.48% for Layout Valley, and 1.54% for Salisbury. Finally, the P_{NaOH} fraction showed the highest values with Morne Prosper 1.53%, Soufriere 1.04%, Castle Bruce 2.14%, Pond Casse 2.18%, Layout Valley 1.23%, and Salisbury 2.32%. These differences underscore the uneven spatial distribution of non-occluded P which would be sparingly available for plant uptake. The non-uniformity vary particularly in function of extractable P fractions which again accentuates P distribution. Under field conditions, it is plausible that micro zones of nutrient enrichment/deficiency simultaneously co-exist.

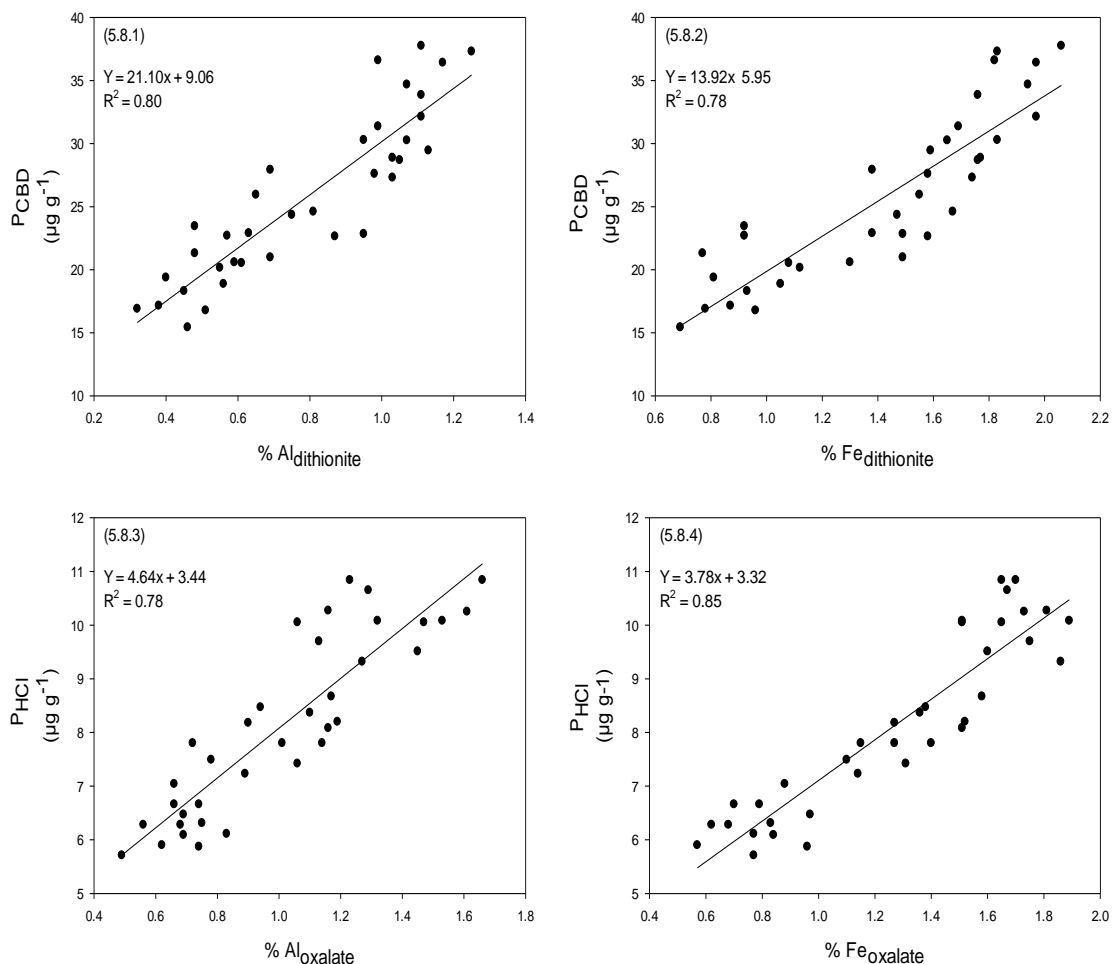


Fig. 5.8. Relationship between oxalate extractable Al ($\%Al_o$), Fe ($\%Fe_o$) and extractable HCl extractable P (P_{HCl}); and dithionite extractable Al ($\%Al_o$), Fe ($\%Fe_o$) and CBD extractable P (P_{CBD}). $n = 36$, $P < 0.001$.

The results (Fig. 5.8) shows the relationships between dithionite extractable Al and Fe with P_{CBD} ; and oxalate extractable Al and Fe with P_{HCl} being significant at $P < 0.001$. Oxalate extractable aluminium (Al_o) as well as oxalate extractable iron (Fe_o) were positively correlated with P_{HCl} . However the relationship was stronger for Fe_o ($R^2 = 0.85$, $P < 0.001$) as opposed to Al_o ($R^2 = 0.78$, $P < 0.001$). In addition, the relationship of P_{HCl} with Al_p ($R^2 = 0.88$) and Fe_p ($R^2 = 0.90$) were stronger than the other Al and Fe forms. Dithionite extractable aluminium (Al_d) as well as dithionite extractable iron (Fe_d) were positively correlated with P_{CBD} but the relationship was marginally equal with regards to dithionite extractable aluminium ($R^2 = 0.80$, $P < 0.001$) when compared to dithionite extractable iron ($R^2 = 0.78$, $P < 0.001$).

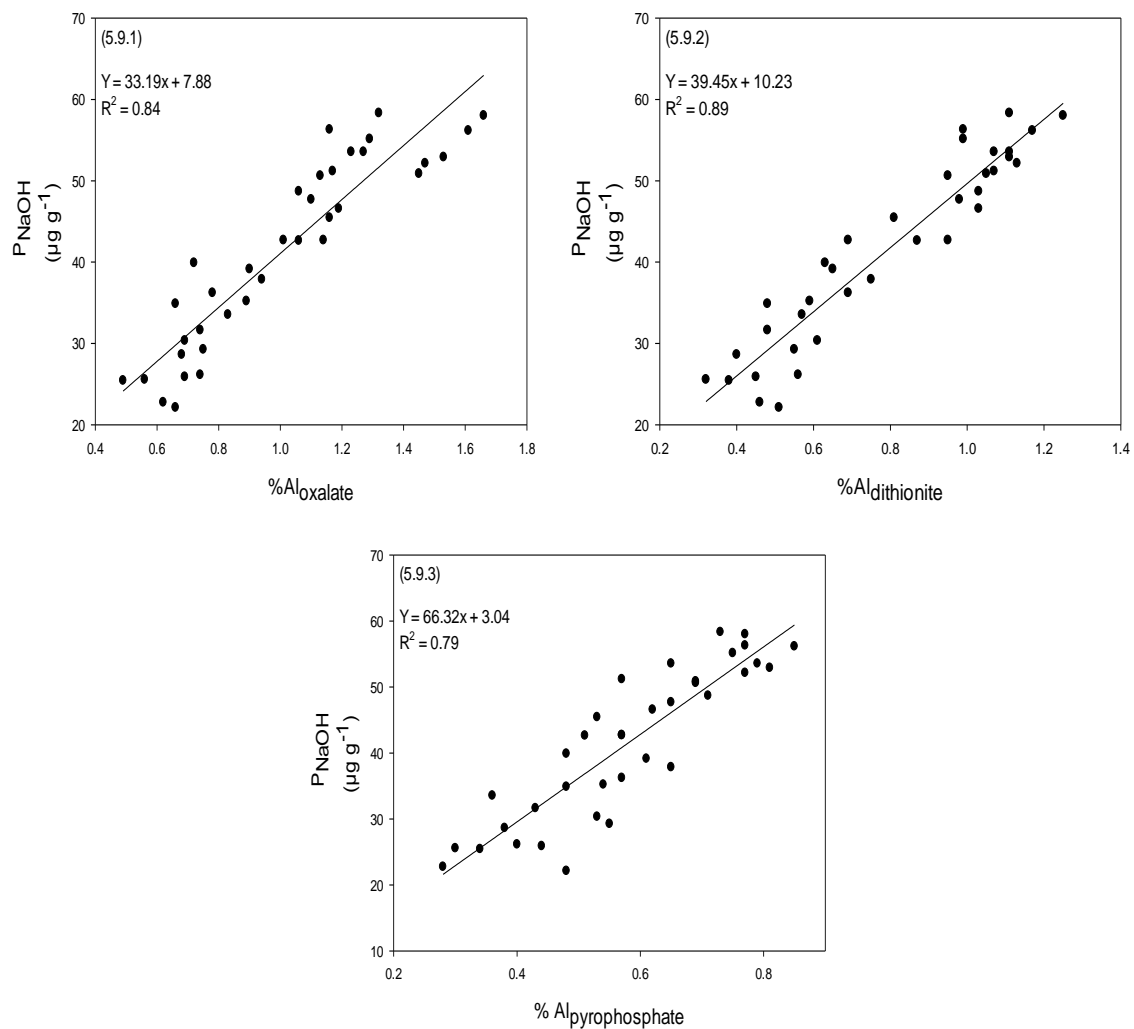


Fig. 5.9. Correlation relationship between oxalate extractable Al, (Al_o), dithionite extractable Al, (Al_d), and pyrophosphate extractable Al (Al_p) with Sodium hydroxide extractable P (P_{NaOH}). $n = 36$, $P < 0.001$.

There was a strong positive relationship between extractable Al in all forms (Al_o , Al_d , and Al_p) and sodium hydroxide extractable phosphorus (Fig. 5.9.). However, the relationship was strongest for the dithionite extractable Al ($R^2 = 0.89$, $P < 0.001$), followed by oxalate extractable Al ($R^2 = 0.84$, $P < 0.001$), with pyrophosphate extractable Al showing the weakest relationship ($R^2 = 0.79$, $P < 0.001$). A totally different trend was observed for the Fe forms (Fig. 5.10) with pyrophosphate extractable Fe (Fe_p) showing an even stronger relationship ($R^2 = 0.90$, $P < 0.001$), followed by oxalate extractable Fe ($R^2 = 0.89$, $P < 0.001$), and finally dithionite extractable Fe (Fe_d) ($R^2 = 0.87$, $P < 0.001$).

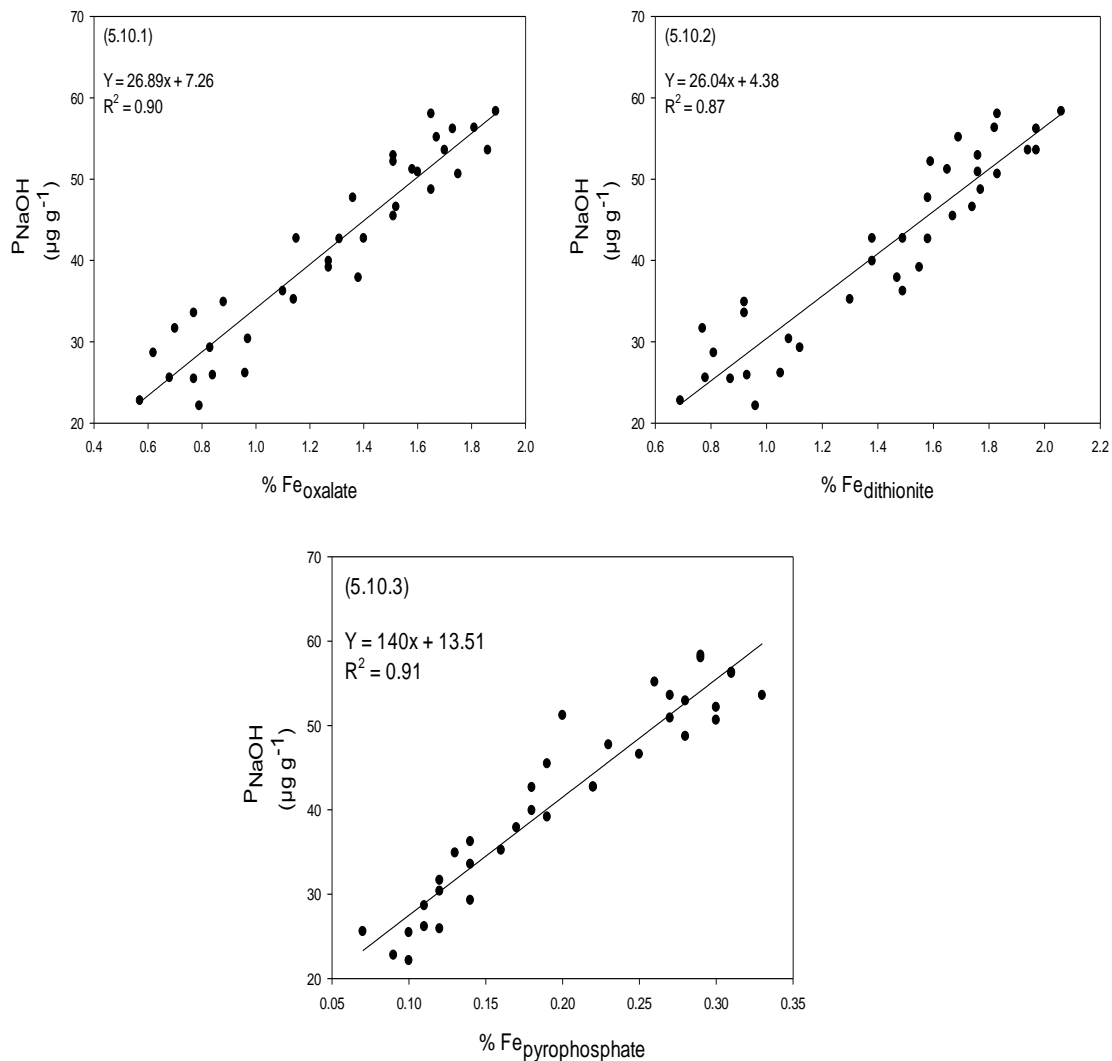


Fig. 5.10. Correlation relationship between oxalate extractable Fe (Fe_o), dithionite extractable Fe (Fe_d), and pyrophosphate extractable Fe (Fe_p) with Sodium hydroxide extractable P (P_{NaOH}). $n = 36$, $P < 0.001$.

4.0 Discussion

4.1 pH NaF

Clay minerals are the primary carriers of fluorine in soil and are known to release a large amount of hydroxide in NaF solutions which has a direct relationship on the amount of OH⁻ released (Perrott et al., 1976a,b; Gilkes and Hughes, 1994; Du et al., 2011). Indeed, the presence of fluorine as a minor constituent of soil minerals does influence SiO₂ content by forming volatile SiF₄ (Arshad et al., 1972) which invariably impacts on soil pedogenic processes. Strong exchanges of fluoride and/or phosphate has been recognized as an important feature of volcanic ash derived soils (Fiantis et al., 2010). The specific adsorption refers to incorporation of anions as ligands in the coordination shell of Fe or Al atoms, which is ranked as a ligand exchange reaction (Hingston et al., 1972; Parfitt, 1979). The reaction of soil minerals with F⁻ is related to activities of different surface-active sites existing on the superficial layers of clay minerals (Hingston et al., 1972; Cade-Menun et al., 2000), with the amount of fluoride increasing significantly by continuously modifying the pH level.

Hingston et al., (1972) and Barrow and Ellis (1986) demonstrated that the effects of increasing pH on fluoride retention by soil could be explained by the interaction between the decreasing charge on the variable charge surfaces and the changes in the proportion of fluoride present as the F⁻ ion. According to Shoji et al., (1993), this type of reaction differs from the ion exchange reactions through: (1) the anions react with active Al and Fe compounds to form covalent bonds or inner-sphere complexes; (2) sorption reactions of these anions are not completely reversible making the sorbed anions difficult to be desorbed; (3) the adsorption capacity for these anions is greater than the amount of positive charges; and (4) the ligands on the surface of active Al or Fe compounds are released by ligand exchange reactions.

In essence, the mechanism involves clay minerals adsorbing H^+ to protonate aluminium-bound surface-active hydroxyl sites in the superficial layers and induce F^- binding (Barrow and Ellis, 1986; Du et al., 2011). To this end, the adsorption of H^+ promotes the adsorption of F^- , and the protonation of Al-OH sites, which then becomes potential adsorption sites (Perrott et al., 1976b; Du et al., 2011). In addition, Huang and Jackson (1965) deduced that the attack of F^- on aluminium in clay minerals results in mineral dissolution, formation of solid AlF_4^- complexes, and the release of hydroxide ions (OH^-). However, it should be noted that the release of OH^- might be re-adsorbed by clay minerals and thus affect pH.

Values of pH (NaF) above 9.5 has been used to assign and differentiate soils with amorphous versus crystalline material (Tsai et al., 2010). Values of pH above 9.5 tend to suggest that amorphous material or active Al-OH groups are dominant in the soil exchange complex. Soils which exhibit such high pH tend to indicate that volcanic parent material may still influence the soil characteristics, even though the soils may have undergone long-term and intense weathering (Tsai et al., 2010). The high reactivity of Al and Fe bound with humus is reflected by the high pH (NaF) and phosphate adsorption values (Fig. 5.1). These are also features common to andic soil samples containing a large amount of humus (Mizota and Wada, 1980; Mizota et al., 1982; Shoji, 1985). More interestingly, Candan and Broquen (2009) demonstrated that aggregate stability tends to increase as pH (NaF) values increases, thus indicating the influence of active Al. According to Yuan et al., (2000), this may be caused by Al interacting with organic matter through an exchange of ligands between the hydroxyls on the allophane surface and the carboxylic groups of humic acids.

A number of authors (Farmer and Fraser, 1982; Barrow and Ellis, 1986; Farrah et al., 1987; Cade-Menun et al., 2000) have highlighted that unlike silica, the chemical form of soluble Al species depends on system pH and fluoride concentration. In the absence of fluoride ions, hydrolysis of Al solutions yields a series of hydroxyl compounds (Farrah et al., 1987;

Mizota and Van Reeuwijk, 1989). Thus, it has been well established that increases in pH of a sodium fluoride solution when in contact with soil is a suitable field and laboratory test for determining the presence of allophane in soils (Perrott et al., 1976a,b; Gilkes and Hughes, 1994) whilst other researchers have confirmed the value of the test for detecting alumina-silicates gels and hydroxyl alumina species in soils (Brydon and Day, 1970). According to Parfitt and Henmi (1980) a rapid reaction usually takes place when NaF is added to allophane samples, which indicates that there are a number of defect sites and broken bonds where F can react with Al and break up the structure.

In the presence of fluoride, competing equilibrium relationships define the pH and it is generally accepted that, as F adsorption proceeds, the solution pH increases, thus depleting the protons in the solution (Du et al., 2011). Despite the usefulness of the test in determining the reactivity of the inorganic fraction of the soil, Perrott et al., (1976b) were instrumental in highlighting that it does not provide specific information with regards to a quantitative measure of the amount of poorly ordered material present. These authors proposed an alternative method which involves the reaction of the soil or clay at 25°C with 0.85 M NaF at pH 6.8 and went on to argue that the amount of OH⁻ released after 25 minutes being taken as the single value characteristic. However, like many methods, it is limited in that it may not be totally suitable for surface soils because of interference by organic matter likewise for carbonate containing soils unless the carbonate content is removed.

4.2 Toluidine Blue Test

Toluidine blue (TB) is adsorbed on negatively charged colloids and exhibits a characteristic colour change (metachromasis) from blue to purplish red (Wada and Kakuto, 1985a,b). Studies have shown that Andosols in which allophane and imogolite predominate in the exchange complex have a small amount of negative charges under the conditions in which they occur in the field (Fernández-Caldas and Herbillon, 1982; Okamura and Wada, 1983;

Wada and Kakuto, 1985a; Ochoa, 2004). To this end, the presence of layered silicates tend to suggest that these soils may have large amounts of negative charges (Uehara and Gillman, 1980). In principle, superficial and sub-superficial soil layers containing large amounts of Al and Fe-humus complexes do not react with TB even in the absence of allophane and imogolite (Wada and Kakuto, 1985a), and according to the stoichiometry of the reaction relatively small amounts of layered silicates can exhibit the metachromasis with TB.

Some researchers have suggested that imogolite-like allophane ($Al/Si = 2$) occurs very frequently in soil horizons with >1 or 2% allophane, suggesting that it is more stable, or is more readily formed, in soils than other allophanes (Wada et al., 1979; Parfitt and Kimble, 1989). In addition, some researchers have argued that imogolite can form only in solutions of $pH < 5$ from a hydroxy-aluminium orthosilicate precursor (Farmer et al., 1983). A $pH > 4.7$ is required for allophane to precipitate and generally, allophane forms from glass (at $pH (H_2O) 5$ to 7), and feldspar and/or biotite (at $pH \sim 5$) in soils with udic moisture regimes and with good drainage (Shoji and Fujiwara, 1984; Nanzyo et al., 1993b). Under these conditions silicic acid and hydroxy-aluminium cations react to give allophane (Shoji et al., 1993; Nanzyo et al., 1993a).

In effect, there are some dissimilarities existing between allophanic and non-allophanic Andosols. Shoji et al., (1993) pointed out that the main forms of active Al and Fe are allophane, imogolite and ferrihydrite whereas in non-allophanic Andosols, they consist largely of Al and Fe complexed with humus, which can be preferentially dissolved by sodium pyrophosphate. In addition, Shoji and Fujiwara (1984) highlighted that in non-allophanic soils the Al of weathering products is present in major amounts in 2:1 layer silicates and in minor amounts in Al-humus complex. On the contrary, the Al of weathering products in allophanic soils is found in large amounts in allophane and imogolite and in small amounts in allophane-like constituents and Al-humus (Shoji and Fujiwara, 1984). These authors further pointed out that the Fe of

weathering products, however, consists mainly of the "free" form, which is largely complexed with humus, with small portions of this element being contained in the layer silicates.

The hydraulic properties of the parent material, possibly together with the time of pedogenesis, can affect the different pedogenetic trends of these soils (Vacca et al., 2003). According to these authors, allophanic soils tend to develop in younger, porous, permeable ash deposits where rapid glass weathering is favoured and Al and Si are readily available for allophane formation. By contrast, non-allophanic soils tend to develop in older, less porous, and less permeable scoria and consolidated tuffs where pedogenesis induces the neogenesis of crystalline clays and hydrated halloysite is probably formed by in situ weathering of volcanic glass. Moreover these authors have argued that allophanic and non-allophanic soils can then coexist in similar landscapes under similar climatic conditions (Vacca et al., 2003, 2009).

It is well documented that allophane formation is influenced by Si solubility (Henmi and Wada, 1976). In effect Si-rich allophanes are present in environments where Si in soil solution is likely to be high, and Al-rich allophanes are present in acid soils where the Si in soil solution is likely to be low (Parfitt and Kimble, 1989). Silicate weathering and leaching results in the removal of Si from soils and the accumulation of Al, Fe and other oxides and these changes are accompanied by decreased Si solubility in water (Buurman et al., 2007; Georgiadis et al., 2013). Evidently, oxalate extractable Si differed much more between these two groups of soils.

The abundance of allophane and imogolite usually increases with an increase in the amount of silica leaching while the abundance of halloysite increases with a decrease in silica leaching or from an enrichment of silica in the soil profile (Parfitt and Kimble, 1989; Mizota and Van Reeuwijk, 1989; Parfitt, 1989b; Gérard et al., 2007). Furthermore, the higher the allophane content the higher would be the active aluminium (Al_o). Likewise, active Fe (Fe_o) is generally higher in soils containing more allophane (Van Ranst et al., 2004, 2008). This suggest that

soils containing a large amount of allophane in the clay fraction would normally have a higher affinity for P, resulting in a lower availability of P for plant growth.

According to Wada and Kakuto (1985b) the high reactivity of Al and Fe bound with humus is reflected by the high pH (NaF) values. These are also features common to andic soil samples containing a large amount of humus (Mizota and Van Reeuwijk, 1989; Shoji and Takahashi, 2002). It is therefore not totally surprising that soil samples which contained allophane and imogolite showed the metachromasis with TB (Table 5.1). Metachromasis was more than likely on account that these soils possibly contained layer silicates and humus reacting with small amounts of TB.

Thus in effect, the presence or absence of allophane will then depend on the rates of production of hydroxyl-aluminium species both locally and by illuviation (Van Breemen et al., 2000; Velde and Barre, 2010), the rates of formation of humic and fulvic acids (Hall et al., 1996; Yuan et al., 2000), the amounts of smectite and vermiculite (Farmer, 1984), and temporal factors (Creton et al., 2008). However, it should be noted that the absence of TB metachromasis is not a reaction specific to allophane and imogolite (Wada and Kakuto, 1985a,b). In essence the test indicates that negative charges are absent or present in very small amounts in a soil as it occurs in the field or that negative charge sites have no access to large cations such as TB in the solution. To this effect, Yuan et al., (2000) demonstrated that ligand exchange occurs between the surface hydroxyl groups of allophane and the carboxylate groups of humic acids and as a result, the allophane-humic acid complexes can acquire negative charges which require the co-sorption of extraneous cations (Ca^{2+} or Na^{+}) for charge balance. These are also features common to andic soil materials with high active aluminium contents (Wada, 1980).

The absence of TB metachromasis can be used as an indication of "andic" soil properties, when the test is applied to samples without H_2O_2 pre-treatment. Notwithstanding the aforementioned, allophanes with variable (high and low) $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios have different

negative charge characteristics (Okamura and Wada, 1983) and selectivities for organic cations (Wada and Tange, 1984) and as such the TB test cannot be applied. However, Henmi and Wada (1976) have suggested that certain allophanes have definite structural arrangements and therefore cannot be considered "amorphous", to the extent that allophane and allophane-like constituents are differentiated by their dissolution characteristics, but not by their morphology. In addition, the colour change from blue to purplish red (metachromasis) positively suggests that TB is adsorbed on negatively charged polymers and colloids. Thus the presence of TB metachromasis suggests that most of the cation exchange sites including those arising from variable negative charges has access to TB in the solution.

4.3 Extractable Al and Fe

Andosols form under conditions of rapid chemical weathering of parent material consisting mainly of volcanic glass that releases large concentrations of Ca, Mg, Al, Fe and silica to the soil solution (Chang and Jackson, 1958). In such soil conditions, Al and Fe hydroxides and silicate ions precipitate from the super-saturated soil solution to give short-range ordered or poorly crystalline alumino-silicates like allophane and imogolite (Parfitt and Henmi, 1982; Theng et al., 1982; Buurman et al., 2007; Hernández et al., 2012).

Citrate-bicarbonate-dithionite, sodium pyrophosphate, and acid ammonium oxalate, each extract a different fraction of the soil Fe (Table 5.2) and Al (Table 5.3). The dithionite procedure extracts crystalline Fe, as well as amorphous and inorganic forms of Fe and Al. Sodium pyrophosphate extracts the Fe and Al associated with organic matter (Donisa et al., 2003). Chang and Jackson (1958) have suggested that the dithionite treatment dissolves iron phosphate but not aluminium phosphate; and aluminium phosphate apparently occludes some iron phosphate in barrandite-like forms. The ammonium oxalate extracts organic Al and Fe plus the amorphous Al associated with allophane and imogolite, and the amorphous Fe of ferrihydrite (Parfitt and Childs, 1988; Mizota and Van Reeuwijk, 1989, Parfitt, 1990).

A measure of the amorphous component is obtained by subtracting pyrophosphate results from the oxalate results. Subtracting the oxalate results from those obtained by dithionite gives the percentage of crystalline Fe (Parfitt and Henmi, 1982; Parfitt and Childs, 1988; Woignier et al., 2007; Matus et al., 2008). The short-range ordered minerals are estimated from the $(Al_o + 0.5 Fe_o)$ index, while organo-metallic complexes are calculated from the $Al_p:Al_o$ ratio (Hernández et al., 2012).

The ratio of pyrophosphate-extractable Al to acid oxalate-extractable (Al_p/Al_o) (Table 5.6) is frequently used to differentiate allophanic from non-allophanic soils (Shoji et al., 1993; Aran et al., 2001; Ndayiragije and Delvaux, 2003). Nanzyo et al., (1993a) have suggested that the Al_p/Al_o ratio is in the range of 0.1 - 0.4 for allophanic Andosols and 0.8 - 1.0 for non-allophanic Andosols. In addition, $Al_o + 0.5Fe_o$ (Table 5.4) is also used in the definition of andic soil properties which is related to the relative atomic weights of Al (~27) and Fe (~56), and by using one-half the weight of Fe the requirements are about the same amount of Fe and Al necessary for surface reactivity and exchange of OH^- groups (Van Ranst et al., 2004).

In the studied soils, the mean Al_p/Al_o ratio ranges from 0.51 (0.02) in soils from Morne Prosper to 0.69 (0.03) in soils from Salisbury. The application of the Si_o method (Parfitt, and Wilson, 1985) yielded an estimated 1.22% allophane in the 20-40 cm horizon of soils from Soufriere to a high of 3.57% in the 0-20 cm of the soils from Pond Cassé (Table 5.2). The application of the method as proposed by Mizota and Van Reeuwijk, (1989) yielded analogous results. Most notably, these results tend to generally suggest that Al was largely incorporated in Al-humus complexes, thus potentially producing an anti-allophanic effect (Shoji et al., 1993; Prado et al., 2007). The low values tend to suggest that active Al was not significantly incorporated into allophane in any of the soils under study. The amount of Si_o extracted (Table 5.2) are low and suggest little attack on silicates. To this end, Bascomb (1968) have suggested that the low values of extractable Si will somewhat reflect the amount of $< 2\mu$ clay present.

However, Dahlgren (1994) and Kleber et al., (2004) have suggested that low Si_o concentrations should not be considered for allophane estimation due to the lack of specificity by acid-oxalate, which may attack the surface of crystalline minerals. Indeed, Arshad et al., (1972) shared similar observations much earlier highlighting that greater dissolution of layered silicates by oxalate can be attributed to its low pH at which Fe (Fe²⁺) and Al are soluble.

Furthermore, hydrological conditions such as water infiltration rate in the soils and specific topographic position have been known to be responsible for lowering Si concentrations in the soil solution, (Georgiadis et al., 2013). In addition Parfitt (1990) have argued that low runoff, the lack of standing water and the high soil permeability will promote the leaching loss of Si from the soil solution thereby allowing for the formation of Al-rich allophane. Based on the aforementioned, parent material becomes evidently important in determining the formation and abundance of allophane in volcanic soils. According to Van Ranst et al., (2004) andesitic tuffaceous ash produces more allophane than basalt-andesitic ash, which in turn produces more allophane than calc-alkaline basaltic ash.

Si solubility, combined with info on phosphate extractable Si, gives information on the extent and degree of Si-saturation of reactive surfaces in soils, and indirectly, information about the crystalline materials as well (Fox, 1982). Undoubtedly, there exist a relationship between Si and phosphate sorption when low phosphate adsorption is accompanied by high Si solubility and high phosphate retention accompanied by low Si solubility (Fox, 1982). As a result, P-adsorption increases with soil weathering as a function of decreasing Si-solubility. From a biogeochemical viewpoint, allophane and imogolite are supposed to form stable organic-mineral complexes through anion and inner-sphere ligand-exchange reactions (Buurman et al., 2007). Pyrophosphate extracts peptizable organic matter and separates amorphous hydrous forms from the less active crystalline oxides (Bascomb, 1968; Arshad et al., 1972; Shang and Zelazny, 2008). However, Loveland and Digby (1984) and Shang and Zelazny (2008) were

quick to point out that the amount of Al and Fe extracted vary with experimental conditions to include centrifugation, flocculation or filtration of extracts.

More importantly, it is fully understood that a limited amount of isomorphic substitution occurs in allophane (Al-Ani and Sarapää, 2008), with the most common type being the substitution of Fe for Al. To that extent, little permanent charge is assumed to be present with the majority being variable charge (Perrott, 1977). Both cation and anion exchange capacities exist, with the relative amounts depending on the pH and ionic strength of the soil chemical environment (Hingston et al., 1972; Yuan et al., 2000; Al-Ani and Sarapää, 2008).

The iso-electric points of Al(OH)₃ and Fe(OH)₃ are between pH 7.0 and pH 8.0, and in this regard, Birrell and Fieldes (1952) have suggested that the dispersion of a soil containing both allophane and free sesquioxides should be possible in a weakly acid medium, provided the anion concentration is sufficiently low, or in a strongly alkaline medium, so long as the cation concentration is low enough. Hence, there seems to be also some critical concentration of iron or aluminium hydroxide in the soil, above which neither acid nor alkaline dispersing media are effective. To this effect, Bascomb (1968) argued that an alkaline pH (pH 10) for extractable pyrophosphate is preferable based on the solubilities of organic matter versus inorganic Fe compounds whereby obtaining the maximum amount of peptizable organic matter and separation of amorphous hydrous forms from the less active crystalline Fe oxides.

High ratios of Al_p/Al_o and Fe_p/Fe_o (>0.8) (Table 5.6) tend to strongly suggest that active Al and Fe were largely complexed with humus (Aran et al., 2001). In essence, the Al_p/Al_o ratios indicate that the proportion of organic-bound Al in the pool of mobile Al. The high affinity of pyrophosphate for organically bound Al has led to its use as an extractant for these Al forms, and in principle gives an estimate of the amount of organic-bound Al. Aluminium reacts with organic matter in many soils to form stable complexes and may be monomeric or it may be in hydroxy polymers (Hall et al., 1996). In most cases Al is quantitatively extracted

from the humus complexes with pyrophosphate reagent (Higashi et al., 1983). Consequently, the effectiveness of sodium pyrophosphate in removing the easily extractable organic matter has been attributed to its ability to chelate with Ca and trivalent metal ions (Hall et al., 1996).

The predominance of organic associated Fe and Al (Table 5.2 and 5.3) tends to reflect the characteristic illuviation of organic matter and organometallic complexes which strongly suggest that some level of podsolization could be occurring especially in the high rainfall areas (Anderson et al., 1982; Buurman and Van Reeuwijk, 1984; Aran et al., 2001). Bascomb (1968) has suggested that pyrophosphate at pH 10 extracts the fractions of Al and organic matter produced in recent weathering and eluviation of soils and peptizes very fine amorphous particles, to some extent irrespective of their chemical nature without serious attack on silicates. However, as pointed out by Cade-Menun et al., (2000), the predominance of organic associated Fe and Al tends to reflect the characteristic illuviation of OM and organometallic complexes.

To this effect Buurman and Van Reeuwijk (1984) and Van Breemen et al., (2000) have argued that allophane will not be found in the eluvial horizon because Al in organic complexes is more stable than in orthosilicates. This contrasts with Fe, which tends to form oxyhydroxide structures (ferrihydrite) which adsorb organic molecules and which are peptized by pyrophosphate reagent (Jeanroy et al., 1984). To this extent Farmer et al., (1983) have found small amounts of Al to be extracted from allophane by pyrophosphate and have suggested that this may contribute to Al extracted by pyrophosphate from allophanic soils. The Si levels extracted by pyrophosphate, however, are usually very low and indicate that very little allophane is dissolved by pyrophosphate reagent in most soils.

Parfitt and Childs (1988) and Cornell and Schwertmann (2006) further noted that pyrophosphate extracts organically bound Fe and Al but not all pyrophosphate-extractable Fe and Al are from organic complexes; and some researchers have argued that pyrophosphate-

extractable Fe and Al are poor indicators of organically bound pools that are of interest to plant nutrition (Bertsch and Bloom, 1996; Loeppert and Inskeep, 1996).

Several authors have highlighted that Al_o gives an estimate of Al in allophane, imogolite and organic matter, and indexes amorphous, short-range order oxides with high surface area and reactivity to soil P (Parfitt and Henmi, 1982; Parfitt and Childs, 1988; Parfitt, 1989b; Cade-Menun et al., 2000; Cornell and Schwertmann, 2006; Richter et al., 2006; Woignier et al., 2007; Matus et al., 2008). Likewise, ongoing acidification protonates these oxides surfaces, rendering them more reactive to a variety of anionic functional groups, (Richter et al., 2006). According to Cornell and Schwertmann (2006) because of the strong complexing ability of oxalate at pH 3.0, organically bound Fe and Al are also extracted in this manner and have suggested that protonation and complexation are two likely mechanisms responsible for the dissolution of Al and Fe in acid oxalate solution under darkness. However, Arshad et al., (1972) noted that oxalate has limitations in its use especially for soils containing trioctahedral minerals such as biotite and magnetite which are often considered to be moderately or the least stable minerals. In practice these authors demonstrated that trioctahedral minerals are affected by oxalate-releasing structural cations, which would be assumed to have been released from amorphous materials.

Al oxalate values also gives an estimate of total translocated Al, although it will also include allophane and/or imogolite as Al forms which form in situ (Childs et al., 1983). Acid ammonium oxalate attacks most silicate minerals, and goethite and hematite only slightly, but it dissolves magnetite and finely divided, easily-weathered silicates such as olivine to a considerable extent, therefore Al_o values tend to arise principally from hydroxyl-aluminium species adsorbed on or within layered silicate clays (Anderson et al., 1982). High Al_p/Al_o and Fe_p/Fe_o ratios ranging between 0.66 (0.03) as is the case of the Castle Bruce soil type and 0.69 (0.03) as is the case of the Salisbury soil type revealed that Al/Fe–humus complexes

predominated over allophanes (Table 5.6). This is consistent with the relative acidity of these soils, as formation of allophane takes place at pH (H₂O) 4.9 (Shoji and Fujiwara, 1984).

Andosols commonly show a striking accumulation of organic carbon, large amounts of active Al and Fe and low pH (Aran et al., 2001). High values have been explained by protection of organic C by allophane (Mizota and Van Reeuwijk, 1989). The presence of amorphous minerals in these soils is compatible with a substantial inhibitory effect on soil C mineralization (Hernández et al., 2012). However, for low pH values pH <5 organic matter plays an anti-allophanic effect (Shoji and Masui, 1972) by formation of metal–humus complexes leaving little or no Al available for co-precipitation with Si to form allophane and imogolite.

Non-allophanic Andosols generally contain high amounts of Al/Fe–humus complexes with strong mobilization and transfer of these complexes. In these soils, current soil-forming processes probably lead to the formation of organo-metallic associations with low carbon to metals ratio, high stability and low mobility resulting in strong accumulation of these complexes. According to Nanzyo et al., (1993a,b), the abundance of organo-metallic associations, with a high physical and biological stability and a low mobility, constitutes an original feature of non-allophanic Andosols.

The role of Al bound to organic matter in the stabilization of soil structure is evident (Shoji et al., 1993). To this extent the fractal pore structure, an important characteristic of soil stability in Andosols, is mainly determined by its allophane content (Candan and Broquen, 2009; Chevallier et al., 2010) and allophanic soils contain up to three times as much SOC as non-allophanic soils (Wada, 1985; Chevallier et al., 2010). However, soil organic carbon bioavailability generally decreases with increasing allophane content. To that extent some authors (Nanzyo et al., 1993a,b) have postulated that non-allophanic Andosols can possibly accumulate more organic C than allophanic ones which is reflected by an increase in organic C content in function of increasing of Al_p/Al_o ratios.

On the contrary, depending on the distribution and proportion of extractable Fe_d , Fe_o , and Fe_p it is possible to estimate the content of secondary iron materials in soil (Childs et al., 1983). In addition, these values give a good estimation of the likelihood of secondary iron being lost from soils possible in a mobile reduced Fe^{2+} (ferrous) state through lateral drainage. Together with citrate-bicarbonate-dithionite, extractable Fe (Fe_d), which gives a measure of the total amount of Fe oxides, Fe_o provides useful information on soil genesis. As for Al, higher levels of Fe soluble in oxalate acid tend to suggest that a higher proportion of inorganic forms of Fe predominate (Anderson et al., 1982).

Data on Fe_o are useful, since ferrihydrite, due to its hydroxylated surface and high specific surface, has an influence on important chemical reactions in soils, such as ion adsorption (del Campillo and Torrent, 1992). In addition, the rate of transformation from ferrihydrite to goethite at any one time is proportionally related to the amount of ferrihydrite left for transformation (Cornell et al., 1974; Schwertmann and Murad, 1983; Cornell et al., 1987). In this regard the data obtained from the calculated concentrations of this mineral (Table 5.5) and the apparent none relationship with soil organic carbon (Fig. 5.3) seems to suggest that goethite is strongly favoured where the concentration of monovalent Fe(III) ions, either $Fe(OH)_2^+$ or $Fe(OH)_4^-$, is at a maximum, with the rate of goethite accumulation slowing down as the pH increases (Hingston et al., 1972; Schwertmann and Murad, 1983; Cornell et al., 1987; Cornell and Schwertmann, 2006).

In effect, residual ferrihydrite in the system tends to decrease with increasing pH, with the proportion and crystallinity varying with pH (Cornell et al., 1974) hence, goethite will be favoured as the concentration of Fe(III) ions in equilibrium with ferrihydrite increases. Therefore it is not surprising that within this soil environment the formation of goethite was retarded. To further highlight this point Schwertmann and Murad (1983) demonstrated that below pH 4, although $(Fe(OH)_2^+)$ increases, it is overridden by the concentration of the divalent

Fe(OH)²⁺ ions which appear to be less favourable for goethite crystal growth than the monovalent form. In the studied soils, Fe_o values were higher than Fe_p, but the Fe_p/Fe_o ratio was generally low and the ratios were relatively equal at all sites (0.13–0.18). Notwithstanding the aforementioned, this is a clue towards the inference that non-crystalline, or poorly crystalline forms of iron, are prevalently ferrihydrite rather than organically bound iron.

Oxalate-extractable Fe (Fe_o) gives a measure of the so-called “active” forms of free Fe which is essentially ferrihydrite and small amounts of organically-bound Fe (del Campillo and Torrent, 1992). The Fe_o/Fe_d ratio has been used as a geochemical index (Buondonno and Coppola, 2005) and relates to the degree of Fe oxides crystallinity (Schwertmann, 1985). It is higher in evolved soils, thus reflecting the degree of soil development from volcanic materials (Malucelli et al., 1999). In effect, the Fe_o/Fe_d ratios lower than two (<0.2) indicate that the crystalline forms are much more abundant than the short-range-order Fe oxides (del Campillo and Torrent, 1992).

In the investigated soils, the Fe_o/Fe_d ratio (Table 5.6) were not significantly different with regards to site (P = 0.169) as well as soil horizon (P = 0.453) with a recorded mean of 0.89 (0.01). However, the absolute values as determined for soils from Layou Valley in the 0 - 20 cm soil horizon, 0.94 (0.01) and the 20 - 40 cm, 0.93 (0.03) was higher than that of soils from Soufriere (0.86 (0.02) and, 0.84 (0.04) for the 0 - 20 cm and 20 - 40 cm respectively. Ferrihydrite also has an influence on the supply of Fe to plants especially grown on calcareous soils, as is evident by the observed inverse relationship between the degree of chlorosis and Fe_o content in soil (Benítez et al., 2002; Reyes et al., 2006; Sánchez-Rodríguez, 2013; Díaz et al., 2013; Sánchez-Rodríguez, 2014). Although essentially applicable to calcareous soils, these insights should act as a guide for future studies especially in areas where calcium might possibly be or has been identified as the dominant exchangeable base.

4.4 Chang and Jackson P fractionation

The total quantity of P and plant-available P often differ greatly in soils of the tropics, which is typically related to weathering intensity (Vitousek et al., 1993; Crews et al., 1995; Herbert and Fownes, 1995; Vitousek and Farrington, 1997). The results from the Chang and Jackson P fractionation show significant differences between the six volcanic soils in terms of total P extracted. Since all the soils under study were originally from more or less the same andesitic parent material it seems plausible that the observed differences in chemical properties (differences of P-fractionation) was primarily brought about most probably by increase weathering and/or leaching due to greater age, and/or higher precipitation and temperatures, land use and management, as well as influence of slope.

Based on these results it is only reasonable that phosphorus fractions separated by the same sequential method are not of equal availability to plants in all soils (Guo and Yost, 1998; Guo et al., 2000). The high adsorption of phosphate can be ascribed to the small particle size of allophane, its high surface area of $\sim 800 \text{ m}^2/\text{g}$ (Parfitt and Henmi, 1980), and the presence at the surface of Al-OH-Al groups and defect sites (Theng et al., 1982). It is not surprising then that the presence of allophane and/or imoglite as dominating minerals will ultimately dictate the phosphate sorption potential of soils. This is further highlighted by the observation of Theng et al., (1982) who demonstrated that imoglite which also has Al-OH-Al surfaces but containing relatively few defect sites where phosphate can be adsorbed in fact has a reduced P-adsorbing potential when compared to allophanes.

In the volcanic soils under study, the total extractable P range from $106.35 \mu\text{g g}^{-1}$ to $60.23 \mu\text{g g}^{-1}$ (Fig. 5.5) with the largest inorganic P fraction in the P_{NaOH} , most likely to have been sequestered in amorphous sesquioxides. Across all sites, the P_{NaOH} fraction (53.32 – 55.12%) is higher than the P_{CBD} (32.5 - 32.27%) and P_{HCl} (11.08 - 9.56%) fractions, suggesting that inorganic phosphate is non-occluded most likely with organically associated Al and Fe.

Indeed, the non-occluded fraction will include (NH₄Cl-P, NH₄F-P, and NaOH-P). Hence, the accumulation of inorganic phosphate as extracted by NaOH strongly suggest that there was substantial adsorption of P onto surface hydroxyls of soil colloids (Cade-Menun et al., 2000).

The term “non-occluded” is believed to represent phosphate ions sorbed at the surface of Fe and Al oxides and hydrous oxides and CaCO₃. Conversely, occluded P refers to phosphate ions present within the matrices of retaining components following diffusive penetration or incorporation within developing coatings and concretions of oxides and hydrous oxides of Fe and Al with continuing soil development (Walker and Syers, 1976).

The distribution of inorganic phosphorus in soils has been used with a high degree of confidence to measure the degree of chemical weathering (Walker and Syers, 1976; Vitousek et al., 1993; Crews et al., 1995; Herbert and Fownes, 1995; Vitousek and Farrington, 1997). The relationship between Si_o and pH NaF ($R^2 = 0.80$, $P < 0.001$) strongly suggest that P-adsorption increases with decreasing Si solubility (i.e. with soil weathering). According to Theng et al., (1982) the chemical weathering sequence usually being calcium phosphate >> aluminium phosphate >> iron phosphate >> occluded phosphate. In addition, based on the observations of Chang and Jackson (1958) the occluded phosphate will invariably include reductant soluble iron phosphate and aluminium-iron phosphate occluded in iron oxides.

The results tend to suggest that the 0-20 cm horizon most likely reflects the P forms and contents of organic matter, and most of the P would be in organic forms, such as orthophosphate monoesters and diesters (Walker and Syers, 1976; Cade-Menun et al., 2000; Shen et al., 2011). Therefore it is not startling to anticipate that inorganic NaHCO₃-P will decrease the most in response to plant P withdrawal in all soils; and the inorganic NaOH-P will also decline with plant P uptake in all soils but most likely in the long term as P pools are replenished. In addition, it should be expected that the chemically and relatively resistant

organic forms of P (P_o) and residual P would vary in these soils on account of land use, vegetation and enhanced mineralization of soil organic matter (Chen et al., 2000).

As soil development proceeds further, P released by weathering would therefore decline as primary minerals are depleted with most P being retained on-site, because both biological and geochemical processes would make P nearly immobile (Uehara and Gillman, 1980; Cross and Schlesinger, 1995). However, each time P cycles through available pools, a small amount may be bound in physically or chemically protected forms, especially as soils acidify over time and a little could be leached in inorganic or organic forms. Thus, upon exposure at or near the surface, weathering of the more labile minerals in primary substrates is likely to increase the biological availability of P (Vitousek and Farrington, 1997; Selmants and Hart, 2010).

The P_{NaOH} fraction being generally high in both soil horizons gives an indication that soil P extracted by NaOH potentially represents the most biologically available P in soil (Cross and Schlesinger, 1995; Schmidt et al., 1996). The HCl fraction of P_i , is often considered to be part of the occluded non-biologically cycling pool of P and very much part of the slowly cycling biogeochemical cycle of P that can supply bioavailable P over decadal time scales (Richter et al., 2006).

From the data obtained, it would appear that given a decreased P_{HCl} fraction in the 20-40 cm horizon, relative to the 0-20 cm ($P < 0.001$), primary P minerals such as apatite might have undergone chemical changes thus reflecting the intensity of weathering (Williams et al., 1969; Walker and Syers, 1976; Stevenson and Cole 1999). However, the correlation ($R^2 = 0.78$, $P < 0.001$) of P_{HCl} to oxalate-extracted Al and P_{HCl} to oxalate-extracted Fe ($R^2 = 0.85$, $P < 0.001$) as reported (Fig.5.8.3) tends to suggest that P sorbed to amorphous Al may have been extracted instead of, or in addition to, low presence of calcium phosphate (Cade-Menun et al., 2000; Richter et al., 2006).

Some researchers (Guo and Yost, 1998; Guo et al., 2000) have suggested that in weathered soils, the HCl-P_i may act as a buffer for the NaHCO₃-P_i in the slightly weathered soils, whereas NaOH-P_i seemed to act as a buffering pool for NaHCO₃-P_i in the highly weathered soils. These authors highlight that residual P in slightly weathered soils is plant-available on a relatively short time scale. In contrast, residual P in the highly weathered soils will accumulate in the presence of intensive plant P removal, indicating that it is unavailable to plants. In defining residual P as the inorganic P present within highly crystalline oxides and hyrous oxides of Fe or highly insoluble phosphate minerals (Walker and Syers, 1976), it would then seem appropriate that organic P (NaHCO₃- and NaOH-P_o) fractions will not be significant contributors to available P in these soils that received high levels of inorganic P.

In a nutshell, the Chang and Jackson phosphorus (P) sequential extraction offers some practical utility in that it groups P fractions of similar availability into three functional pools according to the plant availability of the P fractions: readily available, the reversibly available, and the sparingly available. These grouped pools may simplify practical use of fractionation data and provide insights into differences in availability and cycling of added P in diverse soils.

It is generally accepted that the inorganic P extracted by 0.5 M NaHCO₃ (NaHCO₃-P_i) is readily available in all soils. Furthermore, the reversibly available P fractions will tend to differ between slightly weathered and highly weathered soils. In the slightly weathered soils, the reversibly available P will include the organic P (P_o) (NaHCO₃- and NaOH-P_o), NaOH-P_i, HCl-P, and residual P. On the contrary, in the highly weathered soils, NaOH-P_i and organic P are considered reversibly available. Furthermore, it is expected that no P fractions will appear to be sparingly available in slightly weathered soils. However, it is believed that residual P will be sparingly available P in highly weathered soils. The results tend to suggest that P availability will be greater when added as manure, compost or mineral fertilizer to slightly weathered soils than when added to highly weathered soils as suggested (Guo and Yost, 1998).

5. Conclusion

With a narrow range in chemistry of the parent material of Dominican soils, it has been postulated that the geochemical nature of these soils is dependent almost entirely on the weathering-leaching balance (Lang, 1967). This author suggested that the balance almost exclusively determines the nature of the weathering product in soils which may not show gross morphological differences, and as such soil development is highly dependent on the duration and intensity of the weathering process, leading towards a gradual state of soil maturity.

These soils despite their favourable physical state, are almost completely devoid of available nutrients, with phosphorus being a noted limiting nutrient. The exception will be found in the surface organic horizon which persists under primary and secondary forest and to a lesser degree under conditions of prolonged fallow. However these nutrients will be soon lost under clean cultivation, a clearly visible practice across the Dominican farming landscape, leaving the difficult problem of managing nutrient supply under a continuous and highly efficient leaching mechanism.

From the aforementioned study, a number of conclusion are being drawn which has a direct impact for the future management of phosphorus. In addition, some of the farm husbandry implications coming out from this study include:

(1) The total quantity of P ($136 - 277 \mu\text{g g}^{-1}$) and plant-available P ($28-46 \mu\text{g g}^{-1}$) differs considerable between sites most probably as a result of variation in weathering intensity and/or leaching. This difference in P availability is also related to climatic conditions (precipitation and temperature), land use management as well as the influence of slope. From an agronomic standpoint, this would imply that cost effective nutrient budget strategies needs to be developed and synchronized to soil (site) specific characteristics. Furthermore, in this extremely efficient weathering environment, it would appear that the application of external inputs such as

phosphate fertilizers would have to be frequent and may not be very effective if the organic matter content continues to be depleted.

(2) The total combined quantity of phosphorus extracted by the Chang and Jackson method revealed extremely low levels of total P, ranging from 106.35 – 61.20 $\mu\text{g P g}^{-1}$ soil. As a total percentage of P extracted, NaOH had an average of 52.7% across all sites. Hence, the accumulation of inorganic P as extracted by NaOH strongly suggest that there is a substantial amount of adsorption of P unto surface hydroxyls of soil colloids. Nonetheless, this fraction possibly represents the most biologically available P in soil hence microbial activity has the potential of mineralizing this pool and making P become plant available in the long term. However, soil microbial activity is strongly influenced by among other factors such as the application of pesticides and as such the disparity between long term edaphic health and security versus short term economic returns, through synthetic pest and disease control, is debatable especially as new alternative techniques surface.

(3) There is a very strong exchange of fluoride in these soils as was recorded by the high pH (NaF) values. There was also a high reactivity of Al and Fe bound with humus as is reflected in the high pH (NaF) values. This has implications for slope management in light of the fact that vegetated slopes of over 60° and cultivated slopes of over 50° are very common within the Dominican agricultural landscape. However, within the literature there is evidence that aggregate stability generally increases with increasing pH (NaF) values and by inference with increasing allophane content. It would seem that increasing the application of the concept to address concerns related to slope stabilization (i.e. hillside farming and road construction) could be further understood by the incorporation of allophane chemistry into routine activities.

It is generally accepted that soils formed from volcanic materials have many distinctive properties that are rarely found in soils derived from other parent materials. These soils have high potentials for agricultural production. However, some of them produce well below their

potential capacity due to lack of understanding of the nature and properties and proper management of these soils. In this regard, some general conclusions which are being made from this study include the following:

(1) The calculated concentrations of allophane and ferrihydrite were highest in soils which had corresponding higher values of pH (NaF), as well as oxalate extractable Al and Fe. This gives an indication of the P retention capacity and hence the ability of P to be plant available. Essentially these soils can be separated into two distinct groups. In addition, the soil properties differ much more between these two groups of soils rather than within them.

(2) The ratios for The Al_p/Al_o , strongly suggest that an anti-allophanic effect may in fact be consequential at some of these sites. This gives an indication of the retardation of allophane formation and hence possible increases in P solubility.

(3) The relatively high concentration of non-crystalline alumino-silicate material present in the sub-soil horizon suggests that Al was strongly bonded to clay particles and thus less available in soil solution. This suggest that reduced Al solubility would increase P retention in these soils.

(4) There were significant differences across sites for both amorphous forms of Al and Fe respectively, however the dithionite extracted more amorphous Fe as opposed to Al. In addition, the amorphous forms of Al and Fe were generally higher than the crystalline forms. This indicates that P retention would be closely related to the poorly ordered crystalline forms and P availability would essentially be derived from organic matter.

(5) High amounts of Fe, released from the weathering of Fe-bearing minerals are more than likely transformed into more or less crystalline Fe-oxides. There are noticeable quantities of iron. This is dependable and consistent with the nature of the parent material, containing easily weathered, iron-rich minerals. This indicates that Fe plays a significant role in P retention in these volcanic soils. There was no relationship of goethite with SOC within each group of soil.

CHAPTER 6

THE USE OF PHOSPHORUS SOIL TESTS FOR UNDERSTANDING POTENTIAL P LOSSES IN DOMINICAN VOLCANIC SOILS

Abstract: Although P application is an integral part of profitable agricultural systems, continued input of fertilizer and manure P in excess of crop requirements may lead to a build-up of soil P levels, which is of environmental rather than agronomic concern. To this end, the concept of P saturation and saturation capacity has been comprehensively used in predicting P losses. Within the context of Dominican agriculture, P fertilizer application is usually done through a broad spectrum N-P-K mix and manure/compost application as part of the production strategy. Thus, losses from P applications, in addition to P from organic sources, and from the bulk soil may potentially be important sources of runoff P and soil testing might aid in identifying areas prone to increased dissolved runoff P loss.

The aim of this study is to examine the influence of soil type and soil properties from some major agricultural soils in the Commonwealth of Dominica in order to identify soils vulnerable to P losses and compile information on soil constituents influencing such. To examine potential P losses at six different sites, a series of P extraction procedures were employed, namely: Iron-oxide impregnated paper strip test, water-soluble P, calcium chloride extractable P, Morgan extractable P, Mehlich-III extractable P, and Mehlich-III extractable Al, which were all correlated to other soil properties.

Soils with higher P extractable values are more saturated with P and potentially more vulnerable to P losses through run-off. A sharp difference of reactivity exists between the three classes of Al- and Fe-oxy-hydroxides. Potential P losses associated with humus bound Al-oxides (Al_p) is appreciable as compared to potential P losses on poorly crystalline and crystalline minerals (Al_o , Al_d , Fe_o , Fe_d). P saturation was best predicted by stepwise regression where $P_{sat} = -1.659 + (0.203 \text{ clay}) - (2.519 \text{ Mehlich-III Al}) + (0.535 \text{ Mehlich-III P}) - (0.449 \text{ FeO P}) + 0.0911 P_{des}$ ($P < 0.05$, $R^2 = 0.94$).

Key words: P Saturation, Sorption, Buffering Capacity, Volcanic Soils, Dominica

1. Introduction

When the volcanic soils of Dominica were first studied in a relative detailed way, most soils were found to be inherently deficient in phosphorus (Lang, 1967). As an outcome, during the heydays of citrus, coffee, and coconut cultivation and into the banana industry, regular applications of fertilizer were required, first to increase and then to maintain the P status of these soils for profitable agricultural production (Shillingford, 1972; Evans, 1986). Usually, the application consisted of broad spectrum N-P-K fertilizer mix/manure or composted material which was inopportunately not preceded by environmental soil P testing, notwithstanding efforts within the banana industry at estimating available nutrients (Cornforth and Walmsley, 1971; Ahmad et al., 1973; Twyford and Walmsley, 1974; Walmsley and Twyford, 1976).

The hydrological characteristics of the Commonwealth of Dominica, with a relatively high concentration per surface area of streams, rivers and ravines warrants that P fertilization management be reviewed amidst growing environmental concerns of ecological pollution brought about by poor husbandry practices associated with agriculture (Withers et al., 2001; Withers and Bailey, 2003; Oliver and Heathwaite, 2013); and growing concerns with regard to recreational, drinking and industrial water quality (Drigo, 2001; Bruland and Richardson, 2006; Chase, 2008; Donohoe, 2009), as well as concerns with regards to coastal marine habitats.

It has been widely acknowledged that soil test methods currently used for the determination of plant-available P in soils derived from volcanic parent material either overestimate or underestimate P availability and as such these results might not be reliable in providing a fair assessment of potential P losses (Sacheti and Saxena, 1974; Menon et al., 1989; Self-Davis et al., 2000; Bolland et al., 2003; Bell et al., 2005; Haden et al., 2007; Mason et al., 2010). This unreliability is associated with the fact that different procedures use different reagents, soil:solution ratios, and extraction times to measure P concentrations.

Nevertheless within the contemporary literature, it is known that extractable forms of Al and Fe which affects P sorption capacity in acidic soils (Parfitt, 1979, Shoji et al., 1993; Van Ranst et al., 2004; Pizzeghello, 2011) have important implications for P fertilizer management from both productivity and environmental viewpoints (Burkitt et al., 2002; Edis et al., 2002; Bramley et al., 2003; Brock et al., 2007; Haden et al., 2007; Zhang et al., 2009; Mason et al., 2010; Moody, 2011; Webb and Adeloju, 2013). Furthermore, P availability is influenced by both mineralization and immobilization rates (Mason et al., 2010; McLaughlin et al., 2011), soil pH and soil texture (Moody and Radcliffe, 1986; Edis et al., 2002), as well as tillage and/or other cultural practices such as irrigation schedules and drainage (Soldat et al., 2009).

Sustainable crop production within the Dominican setting requires the regular application of phosphorus (P) containing fertilizers due to the acute low native P reserves and high P fixation associated to Al and Fe soil constituents (Yoshinaga and Aomine, 1962; Follett et al., 1965; Wada, 1967; Wada and Higashi, 1976; Ross, 1980; Childs et al., 1983; Shoji and Takahashi, 2002; Gérard et al., 2007; Churchman, 2010). As a consequence, within the framework of ecological stewardship, keeping agronomic soil P levels well below environmental thresholds is extremely important in developing intensified agricultural systems sustainably, especially for small island developing states like the Commonwealth of Dominica because of its vulnerability to environmental hazards (Benson et al., 2001; Mercer et al., 2007; van der Velde et al., 2007; Barnett et al., 2008), most evident by the passage of tropical storm Erika (27th August, 2015). Indeed due attention now has to be given in terms of the role of soil P and hydrology in P movement; and management practices that can minimize P loss to surface waters. Hence it is more than likely that remedial strategies to reduce the risk of P loss in the short and long-term will need to focus on achieving balance between P inputs in fertilizers and P outputs in production systems (McDowell et al., 2001; Grant et al., 2005).

Based on the aforementioned, the extent of off-site environmental problems associated with agricultural production and soil-derived inputs to stream waters is cause for concern and warrants further consideration (Withers and Bailey, 2003; Schoumans et al., 2015). In this regard, the concept of P saturation and saturation capacity has been widely used for predicting P losses to water (Bolland et al., 2003; Jordan et al., 2005; Sharpley et al., 2009), and the degree of P saturation in soils has been reported as a more meaningful indicator of potential losses to water than the routinely used agronomic soil P test (e.g. Olsen, Bray and Kurtz) since P saturation describes soil in terms of P sorption sites already saturated that is independent of soil type (Yli-Halla et al., 1995; Daly et al., 2001; Ekholm et al., 2005).

Currently, the prediction of potential P losses and the concept of P saturation related to environmental implications are not in routine soil diagnostic testing within the Lesser Antilles far less for the Commonwealth of Dominica. Given the importance of this thematic area to the overall management of P fertilizer applications in these volcanic soils, this exploratory study is carried out with the objective of specifically evaluating the use of the calcium chloride extractable P ($\text{CaCl}_2\text{-P}$), Mehlich-III extractable P (Pm_3), iron oxide extractable P (FeO-P), water extractable P ($\text{H}_2\text{O-P}$), Morgan extractable P (Pm) and Mehlich-III extractable Al as predictors in assessing potential environmental P losses on six agricultural soils from the Commonwealth of Dominica.

The study aims to investigate and compile data on the chemical and mineralogical properties of these same weathered soils which are most likely to influence potential P losses. Thus the study endeavours to obtain an improved comprehension of Dominican soils with the view of applying the concept of potential P losses to practical land use and management exercises related to phosphorus activity in these soils. To this extent, efforts at incorporating measurable parameters such as P saturation in routine soil testing exercises may well prove to be essential in support of agricultural and environmental P management.

2. Materials and Methods

2.1 Description of Study Site [refer to Chapter 3 for comprehensive details]

A small island developing state with an agrarian based economy which sits midway along the Eastern Caribbean archipelago, forming part of the Windward Islands, the southern group of the Lesser Antilles in the West Indies. A comprehensive description of the study sites has been elaborated in Chapter 3 entitled “Geophysical description of the Dominican environment and general characterization of study sites” and as such no further mention will be made.

2.2 Soil Sampling

Soil samples were collected in February 2014. Six sites were visited at which soil samples were taken from surface soil and sub-surface soil. Properties related to available phosphorus were unknown and subject to laboratory analysis. Hence the sites chosen were as diverse as possible representing important agricultural production zones in the country from different geographical locations representing different soil types according to the national soil classification (Lang, 1967).

2.3 Rationale for soil extraction procedures

Within the literature there is no universal consensus of the relationship between the various extractants of P soil test and some essential parameters of soil-P status such as P saturation, inorganic and organic fractions among relevant accompanying soil attributes (Herlichy and McCathy, 2006). Furthermore, the relationship of the various soil P tests with dissolved reactive P (DRP) and biologically available P (BAP), measurements which are related to P saturation, is known to be dependent on the extraction method used (Pote et al., 1996). With all the methods having practical relevance, they were selected in order to unravel which would have better precision for predicting P saturation in these tropical volcanic soils.

2.3.1 Iron oxide paper strip extractable P (FeO-P)

The iron oxide impregnated filter paper test was developed as a soil test for phosphorus in which the FeO paper acts as an infinite sink for P mobilized in a soil solution (Menon et al., 1997). Iron-oxide extractable P (PFeO) was determined according to the method described by (Menon et al., 1989; Menon et al., 1990; Sharpley, 1993; Chardon et al., 1996). In detail the procedure involved cutting a 15-cm disc of ash free, hard filter paper (Whatman No. 42) into rectangles (10 cm x 2 cm) and afterwards immersing the strips in 0.37 M FeCl₃, acidified with 1.32 M HCl for 0.5 hours which retards the formation of goethite.

The paper was left to dry at room temperature for 1 hour. Subsequently, the paper was rapidly and uninterruptedly pulled through a bath for 30 seconds containing 2.7 M NH₄OH (5% w:v) to neutralize the FeCl₃ and produce amorphous iron (hydr) oxide. The strips were consequently rinsed with deionized water to remove adhering particles of FeO and left to air dry. The extraction procedure involved weighing 1 g of air dried soil, which was previously sieved through a 2 mm mesh, into a 50 ml centrifuge tube with the addition of 40 ml 0.01 M CaCl₂ with one filter strip added and shaking end-over-end for 16 hours (overnight). The filter strips were later rinsed with deionized water and dried at room temperature. The FeO with adsorbed P was dissolved by adding 40 ml of 0.1 M H₂SO₄ and shaking for 1 hour. Finally, the determination of P in the acidic extract was done colorimetrically according to the method of Murphy and Riley (1962) using a Biotek™® Powerwave XS microplate spectrophotometer.

2.3.2 Calcium Chloride extractable P (CaCl₂-P)

Calcium chloride extractable P was developed as a soil test for phosphorus in which extractable P corresponds to the P held in soil solution at field conditions (Beauchemin and Simard, 1999; Daly and Casey, 2003; McDowell and Sharpley, 2003; Nair et al., 2004) and therefore favours the intensity component of labile P. Calcium chloride extractable P was determined according to the method described by Self-Davis et al., (2000), McDowell and

Sharpley (2001), Daly and Casey (2005) and Brock et al., (2007). Procedurally, 1 g of air dried soil, which was previously sieved through a 2 mm mesh, was weighed into a 50 ml centrifuge tube and 25 ml of 0.01 M CaCl₂ added. Tubes were subsequently shaken end-over-end for 1 hour at 200 rpm and then centrifuged at 3184 RCF for 10 minutes. The extract was then filtered through Whatman No. 42 filter paper. The extractant was then analysed colorimetrically on a Biotek™® Powerwave XS microplate spectrophotometer, using the Murphy and Riley (1962) molybdate blue method.

2.3.3 Morgan extractable P (P_m)

The Morgan soil test is a universal extraction procedure, meaning it is used to determine all major nutrients and many of the micronutrients simultaneously hence its practicality. The modified method is reported to extract readily available P as well as accumulated P reserves (McIntosh, 1969). Morgan extractable P (Morgan, 1941) was determined according to the modified method proposed by McIntosh (1969), Jokela et al., (1998) and Kleinman et al., (2000). A modified version of the original test was employed as a means of increasing its usefulness in testing acidic soils of different ranges of fertility (McIntosh, 1969).

Procedurally, 4 g of air dried soil previously sieved through a 2 mm mesh sieve was weighed into a 50 ml centrifuge tube. 20 ml of modified Morgan's solution (0.62 M NH₄OH + 1.25 M NH₄OAC) buffered at pH 4.8 was added and tubes were shaken at 180 rpm end-over-end for 30 minutes and then centrifuged at 3184 RCF for 10 minutes. The extract was filtered through Whatman No. 42 filter paper and then analysed colorimetrically on a Biotek™® Powerwave XS microplate spectrophotometer, using the Murphy and Riley (1962) molybdate blue method.

2.3.4 Water extractable P (H₂O-P)

The extraction of some amounts of P which are actually of low availability occurs with many other extractants, whenever they are more acid or alkaline than the soil solution (Self-Davis et al., 2000). The water extraction offers a valid alternative to these extractants, since it extracts those P forms which are mobile by maintaining the soil pH as closely as possible to field conditions (Van der Paauw, 1971). Furthermore, the water extract is interesting from an environmental perspective, because it can simulate the release of P to run-off or leaching water more accurately than any of the stronger chemical extractants used for agronomic purposes (Pote et al., 1996) being closely correlated with dissolved reactive P concentrations in run-off from agricultural land.

Water extractable P was determined according to the method described by Van der Paauw (1971), Hartikainen (1982), Self-Davis et al., (2000) and Daly and Casey (2003). Procedurally, 2 g of air dried soil sieved through a 2 mm mesh was weighed into a 50 ml centrifuge tube. 20 ml of distilled water was added and shaken for one hour end-over-end at 200 rpm. Tubes were subsequently centrifuged at 3184 RCF for 10 minutes. The extract was then filtered through a Whatman No. 42 filter paper and subsequently analysed colorimetrically on a Biotek™® Powerwave XS microplate spectrophotometer, using the Murphy and Riley (1962) molybdate blue method.

2.3.5 Mehlich-III extractable P (Pm3)

The Mehlich-III test, based on the use of an acidic solution containing ammonium fluoride, was developed for routine analyses of P, K, Ca, Mg, Na, and micronutrients. The usefulness of the test is that it may offer the possibility of using one test for P and other nutrients across acid, neutral, and high-pH soils (Mehlich, 1984; Maguire and Sims, 2002a).

Mehlich-III extractable P was determined according to the method described by Mehlich (1984) which was further highlighted by Sims (2000a), Sims et al., (2002), and Brock

et al., (2007). Procedurally, 2 g of air dried soil sieved through a 2 mm mesh was weighed into a 50 ml centrifuge tube. Twenty (20) ml of Mehlich-III extracting solution which was previously buffered to pH 2.5 was added. Tubes were placed on an end-over-end shaker for 5 minutes at 200 rpm. Extracts were subsequently centrifuged at 3184 RCF for 10 minutes. The extractant was finally filtered through a Whatman No. 42 filter paper and subsequently analysed by the Murphy and Riley (1962) molybdate blue method using a Biotek™® Powerwave XS microplate spectrophotometer.

2.3.6 Mehlich-III extractable Al

Mehlich-III extractable Al followed the same procedure for the Mehlich-III phosphorus with the difference being that Al was subsequently analysed by atomic adsorption spectroscopy on a Varian™® Spectra AA – 220 FS.

2.9 Statistical Analysis

Sample analysis was done in triplicate with mean and standard error of the mean (SEM) calculated. Statistical analyses were performed using the SPSS version 20.0 for Windows program (SPSS Inc., Chicago, IL). A general linear model (ANOVA) was used to test for differences in means and generalized t-test to more than two groups. It was used to explain observations, and the observed variance in a particular variable could be portioned into components attributable to different sources of variation.

The significance of differences among means was determined using Tukey's honest significant difference. Effect size was estimated as the proportion of the total variability that could be expressed by the treatment factor and was measured as a partial eta squared (PESq). The Pearson product-moment correlation coefficient was used as a measure of the degree of linear dependence between two variables. Mention of statistical significance refers to alpha = 0.05 was used for type I errors, unless otherwise stated.

3. Results

The results for Mehlich-III extractable Al accentuated significant differences ($P < 0.001$) between sites ($R^2 = 0.87$, $PESq = 0.87$), and significant differences ($P < 0.05$) between soil horizon ($R^2 = 0.87$, $PESq = 0.21$). The mean was 39.04 mg kg^{-1} (2.11). Post Hoc analysis established 5 homogenous subsets with soils from Pond Cassé, 54.42 mg kg^{-1} (2.12) and Layou Valley, 49.53 mg kg^{-1} (3.01) equal at $P = 0.68$. Soils from Layou Valley, 49.53 mg kg^{-1} and Morne Prosper, 43.37 mg kg^{-1} (2.21) equal at $P = 0.45$. Soils from Morne Prosper, 43.37 mg kg^{-1} and Castle Bruce, 36.65 mg kg^{-1} (1.88) equal at $P = 0.35$. Soils from Castle Bruce, 36.65 mg kg^{-1} (1.88) and Salisbury, 27.78 mg kg^{-1} (2.51) equal at $P = 0.12$, with soils from Salisbury, 27.78 mg kg^{-1} and Soufriere, 22.47 mg kg^{-1} (2.08) equal at $P = 0.60$ (Fig. 6.1.7).

These results lend support that potential P adsorption sites are strongest in soils from Pond Cassé and Layou Valley, displaying high phosphate retention characteristics (Allbrook, 1985; Mizota and Van Reeuwijk 1989, Shoji et al., 1993; Fontes and Weed, 1996; Nugroho, 2010) (Chapter 5). However Yli-Halla et al., (1995) contended that soils rich in adsorbed P are also likely to contribute substantially towards eutrophication of receiving water bodies and as such the annual surface runoff becomes critical in assessing annual P load (Sharpley et al., 2003). Hence, although high soil P levels are considered as a potential source of P loss, without favourable hydrological conditions P will most likely not move out from soil.

Site vulnerability to P losses takes into account transport factors such as erosion potential, runoff, leaching, and connectivity to stream channels (Sharpley et al., 2008) as well as climatic conditions, topography and precipitation regimes (Pote et al., 1999). The suggestion being if not managed appropriately, P transfer may possibly be channelled to nearby water bodies and with intensified P input could potentially be problematic in areas such as Pond Cassé and Layou Valley where annual precipitation is $>6000 \text{ mm}$ notwithstanding a gently sloping topography. In addition, P fertilizer applied to Soufriere and Salisbury soils types may

potentially be easily lost through surface runoff and by subsurface drainage and P losses will have to be managed accordingly. In such circumstances, it has been suggested that P may be immobilized, or retained, by amending the soil with additional Fe and Al ions, initiating the formation of new bonds between these elements (Udeigwe et al., 2011). However, taking into account climatic conditions, topography and precipitation regimes (~2000 mm) suggest that the potential of P losses via surface runoff and subsurface drainage might probably be negligible but still cause for concern especially during prolonged and intense rainfall.

The results also tend to suggest that Al associated with allophane, present either as hydrous aluminium oxide and/or organic aluminium complexes (Parfitt, 1979; Farmer et al., 1980) which induces phosphate retention (Allbrook, 1985; Mizota and Van Reeuwijk 1989, Shoji et al., 1993; Fontes and Weed, 1996; Nugroho, 2010) potentially influences the translocation of Al with regards to its mobility (Anderson et al., 1982; You et al., 1999). Moreover phosphate adsorption would be affected by competition for adsorption sites by the presence of positively charged ions of iron and aluminium (Mekaru and Uehara, 1972; Parfitt, 1979; Barrow, 2015) and would thus affect P saturation and potential P losses in these soils.

In contrast and inversely related, the results for the Mehlich-III extractable P showed significant differences ($P < 0.001$) between sites ($F(5, 35) = 25.28, R^2 = 0.88, PESq = 0.85$) and significant differences between the interaction of site with soil horizon ($P < 0.05$). The mean was 27.65 mg kg^{-1} (0.35). Soils from Salisbury, 29.58 mg kg^{-1} (0.40), along with soils from Soufriere, 29.56 mg kg^{-1} (0.50), and the Castle Bruce, 28.70 mg kg^{-1} (0.53) recorded the highest P values without significantly differing from each other at $P = 0.60$. Soils from Layou Valley, 26.92 mg kg^{-1} (0.46), and Pond Cassé, 26.23 mg kg^{-1} (0.34) were equal ($P = 0.80$). Soils from Morne Prosper, 24.87 mg kg^{-1} (0.69) and Pond Cassé, equal at $P = 0.17$ recorded the lowest values (Fig. 6.1).

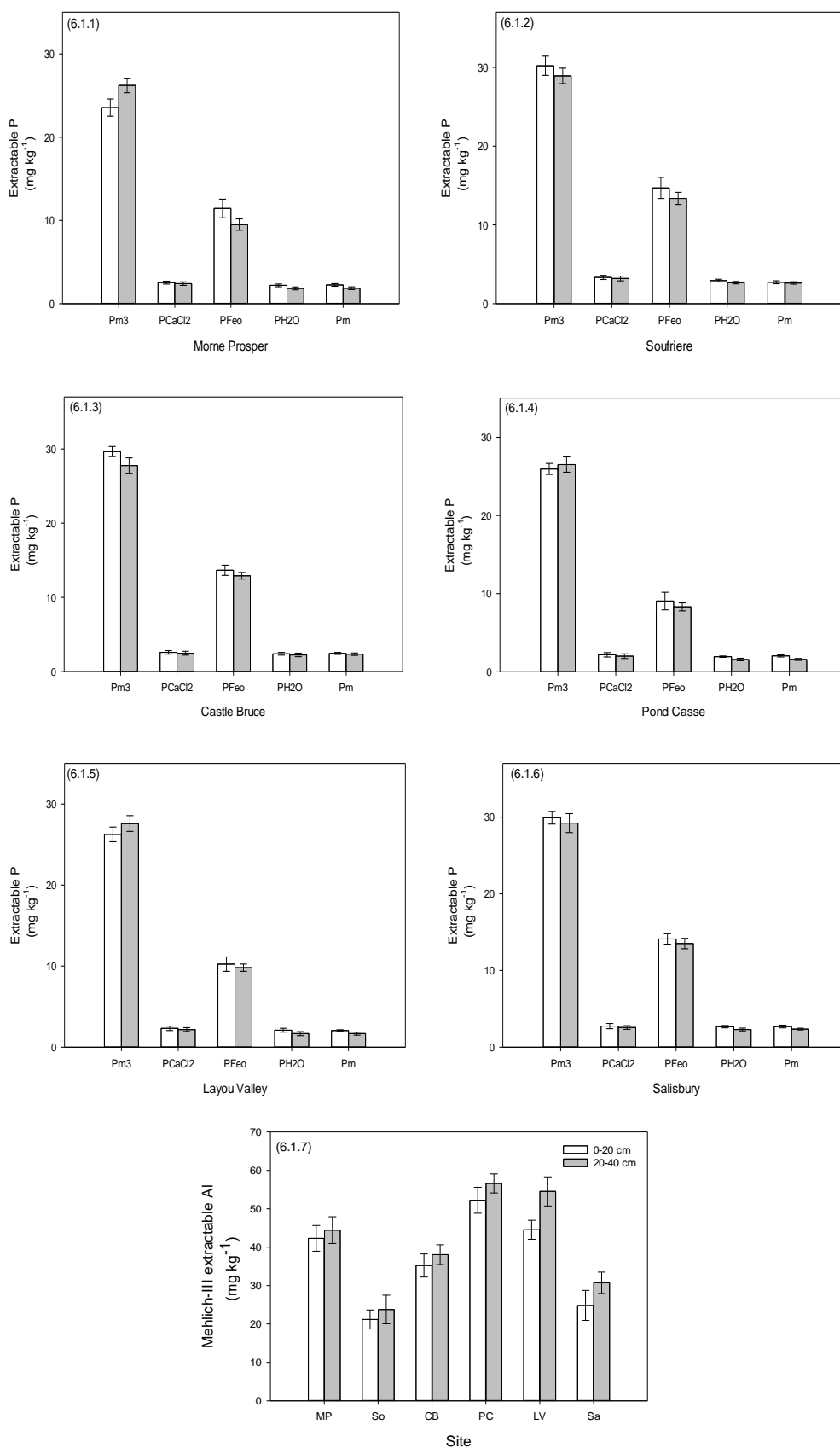


Fig. 6.1. Extractable P in six agricultural soils from the Commonwealth of Dominica. Pm3 = Mehlich-III extractable P, PCaCl₂ = Calcium chloride extractable P, PFeo = Iron oxide extractable P, PH₂O = distilled water extractable P, Pm = Morgan extractable P. Values represent means, error bars represent SEM.

The results for the CaCl_2 extractable P revealed significant differences ($P < 0.001$) between sites ($F(5, 35) = 16.45$, $R^2 = 0.80$, $\text{PESq} = 0.79$) but failed to detect significant differences between soil horizon ($P = 0.09$) and the interaction between site and soil horizon ($P = 1.000$). The mean P content was 2.54 mg kg^{-1} (0.07). The Soufriere soil type recorded the highest P value at 3.27 mg kg^{-1} (0.11), while the Pond Cassé, 2.08 mg kg^{-1} (0.11), Layou Valley, 2.24 mg kg^{-1} (0.10) and Morne Prosper, 2.47 mg kg^{-1} (0.08) recorded the lowest P values (Fig. 6.1).

Similar but stronger trends were observed for the iron oxide extractable P where there were significant differences ($R^2 = 0.93$, $P < 0.001$) between sites ($F(5, 35) = 49.83$, $\text{PESq} = 0.92$), and significant differences ($R^2 = 0.93$, $P < 0.01$) between soil horizon ($F(1, 35) = 13.48$, $\text{PESq} = 0.38$). The mean P content was 11.71 mg kg^{-1} (0.38) (Fig. 6.1). The water extractable P (Fig. 6.1) also showed significant differences ($R^2 = 0.90$, $P < 0.001$) between sites ($F(5, 35) = 31.00$, $\text{PESq} = 0.88$), as well as for soil horizon ($F(1, 35) = 30.61$, $\text{PESq} = 0.58$). The mean P content was 2.21 mg kg^{-1} (0.07). The Morgan extractable P (Fig. 6.1) gave the strongest observed trend with significant differences ($R^2 = 0.91$, $P < 0.001$) between sites ($F(5, 35) = 35.34$, $\text{PESq} = 0.89$), and between soil horizon ($F(1, 35) = 34.18$, $\text{PESq} = 0.61$). The mean P content was 2.22 mg kg^{-1} (0.07).

The results generally show that soils from Soufriere and Salisbury extracted the most P irrespective of the P extraction method used (Fig. 6.1). On the other hand, soils from Pond Cassé, Layou Valley, and Morne Prosper in particular extracted the least amount of P irrespective of the method. Importantly these results show the potential low vulnerability of these soils to P losses and it can be appreciated that soils with the highest percent clay sorbed the least amount of P (chapter 5). High P fixation in these soils means that the risk of phosphorus loss from fields treated with manures and/or fertilizers is potentially less likely to occur, nonetheless close attention has to be paid to erosion potential and sediment P losses.

More interestingly the results (Fig. 6.1) clearly shows that the labile inorganic P in these soils is markedly low and using a Mehlich-III extractable P value of 45-50 mg P kg⁻¹ soil which is generally considered optimum for plant growth and crop yields (Sims, 2000a) lends support to the observation. The iron oxide extractable P used as a “P-sink” method for the determination of available phosphorus (Menon et al., 1989; Chardon et al., 1996) was surpassed only by the Mehlich-III method and the amount of P soluble in CaCl₂ solution was higher than that in H₂O probably due in part to the ionic strength of CaCl₂ and the little enhancement of Ca²⁺ on P sorption by these volcanic soils (Perrott et al., 1993; Jordan et al., 2005). It has been reported that the amount of CaCl₂ extractable P correlates well with the equilibrium P concentrations held in solution at field conditions (Beauchemin and Simard, 1999; Daly and Casey, 2003; McDowell and Sharpley, 2003). Therefore, at the same level of CaCl₂ extractable P, more P would be available in the long-term in soils with high clay content and as such the CaCl₂ soluble P level critical for optimum plant growth would be lower for clayey loam soils than for sandy loam soils (Nair et al., 2004) reflecting the buffer capacity and soil texture.

The values for water extractable P have been reported as being a function of the quantity of P sorbed and the P sorption capacity, or alternatively the degree of P surface saturation (Kuo, 1996). It has also been reported that at comparable solution P concentrations, soils with higher P buffering capacities or clay content should contain more labile P to replenish the solution of P removed by root absorption (Pardo and Guadalix, 1990; Madeira et al., 2007b). Hence soil P availability determined by the quantity of labile P concentration of P in soil solution, and P buffering capacity ultimately governs the distribution of P between the solution and solid phases (Barrow, 1978; Wada, 1978; Moody et al., 1988; Kuo, 1996).

There were significant positive relationships between all the P extraction methods with the most noticeable being the Morgan P having a significant positive relationship with the water extractable P ($R^2 = 0.93$). The relationship of Mehlich-III P and the various soil P test used to

predict potential P losses gave mixed results. The relationship between Mehlich-III P with Morgan P and water extractable P were weaker when compared to the iron oxide extractable P but stronger when compared to that same relationship with CaCl₂ P. In addition, the CaCl₂ extractable P had a significant relationship with the iron oxide (FeO) extractable P but that relationship was even stronger with the water extractable and slightly stronger for the Morgan extractable P (Table 6.1). The iron oxide extractable P (FeO P) had a stronger relationship with the water extractable P when compared to the CaCl₂ and Mehlich-III extractable P however that relationship was even stronger with regards to the Morgan extractable P.

Table 6.1. Relationship between various soil extraction procedures used to predict potential P losses via runoff and subsurface drainage. Correlation coefficient (r) indicated in italics with the corresponding P values. n = 36.

	Mehlich-III P	Extractable Phosphorus (mg kg ⁻¹)			
		CaCl ₂	FeO	H ₂ O	Morgan
*Mehlich-III Al	<i>-0.60</i> P<0.001	<i>-0.75</i> P<0.001	<i>-0.84</i> P<0.001	<i>-0.84</i> P<0.001	<i>-0.84</i> P<0.001
Mehlich-III P		<i>0.49</i> P<0.01	<i>0.69</i> P<0.001	<i>0.58</i> P<0.001	<i>0.55</i> P<0.001
CaCl ₂ P		-	<i>0.67</i> P<0.001	<i>0.74</i> P<0.001	<i>0.76</i> P<0.001
FeO P			-	<i>0.79</i> P<0.001	<i>0.85</i> P<0.001
H ₂ O P				-	<i>0.93</i> P<0.001
Morgan P					-

The relationship of Mehlich-III extractable Al with the various P extraction methods gave significant negative relationships with the strongest negative relationship being observed between Morgan extractable P, H₂O and FeO extractable P. The relationship was weaker between Mehlich-III extractable Al with CaCl₂ P and weakest between Mehlich-III extractable Al with Mehlich-III extractable P.

From these results it can be deduced that potential losses of labile P is related to the P status of the soil. However it can be observed that this is also dependent on the ionic strength and cation species of the extracting solutions (Ryden and Syers, 1975) with FeO, CaCl₂, and H₂O extractable P being better indicators in predicting potential P losses (Pote et al., 1996).

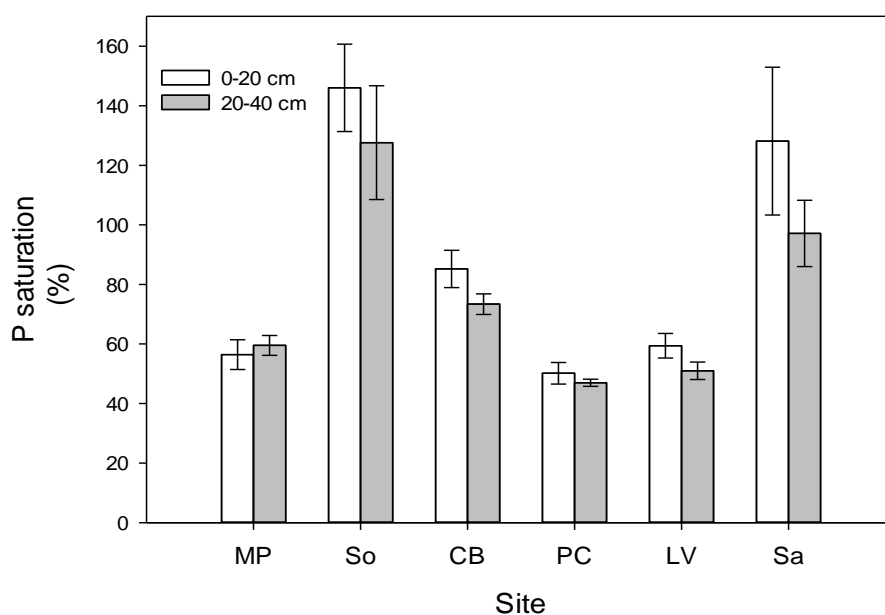


Fig. 6.2. P saturation expressed as a percentage between Mehlich-III extractable P (mg kg^{-1}) and Mehlich-III extractable Al (mg kg^{-1}). Values represent means and error bars represent SEM. NB: Mehlich-III extractable Fe was not determined and as such P saturation tends to be overestimated in the absence of Fe.

The results (Fig. 6.2) indicate that soils from Pond Cassé (PC), Layou Valley (LV) and Morne Prosper (MP) with high clay content, high pH NaF, and higher allophane and ferrihydrite content all had comparatively low P saturation values. Low P saturation is most probably due to the low native P content and fertilizer application, in addition to large amounts of active Al and Fe, ferrihydrite and allophane which is known to be strongly correlated with the capacity of the soil to adsorb P (Shoji et al., 1993; Auxtero et al., 2007).

As the degree of P saturation increases, it should be expected that P will be retained less strongly by the soil and that the soluble P pool will increase (Beauchemin and Simard, 1999). Hence above the P maxima, the retention of P by the soil matrix will tend to decrease in soils from Soufriere as the closeness of the relationship between P solubility and P saturation is dependent on the soil's P sorption properties and associated characteristics of the soil colloids. On a geological timescale, by the time primary minerals would have been depleted most soil P will be more than likely found in recalcitrant inorganic fractions (Peretyazhko and Sposito, 2005; Chirino-Valle, 2013) with increasing demands for fertilizer application.

There were significant ($P < 0.001$) relationships between P saturation and OM ($R^2 = 0.48$), clay content ($R^2 = 0.58$), pH NaF ($R^2 = 0.60$), CEC ($R^2 = 0.62$) and Mehlich-III extractable Al ($R^2 = 0.99$) (Fig. 6.3) which was best described by a polynomial (inverse first order) equation. It is observed that as extractable Al increases there is a corresponding reduction in plant available P. This tendency is brought about by an abundance in available and unoccupied sites which can bond with P thus reducing P saturation (Theng et al., 1982; Barrow, 1984; Bolan et al., 1985).

P availability is governed by an intensity and quantity factor, a diffusion coefficient of P in soils as well as a buffer capacity index (Barrow, 1978; Wada, 1978; Moody et al., 1988). Therefore, as buffer capacity increases there is a corresponding inverse relationship with P saturation which tends to decrease. Hence the inference is that P saturation is the reciprocal product of the soil's buffer capacity as influenced by the presence of Al- and Fe-oxides.

This implies that large applications of P fertilizers will be needed to maintain an optimum level of P in solution as P retention is decreased by the number of binding sites already occupied by P (Madeira et al., 2007b; Barrow, 2015). This is particularly valid for soils for Pond Cassé and Layou Valley. In these soils although the concentration of P in solution is low, the ability of the soil to replenish solution P is high and as such P saturation is decreased.

These results also indicate that the potential P loss via runoff and subsurface drainage is highly attributable to the presence of Al forms in these soils (Kleinman and Sharpley, 2002). Soils from Soufriere with low Al content show a higher P saturation than soils from Pond Cassé and potentially higher tendency of P loss via surface runoff and subsurface drainage. However we contend that the likelihood may increase most probably under equal hydrological events such as rain storms given annual climatic conditions on the leeward side of the island, hence P losses will be more than likely affected by erosion and losses through sediment P.

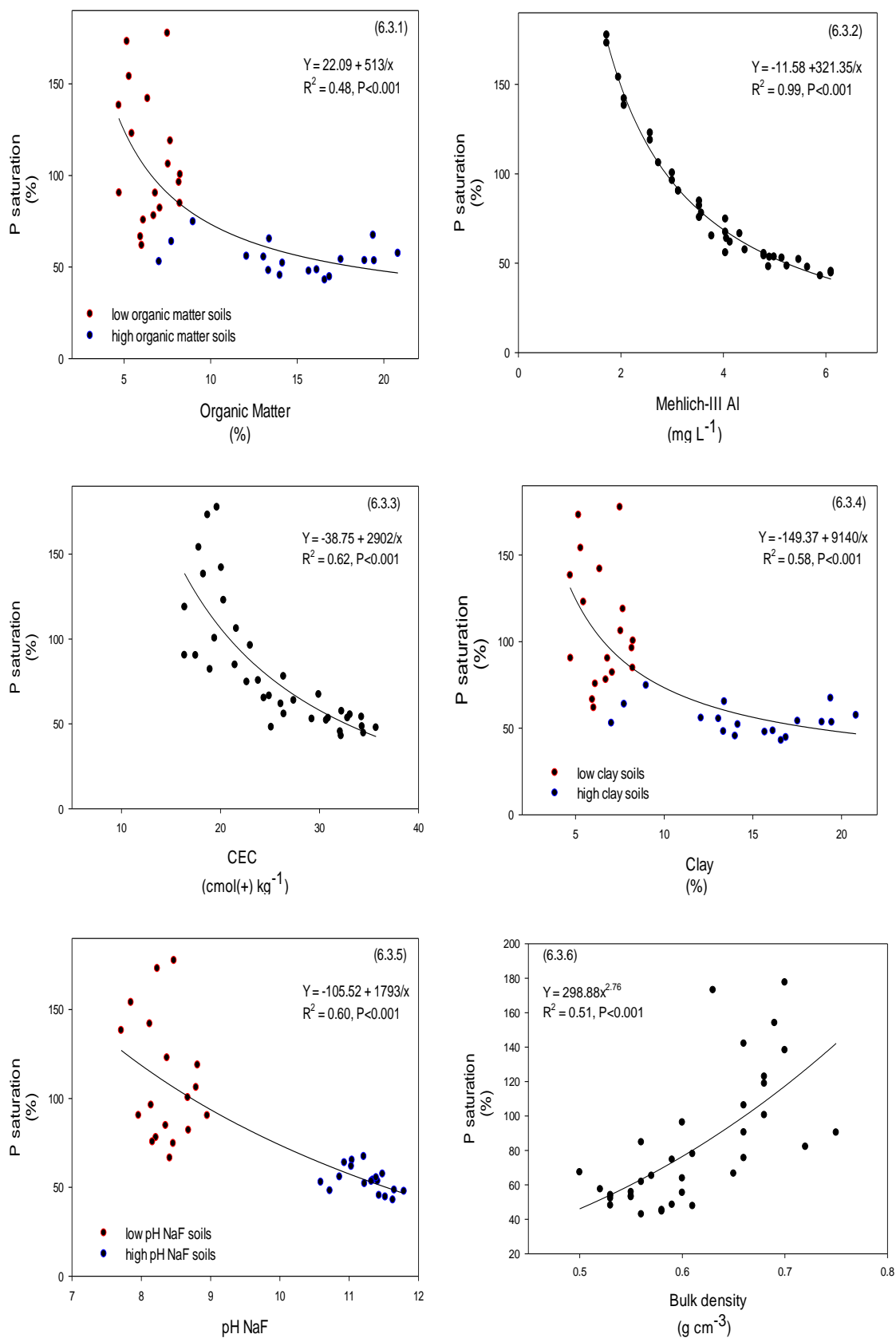


Fig. 6.3. Relationships between percentage P saturation and some selected soil parameters in six agricultural soils from the Commonwealth of Dominica. n = 36. NB: Two distinct group of soils are emerging. Soils with high OM, clay content and pH NaF are showing better relationship with P saturation.

The data also shows (Fig. 6.3.1) that high organic matter soils exhibited low P saturation and tends to suggest that as SOM increases, there are fewer sites, which are usually provided by Al and Fe, for P sorption. More interestingly these results tend to suggest that organic matter may have been producing an acidic environment whereby it interacts with Al and Fe by an eliminative effect and thus blocks P sorption to the solid phase which can be considered a competitive effect (Daly et al., 2001; Daly and Casey, 2003).

In these soils with high organic matter, P may be retained in the soil solution phase where sorption is inhibited. This tends to suggest that P concentrations in soil solution may increase the P saturation potential and the likelihood of potential P losses may increase. This could be more than likely when heavy loads of P fertilizer are applied (i.e. frequent and indiscriminate use of P fertilizers above crop demands) to these high P fixing soils in combination with composted material and animal manure (Robinson and Sharpley, 1996; Siddique and Robinson, 2003) and hence the need to manage manure applications (Sharpley et al., 1996).

Additionally, the results tend to suggest that bulk density, as influenced by soil texture, does have an influence on P saturation. The relationship between these two parameters suggest that as the content of sand increases, which significantly affects bulk density, the ability of the soil to replenish solution P decreases due to the reduced number of binding sites that can be occupied by P as P tends to bind to the clay particles in soil. This suggest that in soils from Soufriere regular applications of P fertilizers would be necessary in order to increase the concentration of P in solution. These results tend to indicate that P saturation related to the molar amounts of P already occupying sorption sites, relative to the number of potential P sites present varies strongly and is inherently dependent on particular soil characteristics such as P buffer capacity, P diffusion coefficient, and P concentration. Differences in these soils may be attributed to variations in annual precipitation as a significant driving factor affecting climatic weathering of primary P minerals but may also be associated to historical and current land use.

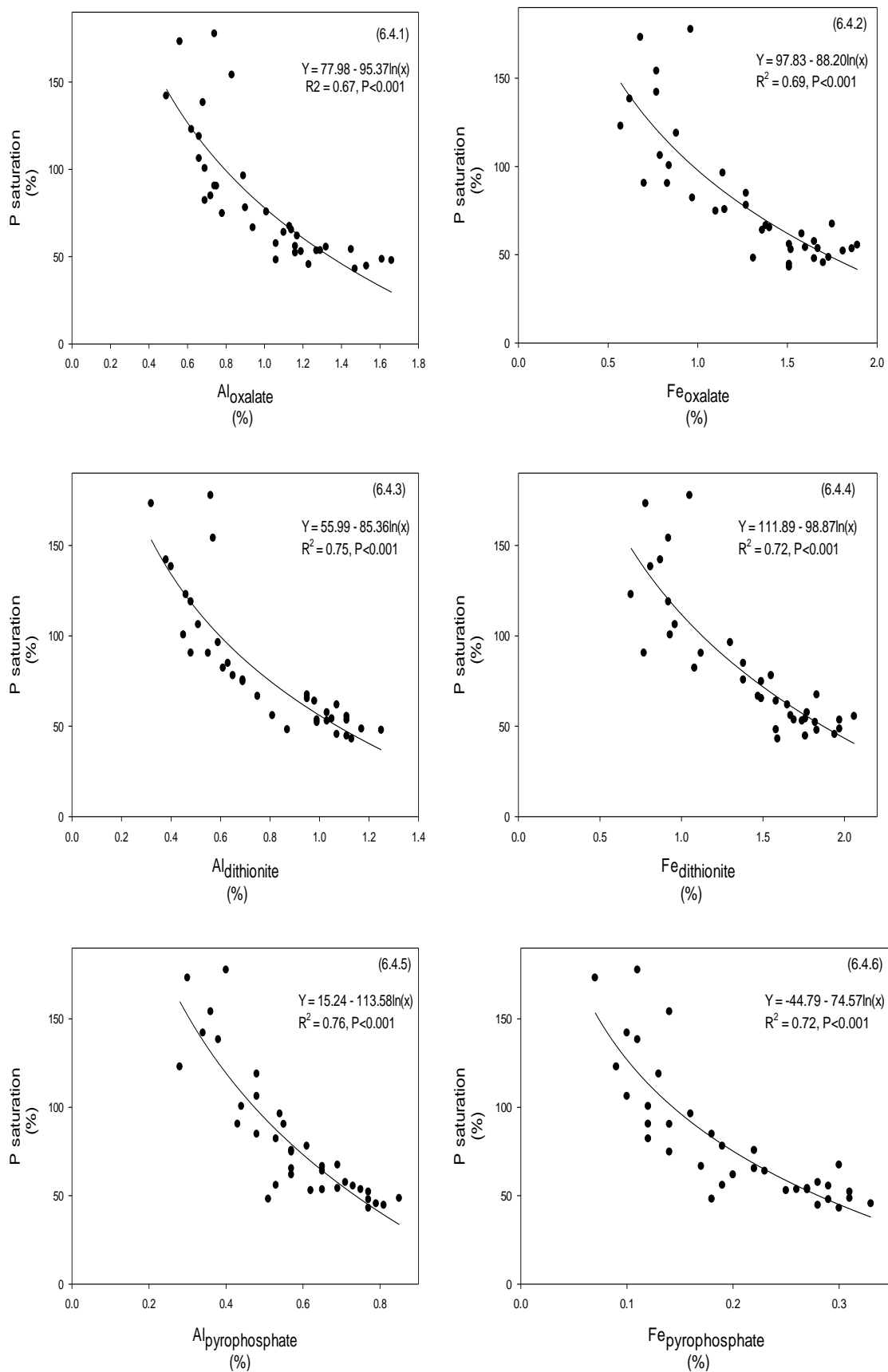


Fig. 6.4. Relationships between P saturation and oxalate, dithionite, and pyrophosphate extractable Al and Fe in six major agricultural soils from the Commonwealth of Dominica. n = 36.

The data (Fig. 6.4) also suggest that in these soils organically bound Al in particular (Al_p) may potentially be more important a driver than crystalline and poorly crystalline amorphous soil constituents in influencing P losses as can be seen from the relationship of P saturation with the various dissolution forms (oxalate, dithionite, and pyrophosphate) of Al and Fe respectively. This suggest that the over application of P by means of composted material and animal manure to the soil can potentially result in significant increases in leachate P concentrations and eventual run-off (Siddique et al., 2000; Kleinman et al., 2003; Siddique and Robinson, 2003; Cornish and Obersen, 2008).

P saturation had a significant negative relationship with Al_o , and Al_p . The relationship with the Fe forms were weaker with Fe_o , Fe_d , and Fe_p . A weaker relationship of Fe_p with P saturation when compared to Al_p is most probably due to Fe having a greater stability in oxyhydroxides as compared to humus complexes and as such concentrations of Fe-humus complexes are typically low (Wada and Higashi, 1976). The relationship of Al_p with P saturation ($R^2 = 0.76$) when compared to Fe_p ($R^2 = 0.72$) can possibly be attributed to the small specific surface area of Fe-oxides (Borggaard, 1983; Parfitt, 1989a; Quang et al., 1996) and most probably the selectivity of the pyrophosphate reagent to Al forms rather than Fe forms (McKeague, 1967) suggesting that aluminium forms a more resilient association with the soil organic matter. Generally Fe has a stronger organic complexation with respect to Al, and Fe is preferentially removed upon dissolution, resulting in the accumulation of Al at the expense of Fe (Farmer et al., 1984; Buurman and Van Reeuwijk, 1984). Moreover, phosphate bound to ferruginous materials are more stable than those bound to Al, because they are less soluble than crystalline/amorphous Al materials (Fontes and Weed, 1996).

The data tends to suggest that the extent to which inorganic anions such as phosphate may be able to compete with Al for surface binding sites is also a function of P saturation (Syers and Iskandar, 1981) and hence the importance of sorption mechanisms in controlling P

dynamics in these volcanic soils (Bridgham et al., 2001) with increasing risk of P release via surface runoff and/or subsurface drainage once the P sorbed exceeds its maxima. Therefore the recommendations of Holford et al., (1974) and Barrow and Debnath (2014) in using P fertilizers related to P adsorption at high energy sites, may likely warrant site specific P management strategies, a concept which is growing in popularity embedded in the principles of precision agriculture.

Moreover, the data tends to suggest that drastic changes to land use affecting organic carbon content will affect the degree of P saturation since potential P losses are partly attributed to the presence of Al_p forms, although the degree of soil P saturation is primarily affected by long-term P application. Nonetheless, the removal of P lowers the soil P concentration (Perrott et al., 1993; Grant et al., 2005), and promotes the release of P from labile pools by desorption of adsorbed soil P and dissolution of slightly soluble P compounds, and as such the potential P losses in the long-term of soils with high P reserves (Schoumans et al., 2015).

P saturation significantly varied according to site (Fig. 6.2) and soil constituents (Fig. 6.3, 6.4). The strong correlation between P saturation and Al_d and Fe_d suggests that large amounts of P can be sorbed by allophane-like materials, as reported by Wada and Gunjigake (1979) and Bell et al., (2005). Nonetheless, added P may cause an even greater increase in soil P when applied to soils that are initially higher in soil P (Pote et al., 2003) and as such increasing soil P levels will most likely promote increased P concentrations in runoff (Yli-Halla et al., 1995) and are usually the result of long-term manure applications, notwithstanding the influence of inorganic P fertilizers in short-term P losses. Thus, it has been recommended that animal manure applications be shifted from high-P soils to lower-P soils to help reduce water quality problems (Sharpley et al., 1996, 2000). However, consideration needs to be given to the spatial distribution of runoff due to hydrological differences in source areas (Pote et al., 2003) with rainfall intensity, duration, and the interval between rainfall events being temporal variables

which influence the discharge and P load. Hence it is of economic and environmental importance to determine how long high-P soils will remain above crop requirements and identify soils where P contents would decrease most rapidly under similar management conditions (Sharpley, 1996; Sims, 1998) which would aid in site specific management actions.

The relationship of P saturation with the various P soil test showed a significant positive correlation ($P < 0.001$) but varied according to the extractant used (Fig. 6.5). The Mehlich-III extractable P gave the weakest relationship ($R^2 = 0.49$) with the water extractable P having the strongest relationship ($R^2 = 0.67$), followed by the Morgan extractable P ($R^2 = 0.65$). The results for the CaCl_2 ($R^2 = 0.58$) and iron oxide extractable P ($R^2 = 0.57$) also gave some insights that the relationship between P soil test and soil P saturation varies, depending on the extraction method (Pote et al., 1996).

The results suggest that the agronomic P soil test (Mehlich-III) as a sole variable was not as effective as the environmentally oriented P soil tests used in this study for predicting potential P losses, results which tend to be in agreement with Magdoff et al., (1999) and Maguire and Sims (2002a,b). This tendency is most probably related to the acidic nature of the Mehlich reagent which extracts P forms that are not necessarily plant available. Hence the results tend to suggest that the high values of Mehlich-III extractable P do not reflect P which is held in soil solution under field conditions in comparison to the Morgan, CaCl_2 and H_2O extractable P which are known to simulate potential P loss dynamics in agro-ecosystems.

In addition and of great interest, the results show that P saturation may be readily estimated by soil laboratories that routinely measure Mehlich-III extractable P, Al, Fe, and Ca as was noted by Kleinman and Sharpley (2002). This is extremely important for small island developing states like the Commonwealth of Dominica, with limited analytical capacity but with an ever growing need to improve its competence as well as to expand the scope with regards to the approaches in soil sampling and analysis.

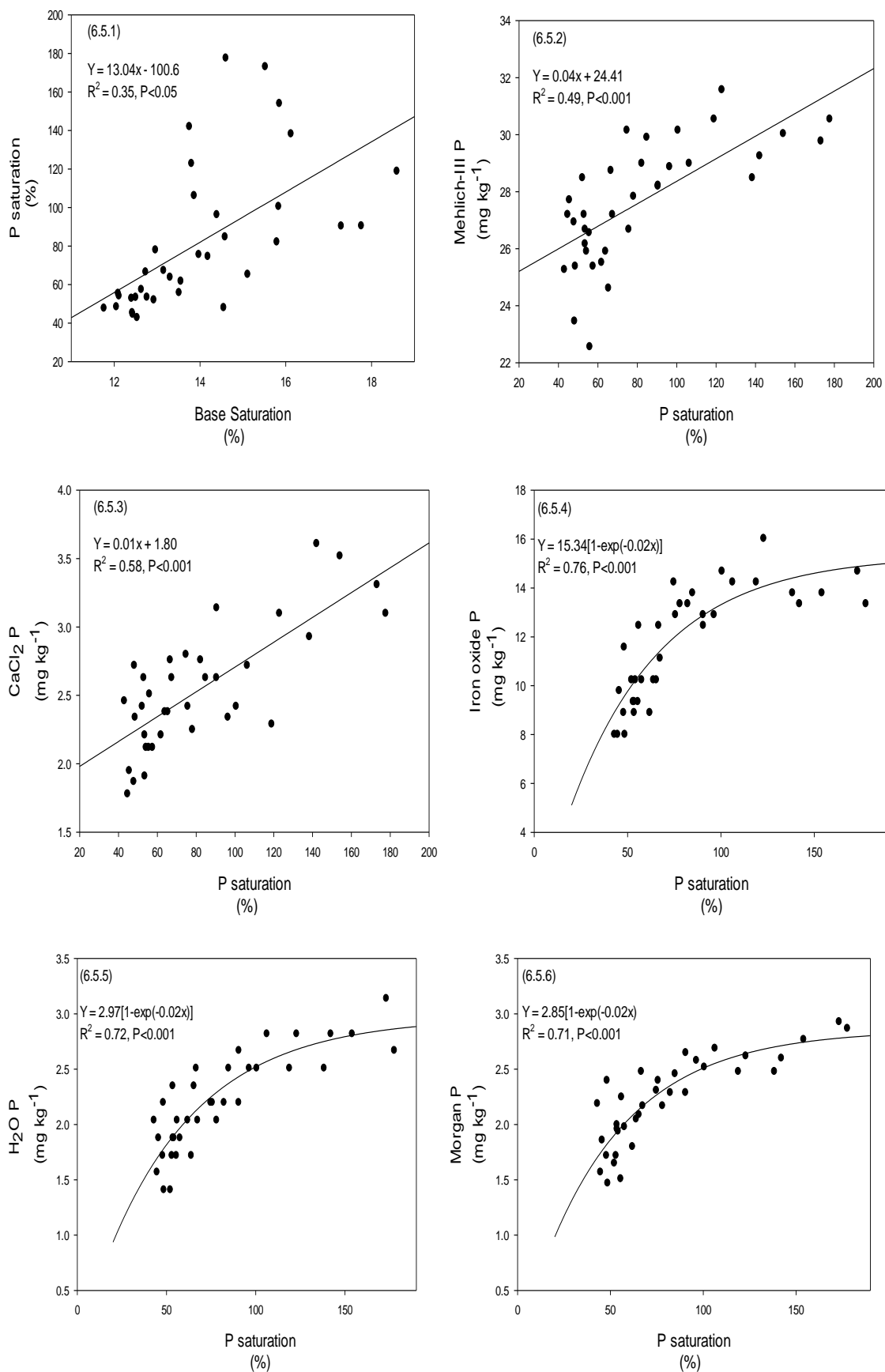


Fig. 6.5. Relationships between P saturation and soil phosphorus test, and P saturation and base saturation in six agricultural soils from the Commonwealth of Dominica. n = 36.

The relationship between P saturation and base saturation showed a significant positive linear correlation (Fig. 6.5.1). The data tends to suggest that the portion of soil binding sites already covered with P as well as the number of basic cations that are held on the soil exchange complex in comparison to the total number of sites are low. This also suggest that the adsorbing surface of soil mineral and organic matter particles with basic cations are not completely occupied and as such P can be added to these soil to a maximum threshold before the potential desorbability of soil P would occur. Indeed a high base saturation value would indicate that the exchange sites on a soil particle are dominated by non-acidic ions, given the fact that in volcanic soils H^+ and Al^{3+} ions tend to find their way on to the surface of the soil mineral and organic particles which lowers the base saturation. Thus as the basic cations of calcium (Ca^{2+}), magnesium (Mg^{2+}), potassium (K^+), and sodium (Na^+) increases, P saturation would tend to decrease (Fig. 6.6) and hence the implication of when a soil should be limed.

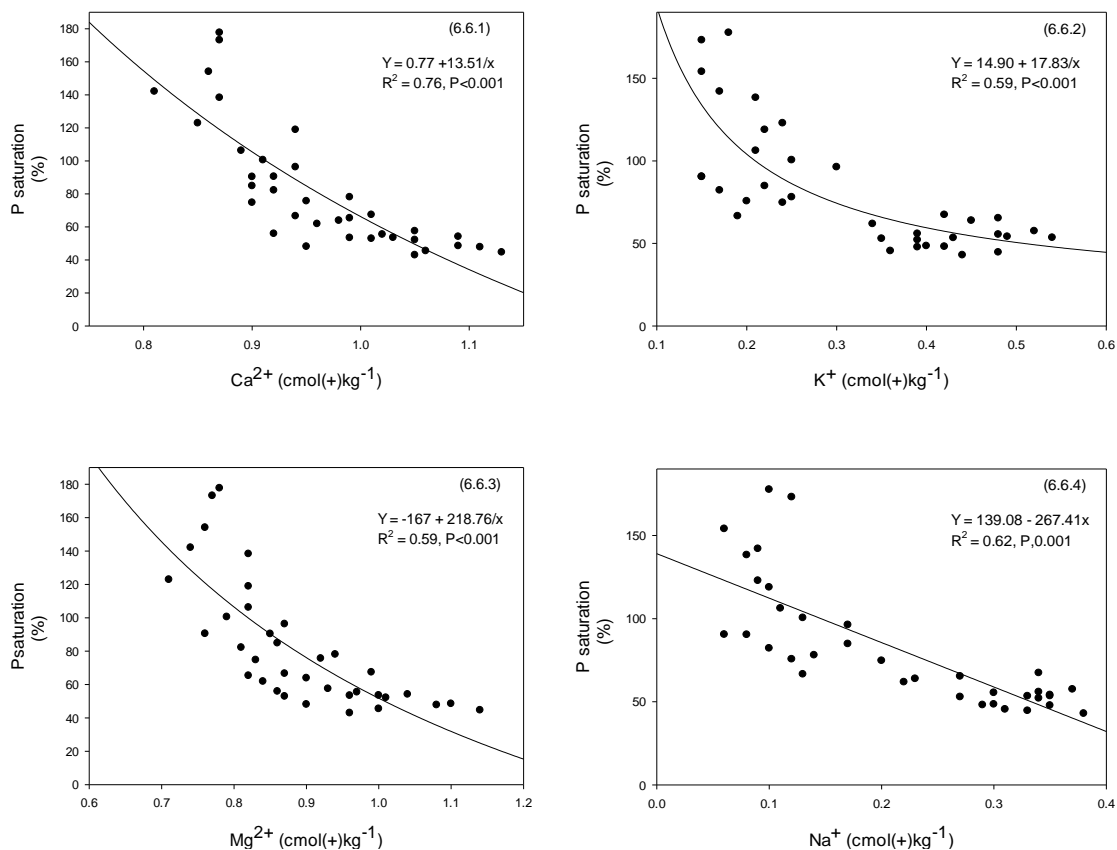


Fig. 6.6. Relationships between P saturation and basic cations in six major agricultural soils from the Commonwealth of Dominica. n = 36.

The relationship of Mehlich-III and CaCl₂ extractable P with P saturation (Fig. 6.5.2-6.5.3) also showed positive linear relationships. These results suggest that due to the low availability of soluble P in these soils, as the portion of the soil binding sites covered with P increases the amount of plant available P increases. However, this also indicates that the potential desorbability of soil P also increases and as such fertilizer management strategies would also have to consider the potential of P losses. However, the relationship of P saturation with iron oxide, H₂O and Morgan extractable P showed a positive correlation which was best explained by an exponential rise to maximum relationship (Fig. 6.5.4 – 6.5.6).

In the case of iron oxide extractable P, these results tend to suggest that in low P fixing soils, with increasing P saturation these soils would not act as P sinks but rather as P sources and hence increase potential of P losses as reflected towards a tendency of maximum rise. With regards to the H₂O and Morgan extractable P, the results suggest that as P saturation increases, the proportion of binding sites associated with mobile P (Van der Paauw, 1971) and accumulated P reserves (McIntosh, 1969) increases to a maximum threshold beyond which P would not be held in soil solution but could either be tightly held by soil colloids in high P fixing soils. In addition, in low P fixing soils this could also lead to P potentially being leached out of the soil solution but more importantly increasing the probability of P losses via run-off since all possible P binding sites would have been fully occupied.

The relationship of the various P soil test with allophane and ferrihydrite all gave significant ($P < 0.001$) negative relationships (Fig. 6.7). The relationship for both allophane and ferrihydrite was strongest with regards to the iron oxide extractable P with correlation coefficients of ($R^2 = 0.84$) and ($R^2 = 0.72$) respectively. The relationship of allophane with the various P soil test (Fig. 6.7.1) gave a mean R^2 value of 0.66 (0.07), with Mehlich-III extractable P having the lowest coefficient ($R^2 = 0.48$). The relationship of the various P extraction with

allophane showed: CaCl₂ extractable P ($R^2 = 0.53$), H₂O extractable P ($R^2 = 0.70$), Morgan extractable P ($R^2 = 0.73$), and iron oxide extractable P ($R^2 = 0.84$).

On the contrary, the relationship of ferrihydrite with the various P soil test (Fig. 6.7.2) gave a mean R^2 value of 0.61 (0.05) indicating the dominant influence of allophane and allophane-like material in P saturation and thus the prevailing effect of allophane in the potential to P losses via surface runoff and subsurface drainage. Mehlich-III extractable P gave the lowest coefficient ($R^2 = 0.43$) followed by CaCl₂ extractable P ($R^2 = 0.54$), H₂O extractable P ($R^2 = 0.66$), Morgan extractable P ($R^2 = 0.70$), and iron oxide extractable P ($R^2 = 0.72$).

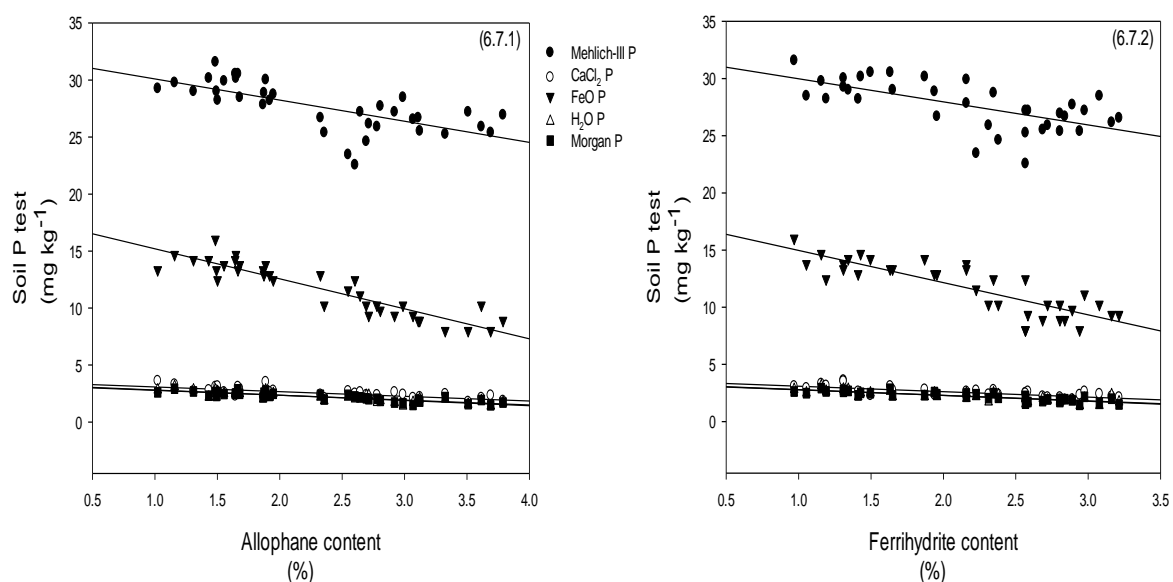


Fig. 6.7. Relationship between allophane and ferrihydrite content and soil P test using various extraction procedures in volcanic soils from the Commonwealth of Dominica. n = 36.

The iron oxide extractable P (Fig. 6.8) had a significant ($P < 0.001$) negative relationship with all the aluminium forms in the order of Al_d ($R^2 = 0.87$) > Al_o ($R^2 = 0.84$) > Al_p ($R^2 = 0.73$). The relationship of the iron oxide extractable P with the various ferruginous forms gave an even weaker correlation in the order of Fe_p ($R^2 = 0.77$) > Fe_o ($R^2 = 0.72$) > Fe_d ($R^2 = 0.69$). The ratio of $Al_o + 0.5 Fe_o$ had a relationship ($R^2 = 0.69$), and allophane + ferrihydrite ($R^2 = 0.68$). This tends to imply that poorly crystalline oxides and organic complexes are important drivers in P adsorption and hence the significant negative relationship with FeO acting as a P sink.

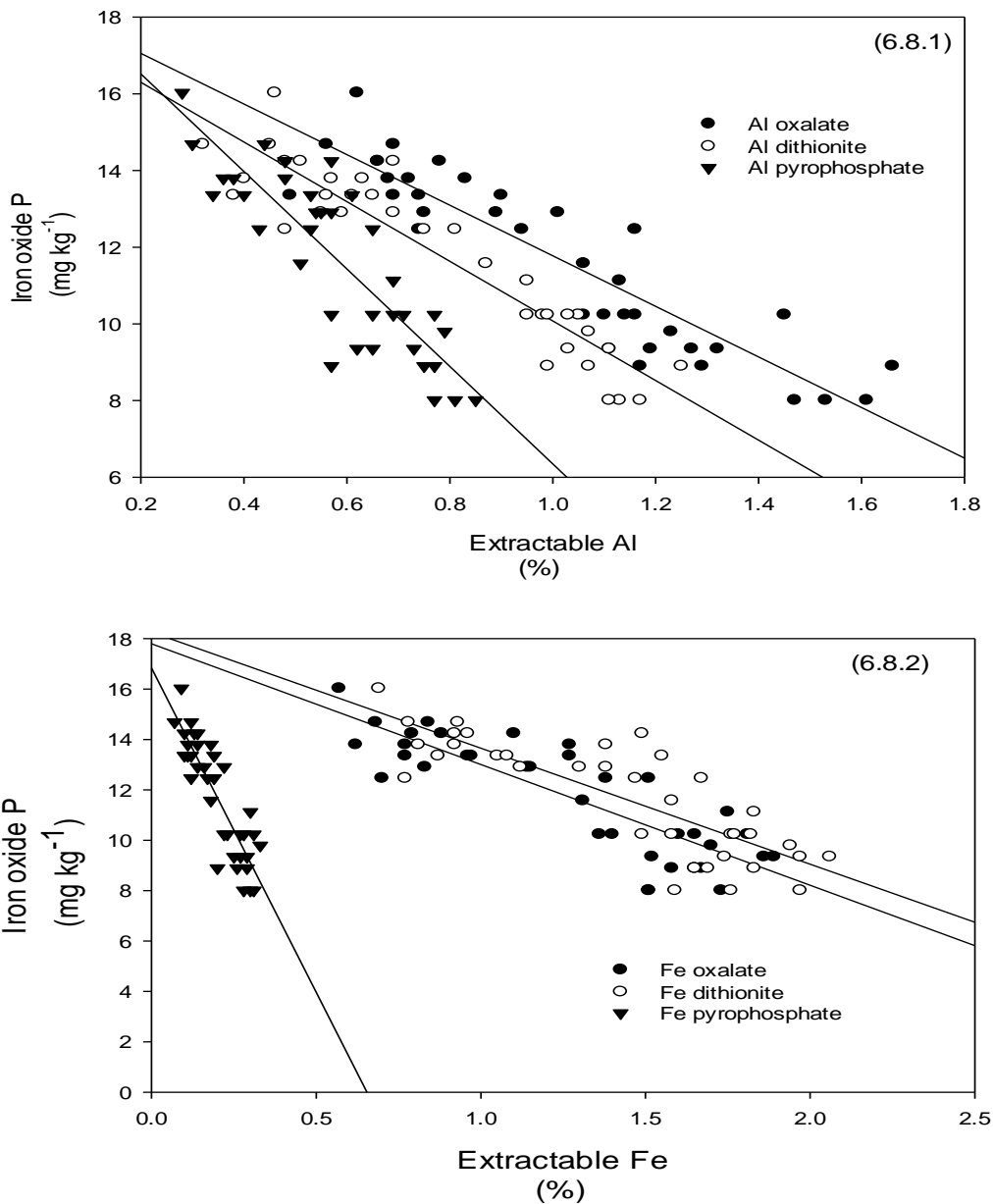


Fig. 6.8. Relationship between iron oxide extractable P and Al and Fe forms in volcanic soils from the Commonwealth of Dominica. n = 36.

Notwithstanding the significant relationships of Al and Fe forms with FeO extractable P, the degree of slope for both Al and Fe pyrophosphate extractable P is much steeper than the dithionite and oxalate forms. This tends to suggest that organically bound Fe and Al has a significant influence on potential P losses. This suggest that the application animal manure and composted material could potentially increase pH by decreasing the concentration of exchangeable Al and increase the availability of soluble P thereby increasing potential P losses.

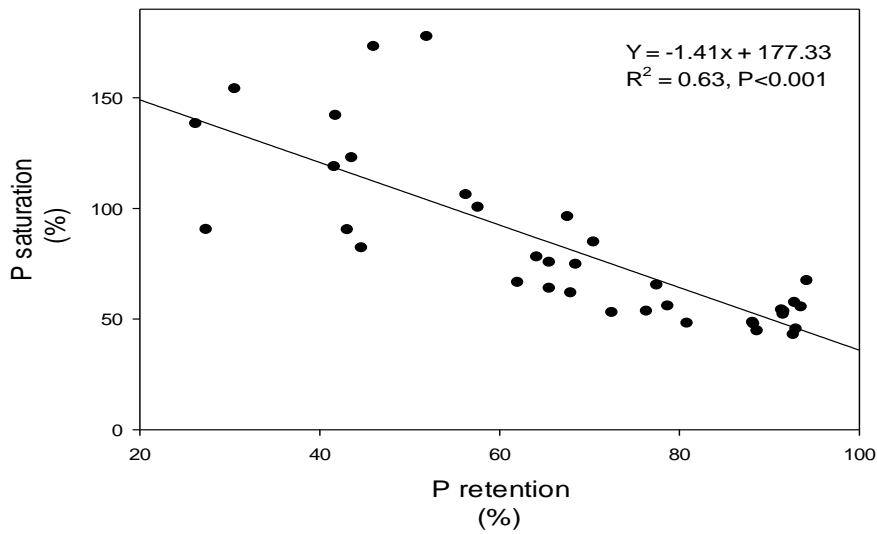


Fig. 6.9. Relationship between P saturation and P retention in six major agricultural soils from the Commonwealth of Dominica. n = 36.

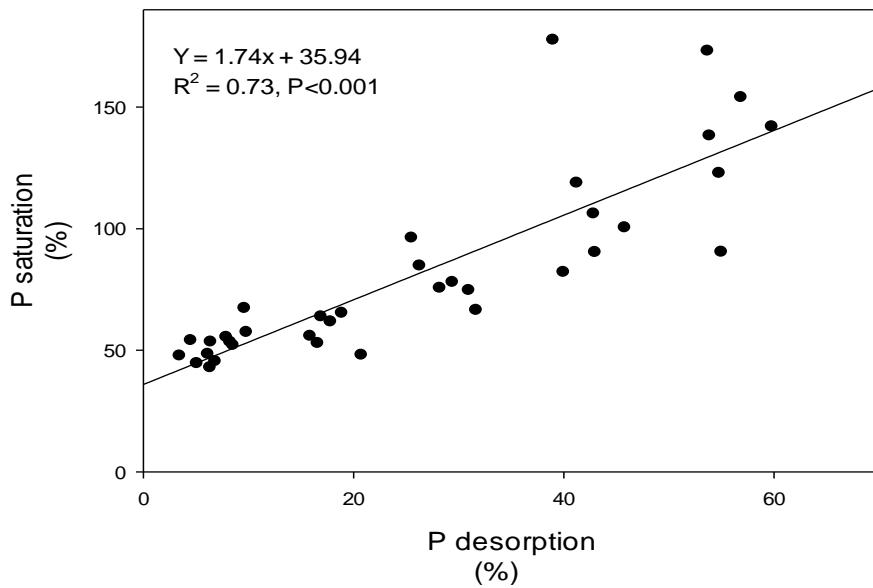


Fig. 6.10. Relationship between P saturation and P desorption in six major agricultural soils from the Commonwealth of Dominica. n = 36.

The relationship between P saturation and P retention (Fig. 6.9) highlight a strong negative correlation ($R^2 = 0.63$, $P < 0.001$) suggesting that the degree of P retention negatively influences P saturation and as such the lower potential of P losses in soils with high P_{ret} values. P retention in soils is generally attributed to hydrous oxides of Fe and Al (Allbrook, 1985; Barrow, 2015). Soils with high P adsorption capacity (Pond Cassé, Layou Valley and Morne Prosper) demonstrated low P saturation and it would be expected that these soil would have a lower

propensity to undergo P losses via surface runoff and subsurface drainage, notwithstanding sediment P loss via soil erosion. Nonetheless, once P is adsorbed onto the soil solid phase, it may undergo biological transformations into organic forms, which may enhance the immobilisation of P (Barrow, 2015) unavailable for plant uptake but susceptible to sediment P losses via erosion.

However, as noted, annual surface runoff becomes critical in assessing annual P load (Sharpley et al., 2003) and site vulnerability to P losses takes into account transport factors such as erosion potential and sediment P loss, runoff, leaching, and connectivity to stream channels (Sharpley et al., 2008) as well as climatic conditions, topography and precipitation regimes (Pote et al., 1999), in addition to the quantitative description of P adsorption on to the solid phase.

Inversely, the relationship between P saturation and P desorption (Fig. 6.10) shows a strong positive correlation ($R^2 = 0.73$, $P < 0.001$) suggesting that the degree of P desorption positively influences P saturation and as such the stronger likelihood of soils with higher P_{des} to potential P losses. Soils with high P desorption capacity (Soufriere and Salisbury) demonstrated higher P saturation and as such it would be expected that these soils would have a higher propensity to undergo P losses via surface runoff and subsurface drainage, hence management strategies which increases P retention may need to be considered (Udeigwe et al., 2011). The presence of Al in high P fixing soils has a significant influence on P retention (Parfitt, 1979; Farmer et al., 1980; Mizota and Van Reeuwijk 1989, Shoji et al., 1993; Nugroho, 2010) thus their vulnerability to P losses in comparison to lower P fixing soils is less likely via run-off and subsurface drainage due to P limited mobility and P fixation unto clays, in addition to the slow diffusion coefficient, estimated to be between $10^{-12} - 10^{-15}/m^2/s$ as has been suggested and reported by Marschner (1995) and thus highlighting the importance of hydrology in the movement of P.

There was a strong negative linear relationship ($P < 0.001$) between P saturation and all the soil constituents of interest. The weakest negative linear relationship was observed between P saturation and SOM, with the strongest negative linear relationship being observed between P saturation and Mehlich-III extractable Al although stepwise regression showed that Mehlich-III extractable Al as a sole variable could account for 85% of the variance. Notwithstanding there was a strong negative linear relationship between P saturation and pH NaF, clay content, and CEC. The linear relationship between P saturation and allophane was not as strong when compared to the relationship between P saturation and ferrihydrite or silica content.

With a number of significant relationships between soils constituents, a forward stepwise regression analysis with P saturation as the dependent variable and the various soil constituents as independent variables showed that P saturation was best explained by a combination of clay content, Mehlich-III extractable Al and P, FeO extractable P, and P desorption. $P \text{ saturation} = -1.659 + (0.203 \text{ clay}) - (2.519 \text{ Mehlich-III Al}) + (0.535 \text{ Mehlich-III P}) - (0.449 \text{ FeO P}) + (0.0911 \text{ P desorption})$ ($R^2 = 0.94$, $P < 0.05$) where clay was significant at $P = 0.019$, Mehlich-III extractable Al significant at $P < 0.001$, Mehlich-III extractable P significant at $P < 0.001$, FeO P significant at $P = 0.012$, and P desorption significant at $P = 0.002$.

4. Discussion

The use of P saturation as an environmental indicator has been routine practice to assess potential P loss from soils since it is a measure of P concentrations in soil relative to the amounts of Al and Fe, which symbolizes P saturation sites in soil (Beauchemin and Simard, 1999; Daly and Casey, 2003). However, whilst soil P testing is not a measure of absolute values of P loss it can provide a good indication of environmental losses in addition to agronomic status (Daly and Casey, 2005; Vadas et al., 2005). It follows that to overcome deficiency, P fertilizers will be required at a rate sufficient enough to raise intensity to a non-limiting level. This rate has been suggested to be negatively related to the initial intensity and

positively related to the P buffer capacity of the soil (Moody et al., 1988), with the latter governing the amount of added P which is adsorbed onto soil surfaces, and hence the amount remaining in solution.

Percentage P saturation is often quoted as an environmental indicator of water-soluble P loss and represents saturation and sorption aspects of soils (Kleinman et al., 2000; Nair et al., 2004). The slightly acidic extract of the Morgan P test has been used in the context of potential losses of P from soil to water. The water extractable (H₂O) P and CaCl₂ P are used as indicators of soil P loss that focuses on simulating desorption and solubilisation of P from soil to solution, which tries to simulate overland flow concentrations (Daly et al., 2001), with the iron oxide extractable P used as a “P-sink” method for the determination of available phosphorus (Menon et al., 1989, 1990; Chardon et al., 1996). Sharpley (1991) has suggested that the iron oxide paper strips removes primarily physically bound extractable P from all soils (approximate 1:1 relationship), with little extraction of amorphous Al and Fe or Ca compounds.

The results on P saturation indicate that P deficiency may be a problem common at all sites, with relatively large inputs of fertilizer required to correct the deficiency owed to low native P content, low P fertilizer applications as well as high P sorbing capacities of the soils (Moody and Radcliffe, 1986). The extent of the problem is likely to be greater in soils from Pond Cassé, Layou Valley and Morne Prosper than those in Soufriere, Salisbury and Castle Bruce owing to the high P retention in excess of 80% for these soils. However, close consideration needs to be given to erosion losses as well as local climatic, topographic, and agronomic factors as these also influence the dynamics of P loss. To this end, attention must be given to the concept of feeding the plant and not the soil in an effort to improve soil P dynamics which should eventually lead to enhanced crop yield (Withers et al., 2014, 2015).

Sorption and storage of P in soils is controlled to a large extent by the presence of ions, such as Al and Fe which have an affinity for P (Parfitt, 1980; Uehara and Gillman, 1981; Fontes

and Weed, 1996; McDowell and Sharpley, 2003) and the concentration of soil solution P is largely controlled by the equilibrium between the soil sorption system, soil solution and precipitated P compounds (McDowell and Sharpley, 2003). When P sorption capacities are large, reserves of P tend to build up in soils owing to their buffering capacity (Moody and Radcliffe, 1986; Pardo and Guadalix, 1990) which might be plant available in the long-term.

Desorption involves the removal of ions from solid soil surfaces rather than the root, and as ions are removed from soil solution by plant root uptake, ions from the solid phase go into solution (Barber, 1995). Soils from Pond Cassé, Layou Valley and Morne Prosper which have higher P sorption capacities when compared to soils from Soufriere, Salisbury and Castle Bruce may function as potential sinks for P at the landscape scale and if so, play a central role in maintaining water quality in these areas (Bruland and Richardson, 2006). This attribute is most relevant to soils from Layou Valley in particular which is home to one of the 10 watersheds found on the island (Chapter 3, Fig. 3.6). Furthermore on-farm best management practices (BMPs) will need to be considered for the Castle Bruce catchment since it is also home to an important watershed. Hence, in the short-term, desorption processes involving organo-metal complexes (Al_p , Fe_p) are likely to dominate but over the long-term, the dissolution of crystalline P species will be the rate limiting step in P release (Sparks, 1999; McDowell and Sharpley, 2003) which will be related to the degree and intensity of weathering processes.

Although low-intensity land management systems are predominant in these agri-environments, new approaches have to be considered with regards to P application. With an ever increasing expansion of land for the cultivation of crops from the *Araceae* family as an example, and with corresponding increases in anthropogenic nutrient inputs in areas like Pond Cassé and Layou Valley, attention now has to be given to the hydrological connectivity between the catchment surface and stream channels (Sharpley et al., 1996; Jarvie et al., 2008). Due consideration must be given to nutrient delivery from diffuse sources, owing to

impermeable clay and sub-surface drainage at Pond Cassé as an example. In contrast, at Morne Prosper, the loamy soils are more permeable and it would be expected that greater water retention and buffering of nutrient concentrations in these areas when compared to the drier grasslands of Salisbury and the natural and semi-improved pasture areas of Soufriere.

While the results highlight higher P sorption for soils from Pond Cassé, Layou Valley and Morne Prosper owing to the presence of ions such as Al and Fe, long-term losses of P from soil as a result of a build-up in soil P concentrations caused by indiscriminate and/or repeated application of inorganic fertilisers and manure cannot be ignored or even be overlooked as these constitute important sources of nutrient additions within these agro systems and hence the need for appropriate management (Robinson and Sharpley, 1996; Cornish and Obersen, 2008; Brennan et al., 2012; Sharpley et al., 2013). In addition, incidental P losses arising from rainfall events following land application of phosphate fertilizers, animal manure and/or amended compost could be quite significant (Withers et al., 2003; Withers and Bailey, 2003) given on-island precipitation regimes (Chapter 3, Fig. 3.5) and the propensity of these events occurring at Morne Prosper, Layou Valley and Pond Cassé should be of great concern given current soil husbandry practices especially at Morne Prosper as an example (Chapter 3, Fig. 3.16).

As an outcome, incidental P losses would therefore be dependent on factors such as: the amount and type of fertilizer or manure applied (Kleinman and Sharpley, 2003; Warren et al., 2009), timing of rainfall events after application of fertilizer or manure (Smith et al., 2007), the volume of runoff generated, antecedent hydrologic conditions, field position, and flow path length (McDowell and Sharpley, 2002), vegetative cover (Zhang et al., 2002), surface slope (Alaoui et al., 2011) and soil type and associated soil characteristics (Borie and Zunino, 1983; Quang et al., 1996; Kleinman et al., 1999; Withers and Haygarth, 2007).

The rapid disappearance of phosphate from an equilibrating solution is kinetically related to adsorption capacity (Imai et al., 1981) and mechanistically to adsorption reactions on to active allophanic colloids (Borie and Zunino, 1983; Moody and Radcliffe, 1986). Hence this disappearance may be potentially balanced by organic P accumulation under a wet moisture regime (Peretyazhko and Sposito, 2005). In addition to high P retention, this would lend support in explaining the slow disappearance of P in Pond Cassé, and Layou Valley where annual precipitation of >6000 mm (Chapter 3, Fig. 3.5) occurs which favours organic P accumulation. Hence it has been suggested that when the moisture regime changes from dry to wet, periods of anoxic soil conditions tend to increase in intensity and duration, and thus depleting Fe(III) (hydr)oxides and releasing sorbed P, but also slowing organic matter turnover, and as such shifting the repository of soil P from minerals to humus (Peretyazhko and Sposito, 2005).

Taking into consideration hydrological events, rapid runoff generated from impermeable areas such as Pond Cassé and to a lesser extent Salisbury during the active hurricane season (July-October) could possibly result in significant delivery of nutrients during these ecologically sensitive periods (Edwards and Withers, 2008) with phosphorus tending to have a high transport dependence upon hydrology (Kleinman et al., 2000; Sharpley et al., 2003). In addition, changes in land-use including artificial drainage (King et al., 2015) could possibly result in the accelerated mineralization of organic P pools (Hedley et al., 1982; Tiessen et al., 1984; Walker and Syers, 1976; Solomon et al., 2002; Chirino-Valle, 2013) and the release of P into surrounding water bodies (Sharpley et al., 2000; McDonald et al., 2002; Foley et al., 2005; Valentin et al., 2008; Börjesson and Tufvesson, 2011) hence the need for small island based agrarian economies to encompass the concept of P saturation and proactively develop management systems which would mitigate against potential P losses.

5. Conclusion

P saturation was related to potential P losses at these different sites as determined by the iron-oxide impregnated paper strip test, water-soluble P, calcium chloride extractable P, Morgan P, Mehlich-III extractable P, and Mehlich-III extractable Al, highlighted the potential vulnerability. The degree of P saturation (DPS) of the soil's P sorption capacity (PSC), based on the Mehlich-III extractable P, and Mehlich-III extractable Al provided a good prediction of potential P losses. The usefulness of the DPS is attributed to the fact that it simultaneously takes into account both P quantity and P buffering capacity factors in predicting potential P losses and indirectly P availability (Daly et al., 2001; Bolland et al., 2003; Jordan et al., 2005; Sharpley et al., 2009). Moreover, these results suggest that observed relationships between specific P soil tests, and P export potential will have limited utility where different soil tests are used, as the differences in the relationship between soil test P and P loss potential are compounded by between test variations (Vadas et al., 2005).

Potential P losses, attributed to biologically available phosphorus (P) is divided operationally into two sources, dissolved reactive P (DRP) usually determined by the dilute CaCl_2 extractable soil P, and bioavailable particulate P (BPP) usually determined by P desorbed to iron-oxide impregnated filter paper (Moody, 2011). The appropriate benchmark method used to assess environmental risk will depend on whether DRP, BPP, or both are considered to be the major source(s) of bioavailable P (Ekholm and Krogerus, 1998; Ekholm et al., 2005). This assessment will also depend on land use, the main form in which P is being transported off-site to include in solution or sorbed on suspended sediment, the nutrient enrichment ratio, and the effectiveness of the delivery pathway to the receiving water (Sharpley, 1993; Yli-Halla et al., 1995; Sharpley and Kleinman, 2003; Cade-Menun et al., 2006). This is of interest to the Commonwealth of Dominica given its vulnerability to soil erosion and flash flooding as was most evident by the passage of tropical storm Erika (27th August, 2015) whereby in excess of

300 mm of rainfall was recorded within 8-12 hours causing significant loss of soil and hence P losses via erosion (Chapter 3, Fig. 3.3) and surface runoff leading to sediment P losses.

Where erosion is a risk to water quality, BPP usually comprises the primary P source (Sharpley, 1993). The use of water and CaCl_2 extraction of surface soil is suggested to estimate surface runoff P and subsurface drainage P, and determines the change point in P soil test which may be used in support of agricultural and environmental P management (McDowell and Sharpley, 2001). In general, soils with high P soil test values were relatively more saturated with P and potentially more vulnerable to losses to water by P desorption. More interestingly, soils with higher P sorption capacities were inherently high in extractable Al. However, P-sorption on humus bound Al-oxides (Al_p) was appreciable as compared to P-sorption on poorly crystalline and poorly crystalline amorphous Al-minerals (Al_o , Al_d) highlighting the need to manage the application of manure and composted material to the benefit of ecosystem health.

Extractable soil P decreased with sample depth, such that the 0-20 cm soil profile had the higher P saturation concentrations when compared to the 20-40 cm (Fig. 6.2). Daly and Casey (2005) conducted in-depth studies on seven grassland sites in Ireland at soil depths of 2, 5, and 10 cm. These authors noted that the current standard sample depth (10 cm) had a good correlation with surface soil samples (2 and 5 cm) and concluded that potential surface P losses can be consistently estimated from current standard depth employed in routine sampling.

Fe-oxy-hydroxides had a stronger affinity for P than Al-compounds with this tendency closely associated to crystalline and poorly crystalline amorphous forms and hence the soil P content. It can be deduced that the forms of P fertilizers to include organic and inorganic forms potentially represent factors affecting P status in these soils as they tend to have limited reserves of P in low P fixing soils. Arguably, the concept of P build-up does not realistically exist for these soils and applied P tends to remain in the soil solution, or as readily-available P if not

immediately taken up by the crop. In this context surplus P would be lost to water if overland flow occurs most probably when large quantities are applied to the soil.

To this end, McDowell et al., (2003) working on pastoral soils of New Zealand demonstrated the greater risks of incidental P losses from soluble P fertilisers such as superphosphate, and conversely the potential environmental benefits from reactive rock phosphate fertilisation of soils at-risk of P loss, where much overland flow occurs such as in very wet soils and near stream channels. However, it has been suggested that in order to minimize P fertilizer inputs and maximize production, potential cash crops will need to be selected for their ability to produce maximum yield at low solution P concentration. This ability will most probably depend not exclusively, on the establishment of an effective mycorrhizal infection (Wu et al., 2005; Adesemoye and Kloepper, 2009; Jones and Oburger, 2011; Heydari, 2013), and precision fertilizer placement and frequency of application (Holford et al., 1974; Moody and Radcliffe, 1986; Barrow and Debnath, 2014) may offer additional means of increasing the utilization of fertilizer P in high-sorbing soils.

This study, exploratory in nature, aimed at establishing the relationship of P saturation with different soil constituents. The suggestion is that broader studies are needed to determine the relationships between P soil tests for Dominican soils, whereby standard protocols for assessing the potential for P loss could then be developed and be gradually incorporated into routine soil analysis. Future studies will have to be based on hydrologic principles that frequently occurring storms do initiate significant surface runoff from fields. Hence it becomes critically important in designing such studies that nonpoint-source losses of P at field and watershed scales can be quantified to facilitate selection and placement of P control measures. Mitigation strategies will need to address P management from the perspective of controlling loss of P in runoff from the soil to sensitive waters via exploration of conservation and/or zero tillage, buffer zones, agroforestry systems and cover crops to intensified fallow systems.

CHAPTER 7

PHOSPHORUS RETENTION AND DESORPTION CAPACITIES OF VOLCANIC SOILS FROM THE COMMONWEALTH OF DOMINICA

Abstract: Most volcanic soils contain large amounts of organic C, active Al and Fe, and short-range-ordered minerals such as ferrihydrite and allophane, which has been found to be strongly correlated with the capacity of the soil to adsorb as well as to desorb P, and indeed a close relationship exists between phosphate sorption and crystalline and amorphous Fe/Al oxides. The predominance of these constituents in most volcanic soils ultimately influences their capacity to adsorb and desorb P, and thus impacting on soil fertility, particularly P availability.

The capacity of the soil to adsorb and desorb P has been successfully described by adsorption isotherms as well as by sequential extraction. In this context, the aim of this study is to (1) determine the P retention characteristics of tropical volcanic soils of the Commonwealth of Dominica by employing radioisotope techniques and use of the Langmuir and Freundlich equations and, (2) assess the ability of these soils to desorb proportions of added P by the successive extraction with 0.01 M CaCl₂ (P desorption) and thus relating the influence of P sorption to selected soil constituents.

The results highlight a wide range of P retention values, 44.33% (1.23) – 94.68% (0.35). P desorption ranged from 5.49% (0.49) to 55.89% (0.95). The relationship of P_{ret} was significantly correlated ($P < 0.001$) with allophane ($R^2 = 0.61$) but even stronger with ferrihydrite ($R^2 = 0.86$). Forward stepwise regression analysis showed that P_{ret} was best explained ($R^2 = 0.92$, $P < 0.001$) by: [$P_{ret} = 43.99 - (2.16 \text{ base saturation.}) + (1.43 \text{ organic matter}) + (27.13 \text{ Fe}_d)$], with P desorption best explained ($R^2 = 0.95$, $P < 0.001$) by: [$P_{des} = 84.81 - (5.51 \text{ allophane} + \text{ferrihydrite}) - (19.37 \text{ Fe}_d) - (0.59 \text{ organic matter})$]. Provided that the concentration range was limited to 0.01 – 1.0 g P L⁻¹, the Freundlich equation best described the relation between sorption and concentration.

Key words: Phosphate, sorption, allophanic soils, P availability, Dominica

1. Introduction

Due to the presence of active and amorphous Al- and Fe- compounds, Al- and Fe-organic matter complexes, and high variable charge in the soil colloidal system, a high ability to retain P is one of the characteristics of volcanic soils (Mizota and Van Reeuwijk 1989; Shoji et al., 1993; Fontes and Weed, 1996; Nugroho, 2010). P availability is governed by an intensity and quantity factor and a buffer capacity index, either singly or in combination, depending on the relative variations of these factors in the soil system (Barrow, 1978; Wada, 1978; Moody et al., 1988). Soil solution P is closely related to adsorbed P, and mineralogy of the clay fraction plays a major role in this relationship, with Al- and Fe- oxides being important P-adsorbers (Iñiguez and Val, 1984; Moody and Radcliffe, 1986; Gilkes and Hughes, 1994; Fontes and Weed, 1996; Quang et al., 1996; Bruland and Richardson, 2006).

The reaction of phosphate in soil with iron and aluminium oxides may consist of a sequence of steps (Bolan et al., 1985). If one of these steps should be very much slower than the others then the overall reaction proceeds at a rate controlled by the slowest step (Bockris and Reddy, 1973). Olsen and Watanabe (1963) estimated that the quantity of P transported by diffusion is dependent on the concentration of P in the soil solution (intensity factor), the ability of the soil to replenish solution P (buffer capacity) and the diffusion coefficient of P in soil. Therefore as buffer capacity increases, the ease of desorption of a given quantity of P tends to decrease (Barrow, 2015), with a concomitant reduction in P availability (Moody et al., 1988) and the release of OH^- , SO_4^{2+} , and SiO_2 (Rajan and Fox, 1975).

The reaction between divalent phosphate ions, and soil with variable charge surfaces, is rapid at first and linked to adsorption on external surfaces (Imai et al., 1981). It then becomes slower and continues for a long time without reaching any true equilibrium (Barrow, 1983; Bolan et al., 1985). This step is generally associated with adsorption on internal surfaces and with new reactive areas, exposed increasingly with time, to phosphate ions in solution (Imai et

al., 1981; Parfitt, 1989a,b; Pardo and Guadalix, 1990) and hence the decrease in P concentration in the presence of Fe-OH, or Al-OH, is partly due to the retention of phosphate by these hydroxides. As a result, P-retention is decreased by the number of binding sites that are already occupied by phosphate (Madeira et al., 2007b; Barrow, 2015).

Andic soil properties exhibit phosphate retention of >85% (Aran et al., 2001; Arnalds, 2004) and P sorption of these soils is known to be related to soil constituents such as oxalate extractable Al and Fe (Auxtero et al., 2008). The rapid disappearance of phosphate from an equilibrating soil solution is related to adsorption reactions onto active allophanic colloids (Borie and Zunino, 1983) when the average phosphate ion concentration in the ambient solution is sufficiently high to enable their penetration of the allophane microstructure (Parfitt and Henmi, 1980; Imai et al., 1981). As a result, adsorbed phosphate into the interior of the particles of iron and aluminium hydroxides by solid-state diffusion (Bolan et al., 1985) coupled with specific surface area, is of importance in phosphate adsorption in soils (Barrow et al., 1980; Fontes and Weed, 1996) particularly as it relates to rates and frequency of P fertilizer application (Barrow and Debnath, 2014) governed by the ability of soil to replenish solution P.

In this respect P-sorption data related to soil properties is a helpful management tool (Parfitt, 1979; Imai et al., 1981; Barrow, 1984; Bolan et al., 1985; Singh and Gilkes, 1991). Such studies have been carried out in many regions and on different soil types of the humid tropics (Quang et al., 1996; Van Ranst et al., 2004; Yatno and Zaayah, 2008; Wisawapipat et al., 2009), but little to no information exists on the P-sorption characteristics of the major soil types in the Commonwealth of Dominica. These tropical volcanic soils generally have high agricultural potential (Navarrete et al., 2008; Nugroho, 2010). However, some of them produce well below their prospective capacity due to lack of understanding of their characteristic properties (Barrow and Debnath, 2014; Barrow, 2015), leading to improper management which results in low crop productivity as well as negative ecological and environmental impacts.

Many attempts have been made to clarify the reaction mechanisms of soil components with anions, especially phosphate, because of its practical importance in agriculture (Theng et al., 1982; Aran et al., 2001; Barrow and Ellis, 1986; Arnalds, 2004; Auxtero et al., 2008; Barrow, 2015). Several kinetic equations have been used either to deduce the mechanisms or simply to interpret the results of this continued removal of phosphate from solution (Bolan et al., 1985) and the various kinetic equations assume different rate determining steps in the reaction of phosphate with soil and its constituents.

In the first order kinetics (Griffin and Jurinak, 1974), the rate of change in concentration is proportional either to the concentration in solution or to the number of empty sites.

$$\text{Log } C = \text{log } C_0 - Kt \quad [18]$$

However in the second order kinetics (Kuo and Lotse, 1973), the rate of change in concentration is proportional to both the concentration in solution and number of empty sites.

$$(1/C_0) - (1/C) = Kt \quad [19]$$

Furthermore, in the diffusion equation as highlighted by Cooke (1966) the rate limiting step is the diffusion of phosphate ions either from the solution to the surface or from the surface to the interior of the particle.

$$X = \sqrt[3]{t + b} \quad [20]$$

McLaughlin et al., (1977) in the modified Langmuir equation highlighted that the rate of adsorption is proportional to the concentration in the solution and the number of empty sites.

$$X = b_1 + \Delta b_1 + \frac{b_{11} K_{11} C}{1 + K_{11} C} + \frac{b_{111} K_{111} C}{1 + K_{111} C} \quad [21]$$

Where X is the amount of phosphate sorbed, C_0 and C are the initial and the final concentration of phosphate in solution, t is the time and all others are parameters.

Barrow and Shaw (1975a, b) in the modified Freundlich equation demonstrated that phosphate reactions in a soil system contains three compartments, A, B and C and react according to $A \leftrightarrow B \leftrightarrow C$, with the rate limiting step being $B \rightarrow C$.

$$X = KC^b t^{b_1} \quad [22]$$

Chien and Clayton (1980) through the Elovich equation demonstrated the importance of the soil's mineralogy whereby the activation energy of adsorption increases linearly with surface coverage.

$$X = (1/\beta) \ln(\alpha/\beta) + (1/\beta) \ln t \quad [23]$$

However, Bolan et al., (1985) subsequently discussed that the limitation in applying these equations to phosphate sorption kinetics is that sorption of phosphate ions by charged surfaces involves changes in surface charge. Barrow (1983) initially proposed a mechanistic model for phosphate reaction with soils which encompasses solid-state diffusion of adsorbed phosphate into the particles involving a number of assumption which are captured by the models of variable charge surface (Bowden et al., 1980), normal distribution of initial electrostatic potential (Snedecor and Cochran, 1967), diffusion of phosphate into particles (Crank, 1964), and electrostatic potential (Posner and Barrow, 1982).

Sorption of phosphate ions by charged surfaces involves changes in surface charge (Allbrook, 1985; Bolan et al., 1985) and P sorption curves describe the relationship between adsorbed P on the soil surface and solution P, and can be used to (1) characterize soils in terms of P buffer capacity and equilibrium solution P concentration; (2) identify the soil chemical and mineralogical properties which determine the magnitude of P sorption; and (3) estimate P fertilizer requirements based on the premise that these requirements are related to the amount of sorbed P at a supernatant concentration known to be non-limiting to plant growth (Moody and Radcliffe, 1986). In addition, several studies have demonstrated the effect of different Fe_o/Al_o , Fe_p/Al_p and Fe_d/Al_d concentrations on P-retention and phosphate immobilization to

both non-crystalline Al/Fe colloids and Al/Fe humic complexes (Arshad et al., 1972; Uehara and Gillman, 1981; Moody and Radcliffe, 1986; Quang et al., 1996; Auxtero et al., 2008).

Initial studies conducted within the wider scope of this research (Chapter 4) have shown that there are potentially significant differences between these soils in the rate at which they react with phosphate based on their reactions with sodium fluoride (pH NaF), which has been used as a quick test for predicting the P sorption capacity of soils (Singh and Gilkes, 1991; Gilkes and Hughes, 1994). These differences have potentially large effects on the residual value of phosphate fertilizer (Barrow, 1978, 1980) taking into consideration that a P concentration of around 0.2 mg L^{-1} in the soil solution can be ascribed as a reference for satisfactory plant growth (Gilkes and Hughes, 1994; Quang et al., 1996). Given the importance of this thematic area in the management of tropical volcanic soils, the objectives of this study are to: (1) determine which soil types within the Dominican agricultural environment have the highest P sorption capacity; (2) identify which soil properties best explained the variability in P sorption.

2. Materials and Methods

2.1 ^{33}P adsorption studies

P adsorption studies were performed by weighing 1 g of air dried soil, previously sieved through a 2 mm mesh, into 50 ml plastic centrifuge tubes and adding 5 ml of KH_2PO_4 at P concentrations of 0.01, 0.025, 0.05, 0.1, 0.25, 0.50, 0.75 and 1.0 g L^{-1} in the presence of 5 ml of 0.01 M KCl solution used to keep the ionic strength of the suspension constant (Van Ranst et al., 2004). ^{33}P was adsorbed as labelled potassium di-hydrogen phosphate ($\text{KH}_2^{33}\text{PO}_4$). The initial activity of the ^{33}P isotope (10,000 DPM = 0.17 kBq) was selected on the basis of a back calculation, allowing for decay, to achieve a sample with sufficient activity so as to be in the optimal range for accurate scintillation counting (P. Tallboy, personal communication).

Soil samples were subsequently shaken end-over-end for 30 minutes. After a centrifugation step (5 minutes at 10,621 RCF), an aliquot of the supernatant (0.5 ml) was analysed for ^{33}P activity by Cerenkov counting using a Wallace®™ 1404 liquid scintillation counter (EG&G Ltd., Milton Keynes, UK) with Wallace®™ Optiphase 3 liquid scintillation fluid (4 ml) as a carrier. Adsorption isotherms were constructed using the Freundlich equation by plotting P concentration (mg L^{-1}) versus mass of P sorbed (mg g^{-1}). The adsorption of phosphate was described by:

$$P_s = ac^{b_1} \quad [24]$$

Where P_s is the phosphate adsorbed by the soil, c (mg P L^{-1}) is the solution concentration of phosphate and a and b_1 are coefficients (Barrow and Shaw, 1975a,b; 1979).

P sorption isotherms were also constructed following a linearized form of Langmuir equation (Woodruff and Kamprath, 1965), as:

$$C/P = C/P_m + 1/k P_m \quad [25]$$

Where: C is the equilibrium P concentration (mg L^{-1}), P is the amount of P sorbed (mg g^{-1}), P_m is the Langmuir sorption maxima and k is a constant related to the P binding strength.

The plot between the values of C/P and C was drawn and the linear curve was fitted to the scattered points to obtain $y = a + bC$. The inverse value of b ($1/b$) obtained from this linear fit was made to represent the value of P_m .

A comparison of the data was also conducted by fitting the adsorption results to the modified Langmuir equation (McLaughlin et al., 1977) which was written as:

$$S = \frac{N_t k c}{1 + k c} \quad [26]$$

Where S is the amount of anion adsorbed, N_t is the maximum adsorption, k is an affinity term, and c is the concentration of adsorbate in solution.

2.2 P desorption studies using 0.01 M CaCl₂

P desorption studies were performed by weighing 1 g of air dried soil, previously sieved through a 2 mm mesh, into 50 ml plastic centrifuge tubes and adding 25 ml of 0.01 M CaCl₂ containing a P concentration of 10 mg L⁻¹ as KH₂PO₄ and two drops of chloroform to suppress microbial growth (Self-Davis et al., 2009). Samples were mechanically shaken twice daily for 30 minutes at room temperature over 7 days to achieve equilibrium and then centrifuged for 10 minutes at 3184 RCF and filtered through Whatman No. 42 filter paper. P in the supernatant solution was then analysed colorimetrically on a Biotek™® Powerwave XS microplate spectrophotometer measured at 880 nm, using the Murphy and Riley (1962) molybdate blue method. This represented the initial P content (mg kg⁻¹) corresponding to extraction zero.

Successive extractions were done by adding 25 ml of 0.01 M CaCl₂ to each sample, followed by 16 hours of shaking using a reciprocal shaker. Samples were then centrifuged at 3184 RCF for 10 minutes and filtered through Whatman No. 42 filter paper. To correct for the entrained solution left in the tube after filtration, the tubes were weighed and sufficient amount of 0.01 M CaCl₂ added to bring the volume of solution back to 25 ml. This procedure was repeated through eight successive extractions (Auxtero et al., 2008). The P content from each filtered extract was determined by the molybdate blue method of Murphy and Riley (1962). The total amount (mg kg⁻¹) of P desorbed (P_{des}) was calculated from the difference between the actual amount of P desorbed at the initial extraction with CaCl₂ and the sum of P desorbed after eight successive extractions with CaCl₂. This ratio between the sum of P extracted after eight successive extractions and P in soil after the initial extraction with CaCl₂ was expressed as the percentage of P desorption.

2.3 Soil Sampling

Soil sampling has been described in chapter 3 “geophysical description of the Dominican environment and general characterization of study sites” and as such no further mention will be made.

2.4 Calculations used in ³³P radioisotope

$$\text{Total P content} = \text{Volume of PO}_4 \text{ added (L)} \times \text{Concentration Blank (mg L}^{-1}\text{)} \quad [27]$$

$$\% \text{ P in solution} = \frac{\text{CPM}}{\text{CPM Blank}} \quad [28]$$

$$\text{Mass of P} = \text{Total P content (mg)} \times \% \text{ P in solution} \quad [29]$$

$$\text{P concentration (mg L}^{-1}\text{)} = \frac{\text{Mass of P}}{\text{Total volume}} \quad [30]$$

$$\% \text{ P sorbed} = (1 - \% \text{ P in solution}) \times 100 \quad [31]$$

$$\text{Mass of P sorbed} = \frac{[\% \text{ P sorbed} \times \text{Total P content (mg)}]}{100} \quad [32]$$

2.5 Statistical Analysis

Sample analysis was done in triplicate with mean and standard error of the mean (SEM) calculated. Statistical analyses were performed using SPSS version 20.0 for Windows program (SPSS Inc., Chicago, IL). Significant differences between groups means was determined by analysis of variance (*t*-test and ANOVA) and Tukey’s test was used for multiple comparison between the sample means where the ANOVA *F* statistics was significant.

3 Results

Table 7.1. Selected soil properties (0-40 cm) of the volcanic soils of the Commonwealth of Dominica. Values represent mean of three replicate with SEM indicated in parenthesis. n = 36.

Soil Type	OM (%)	CEC (cmol(+)kg ⁻¹)	pH NaF (2 mins)	Base Sat (%)	Sio (%)	Al _o (%)	Al _p (%)	Al _d (%)	Fe _o (%)	Fe _p (%)	Fe _d (%)	Al _o + 0.5 Fe _o (%)
Morne Prosper	9.93 (1.38)	26.43 (0.70)	10.86 (0.07)	13.74 (0.39)	0.49 (0.03)	1.14 (0.02)	0.58 (0.02)	0.96 (0.04)	1.45 (0.04)	0.22 (0.01)	1.62 (0.04)	1.86 (0.04)
Soufriere	5.28 (0.24)	18.58 (0.60)	8.04 (0.10)	15.47 (0.62)	0.25 (0.02)	0.66 (0.05)	0.35 (0.02)	0.44 (0.04)	0.69 (0.03)	0.10 (0.00)	0.81 (0.03)	0.99 (0.05)
Castle Bruce	7.35 (0.52)	23.70 (0.71)	8.29 (0.05)	13.80 (0.31)	0.35 (0.020)	0.87 (0.04)	0.57 (0.02)	0.67 (0.02)	1.22 (0.04)	0.18 (0.01)	1.43 (0.04)	1.48 (0.05)
Pond Cassé	16.94 (0.47)	33.95 (0.52)	11.55 (0.07)	12.27 (0.14)	0.61 (0.01)	1.50 (0.05)	0.78 (0.02)	1.12 (0.04)	1.61 (0.04)	0.29 (0.00)	1.77 (0.05)	2.31 (0.06)
Layou Valley	16.80 (1.40)	31.48 (0.48)	11.35 (0.05)	12.62 (0.15)	0.52 (0.02)	1.20 (0.04)	0.72 (0.02)	1.04 (0.03)	1.78 (0.04)	0.30 (0.00)	1.90 (0.04)	2.09 (0.06)
Salisbury	7.47 (0.20)	18.89 (0.74)	8.73 (0.07)	16.00 (0.71)	0.32 (0.02)	0.70 (0.02)	0.48 (0.02)	0.53 (0.02)	0.88 (0.03)	0.12 (0.00)	1.01 (0.03)	1.14 (0.02)

Soil Type	Allophane (%)	Ferrihydrite (%)	Al Mehlich-III (mg kg ⁻¹)	P total (mg kg ⁻¹)	P Mehlich-III (mg kg ⁻¹)	P _i (mg kg ⁻¹) 0.01 M CaCl ₂	P _f (mg kg ⁻¹) 0.01 M CaCl ₂	P desorption (mg kg ⁻¹) 0.01 M CaCl ₂	P-desorption (%)	³³ P-retention (%)
Morne Prosper	2.78 (0.09)	2.46 (0.07)	43.37 (2.21)	257.09 (7.13)	24.88 (0.69)	3.65 (0.03)	3.00 (0.03)	0.65 (0.00)	17.81 (0.73)	82.21 (0.99)
Soufriere	1.46 (0.13)	1.16 (0.06)	22.47 (2.08)	131.12 (3.75)	29.57 (0.49)	5.01 (0.07)	2.22 (0.03)	2.80 (0.04)	55.89 (0.95)	44.33 (1.23)
Castle Bruce	1.84 (0.13)	2.07 (0.07)	36.65 (1.88)	176.83 (6.21)	28.71 (0.53)	4.83 (0.17)	3.44 (0.12)	1.38 (0.05)	28.57 (1.00)	71.35 (0.86)
Pond Cassé	3.51 (0.10)	2.74 (0.06)	54.42 (2.12)	264.20 (8.27)	26.23 (0.34)	2.37 (0.02)	2.24 (0.02)	0.13 (0.00)	5.49 (0.49)	88.86 (5.22)
Layou Valley	2.76 (0.10)	3.02 (0.06)	49.53 (3.01)	259.07 (7.61)	26.92 (0.45)	2.95 (0.05)	2.70 (0.02)	0.25 (0.03)	8.47 (0.45)	94.68 (0.35)
Salisbury	1.61 (0.08)	1.50 (0.05)	27.78 (2.51)	145.92 (5.01)	29.57 (0.40)	4.64 (0.10)	2.69 (0.06)	1.95 (0.04)	42.03 (1.00)	58.05 (1.72)

Symbols: OM = Organic Matter; CEC = Cation Exchange Capacity; Al_o/Fe_o = Oxalate extractable; Al_d/Fe_d = Dithionite extractable; Al_p/Fe_p = Pyrophosphate extractable, P_i = P content from initial 0.01 M CaCl₂ extraction, P_f = Final P content after eight successive extractions with 0.01 M CaCl₂.

The results from the studies using ^{33}P radioisotopes revealed a wide range of P retention (P_{ret}) values (44.33% – 94.68%) in the soils (Table 7.1), and varied according to site and differences in soil constituents. The lowest P_{ret} values were observed in soils from Soufriere, 44.33% (1.23) and Salisbury, 58.05% (1.72), which showed low Mehlich-III extractable Al values, 2.25 mg L⁻¹ (0.21) and 2.78 mg L⁻¹ (0.25) respectively and also low pH (NaF) values of 8.04 (0.10) and 8.73 (0.07) correspondingly. These soils also had the lowest extractable Al and Fe forms (Table 7.1) and as such the P buffering capacity is lower in soils from Soufriere and Salisbury consistent with a lower allophane content and higher base saturation. Soils from Layou Valley, Pond Cassé, and Morne Prosper had the highest P_{ret} values with means of 95% (0.35), 89% (5.22), and 82% (0.99) respectively (Table 7.1). These results suggest that the higher P_{ret} values are related to the higher content of the various Al and Fe forms (Moody and Radcliffe, 1986; Quang et al., 1996; Van Ranst et al., 2004; Bruland and Richardson, 2006).

These results indicate that while soils from Layou Valley and Pond Cassé have strong ability to adsorb P, they simultaneously have low ability to desorb P and hence a high tendency to retain P, which may become unavailable for plant use, requiring large amounts of preferably fast P-releasing fertilizers for annual crops/slow releasing P fertilizers for perennial crops (Barrow, 1980; Borie and Zunino, 1983; Barrow and Debnath, 2014). Soils from Layou Valley and Pond Cassé meet the criteria in defining Andosols with P retention values greater than 85% (FAO, 1988; Parfitt and Clayden, 1991; Shoji et al., 1993; Arnalds et al., 1995; Aran et al., 2001; FAO, 2006). A P retention of >85% is one of three defining characteristics of criteria one in meeting andic properties (FAO, 1988, 2006). However, soils from Morne Prosper, 82% (0.99) and to a lesser extent Castle Bruce, 71% (0.86) tend to show inclination to retain P which reflects the presence of allophane and or layered silicates in these soils (Arnalds and Kimble, 2001) as was revealed by their pH NaF values post two minutes, as well as the 70% P retention index used by soil taxonomy classification (SSS, 2003) in defining soils with andic properties.

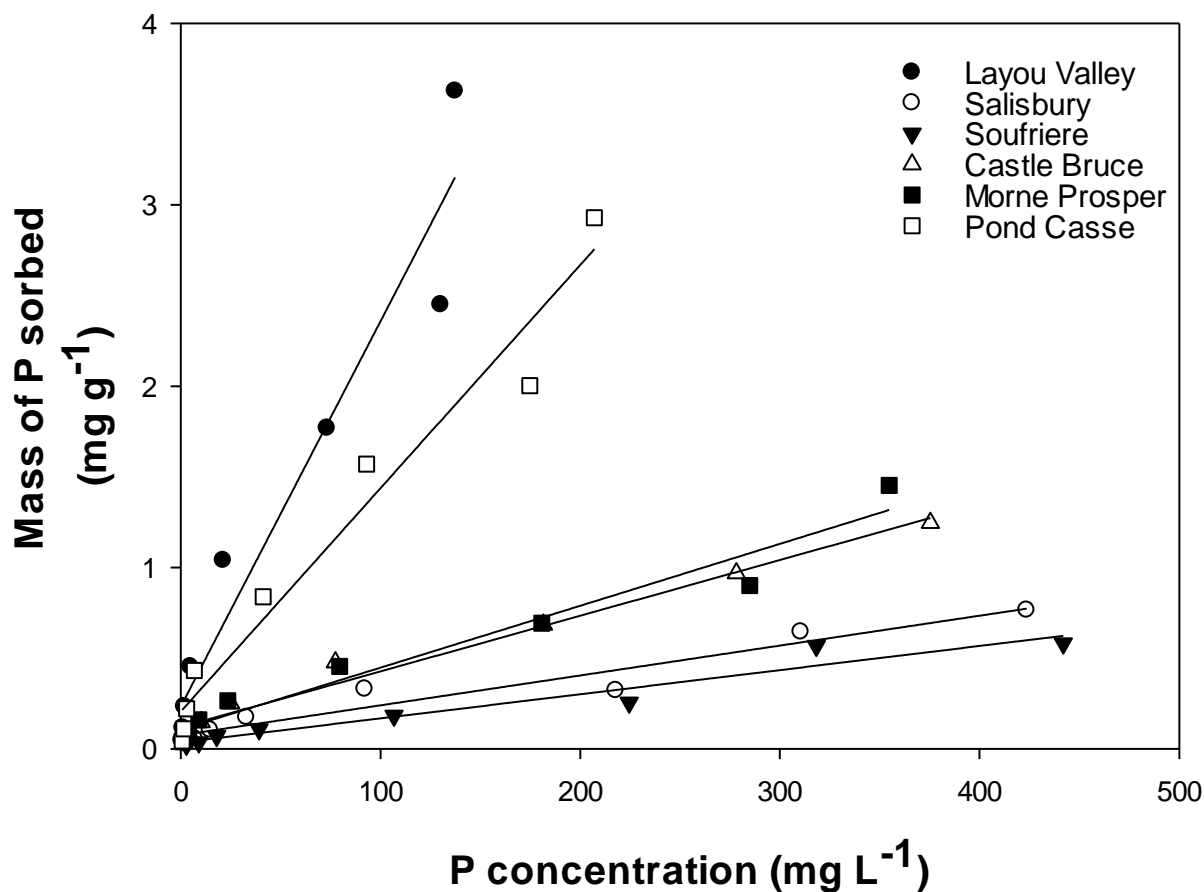


Fig. 7.1. Phosphorus adsorption isotherms of six major agricultural soils from the Commonwealth of Dominica. Data fitted to the modified Langmuir equation. $S = \frac{ntkc}{1+kc}$. Data points represent the mean of three replicates. Correlation equations show the following: Layou Valley ($R^2 = 0.93$, $Y = 0.02x + 0.24$); Salisbury ($R^2 = 0.82$, $Y = 0.002x + 0.08$); Soufriere ($R^2 = 0.75$, $Y = 0.001x + 0.04$); Castle Bruce ($R^2 = 0.95$, $Y = 0.003x + 0.12$); Morne Prosper ($R^2 = 0.85$, $Y = 0.003x + 0.12$); Pond Casse ($R^2 = 0.94$, $Y = 0.01x + 0.21$).

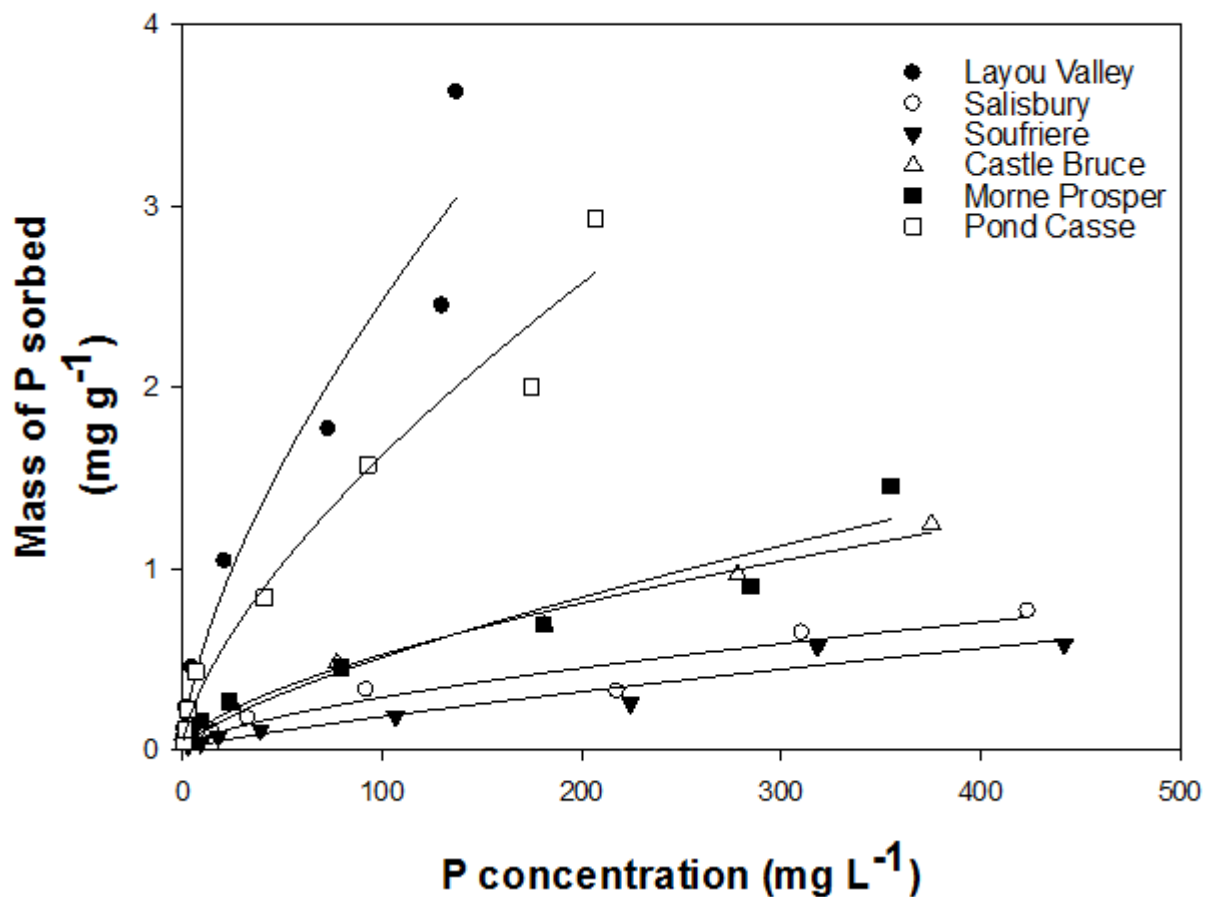


Fig. 7.2. Phosphorus adsorption isotherms of six major agricultural soils from the Commonwealth of Dominica. Data fitted to the Freundlich equation. $Y = ax^b$. Data points represent the mean of three replicates. Correlation equations show the following: Layou Valley ($R^2 = 0.98$, $Y = 0.13x^{0.65}$); Salisbury ($R^2 = 0.96$, $Y = 0.02x^{0.60}$); Soufriere ($R^2 = 0.94$, $Y = 0.01x^{0.64}$); Castle Bruce ($R^2 = 0.99$, $Y = 0.03x^{0.62}$); Morne Prosper ($R^2 = 0.98$, $Y = 0.04x^{0.56} - 0.18$); Pond Casse ($R^2 = 0.96$, $Y = 0.09x^{0.64}$).

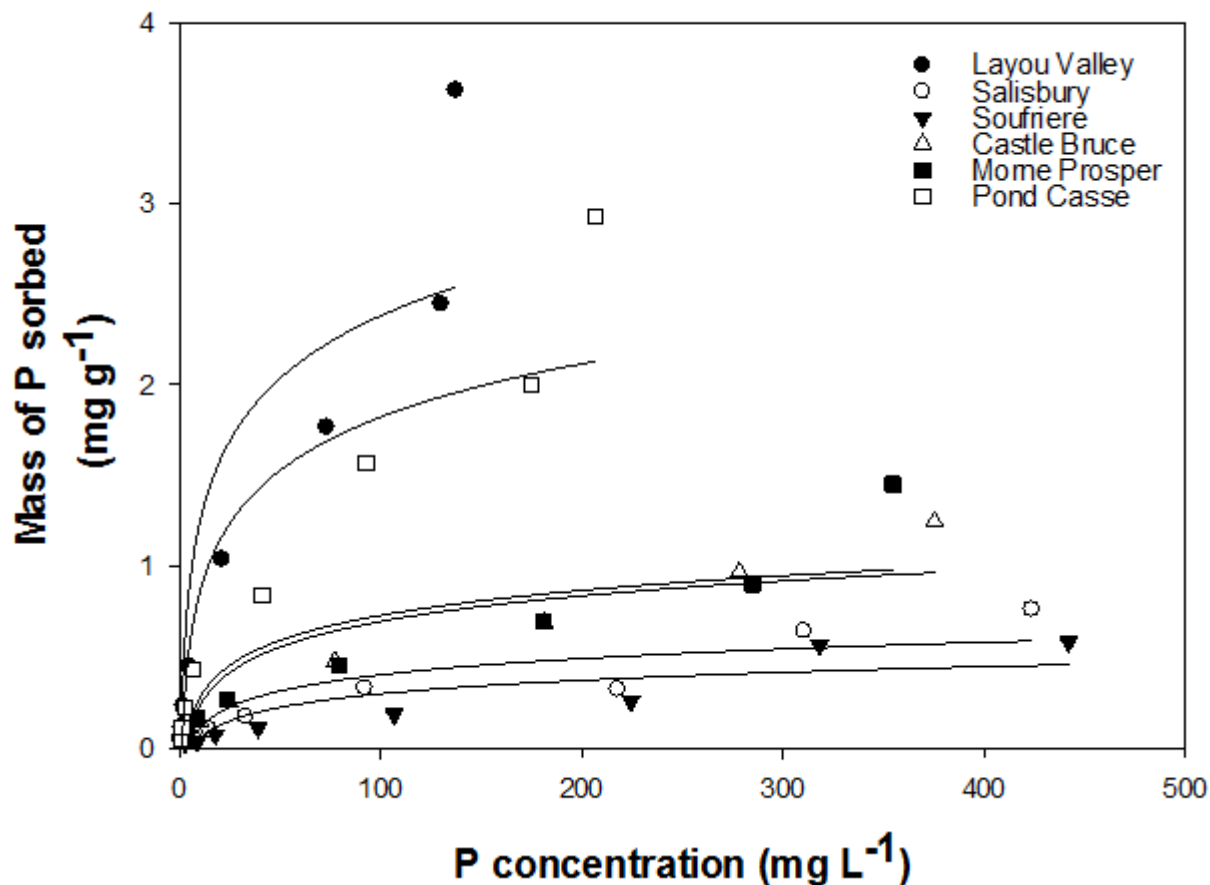


Fig. 7.3. Phosphorus adsorption isotherms of six major agricultural soils from the Commonwealth of Dominica. Data fitted to the linearized Langmuir equation: $C/x/m = C/k + 1/k_b$. Data points represent the mean of three replicates. Correlation equations show the following: Layou Valley ($R^2 = 0.81$, $Y = 0.49\ln(x) + 0.09$); Salisbury ($R^2 = 0.73$, $Y = 0.13\ln(x) - 0.19$); Soufriere ($R^2 = 0.63$, $Y = 0.11\ln(x) - 0.20$); Castle Bruce ($R^2 = 0.84$, $Y = 0.20\ln(x) - 0.24$); Morne Prosper ($R^2 = 0.71$, $Y = 0.20\ln(x) - 0.18$); Pond Casse ($R^2 = 0.82$, $Y = 0.41\ln(x) - 0.09$).

A tendency towards linear relationships was observed when the data sets, P concentration against mass P sorbed, were plotted according to the modified Langmuir equation (Fig. 7.1) and the Freundlich equation (Fig. 7.2). However, a tendency towards curvilinear relationships was obtained when the data sets were plotted according to the linearized Langmuir equation (Fig. 7.3). The goodness of fit varied markedly with the various equations employed. Provided that the concentrations were restricted to the range of 0.01-1.0 g P L⁻¹, the Freundlich equation best described the relation between adsorption and concentration which is in agreement to the findings of Barrow (1978, 1980).

It has been cited in the literature that the model of P adsorption isotherms by the Langmuir equation is preferred to other models because it provides a value of P sorption maxima (Olsen and Watanabe, 1957; Woodruff and Kamprath, 1965). However Harter and Baker (1977) argued that the commonly reported curvilinear nature of the C/x/m vs. C plots (Fig. 7.3) is simply the result of not considering the effect of desorbed ions in the equilibrium solution, rather than being due to multiple adsorption mechanisms, and only becomes important when attempts are made to understand adsorption dynamics and bonding strengths.

In addition, according to Veith and Sposito (1977) and Sposito (1982), the Langmuir equation may be statistically limited in determining whether adsorption or precipitation is occurring during anion fixation reactions in soils and that the parameters in the Langmuir equation cannot be interpreted in terms of surface reactions without additional, independent evidence that only adsorption is involved in anion fixation. However, according to Harter and Baker (1977), this error is of no great importance when the equation is merely used to obtain a calculated adsorption maximum for comparison to other adsorbent properties. Harter (1984) went on to further clarify the use of the Langmuir equation with caution as it does not always adequately estimate adsorption maxima because the plotting of concentration/adsorption as a function against itself reduces data variability and always provides a statistically significant

correlation coefficient. Furthermore, when isotherms do not have the correct shape and only low concentration data is used, the equation can provide estimates of the adsorption maximum that are in error by 50% or more (Harter, 1984).

The results from both the Langmuir and Freundlich equation highlighted the variability of the P retention characteristics of these soils. The modified Langmuir fit gave a mean R^2 value of 0.87 (0.03) while the Freundlich equation gave an increase in the mean R^2 value of 0.96 (0.01). It can be noted that the Langmuir adsorption model deviates significantly in all cases, primarily because it fails to account for surface irregularity of the adsorbent (Barrow et al., 1980; Fontes and Weed, 1996). It has been reported that defect surfaces have multiple site-types available for adsorption, and some parameters vary from site to site, such as the thermal energy of adsorption (Imai et al., 1981, Bolan et al., 1985; Parfitt, 1989a,b).

Adsorption of phosphorus showed a closer relationship with the Freundlich isotherm than with the Langmuir isotherm, in agreement with results of Barrow (1978, 1980) but contrary to that obtained by Olsen and Watanabe (1957), who demonstrated that adsorption of phosphorus by soils from dilute solutions showed a closer agreement with the Langmuir isotherm than with the Freundlich isotherm which they related to the bonding energy of the soil for phosphorus. There was a noticeable marked difference with regards to the fit with the linearized Langmuir equation: $C/x/m = C/k + 1/kb$. The mean R^2 value was 0.75 (0.03) (Fig. 7.3). According to Harter and Baker (1977), when the equation is modified by considering desorbed ions, the isotherm tends to show linearity (Fig. 7.2). In addition, it has been argued that the constant parameter of the Langmuir equation is not simply related to the bonding energy of the adsorbed ion, but to the ratio of adsorbed and desorbed ion bonding energies (Holford et al., 1974).

The results from the ^{33}P radioisotope studies generally show that soils from Soufriere and Salisbury with the highest concentrations of P (Fig. 7.1-7.3) followed by Castle Bruce and

Morne Prosper respectively. Soils from Pond Cassé and Layou Valley recorded the lowest P concentrations which were related to the percentage P in solution (Fig. 7.5) as well as to the P concentration (Fig. 7.6). On the contrary mass of P sorbed were highest in soils from Layou Valley and Pond Cassé respectively (Fig. 7.7) owed to the high aluminosilicate content.

High P sorption capacity in these soils is due to the very large specific surface, calculated to be $\sim 800\text{-}1000\text{ m}^2\text{ g}^{-1}$ (Theng et al., 1982; Allbrook, 1985; Al-Ani and Sarapää, 2008; Creton et al., 2008) and reactivity of allophane (Iñiguez and Val, 1984; Allbrook, 1985; Lizcano et al., 2006). The percentage of P sorbed decreased with corresponding increases in the concentration of added P in the solution (Fig. 7.4). The data tends to suggest that as the percentage of P sorbed increases, the amount that can later be released also increases (Pardo and Guadalix, 1990). A decrease in concentration of P in the presence of Fe-OH, or Al-OH, was due to the retention of phosphate by these hydroxides. P retention is decreased by the part of the binding sites that is already occupied by phosphate (Madeira et al., 2007b) and as more P is sorbed an increasing displacement of OH⁻ is usually observed (Pardo and Guadalix, 1990).

Borie and Zunino (1983), Allbrook (1985), and Óskarsson et al., (2012) highlighted that allophanic soils have the characteristic of high phosphate retention, because of their anion adsorption capacities, observations which were expressed by Gustafsson et al., (1995), and Van Ranst et al., (2004). Thus the conclusion has been reached that phosphate retention in allophanic soils is mainly due to the ability of allophane to strongly adsorb phosphate ions specifically by ligand-exchange (Parfitt, 1980; Borie and Zunino, 1983; Van Ranst et al., 2004; Verde Vilanova, 2009). Consequently, phosphate sorption has been reported to be closely related to the amounts and particle sizes of the hydroxides of iron and aluminium rather than to silica, clay or silt plus clay, suggesting sesquioxides as reactive constituents in highly weathered soils of the tropics (Jones et al., 1982; Sollins et al., 1996; Auxtero et al., 2013).

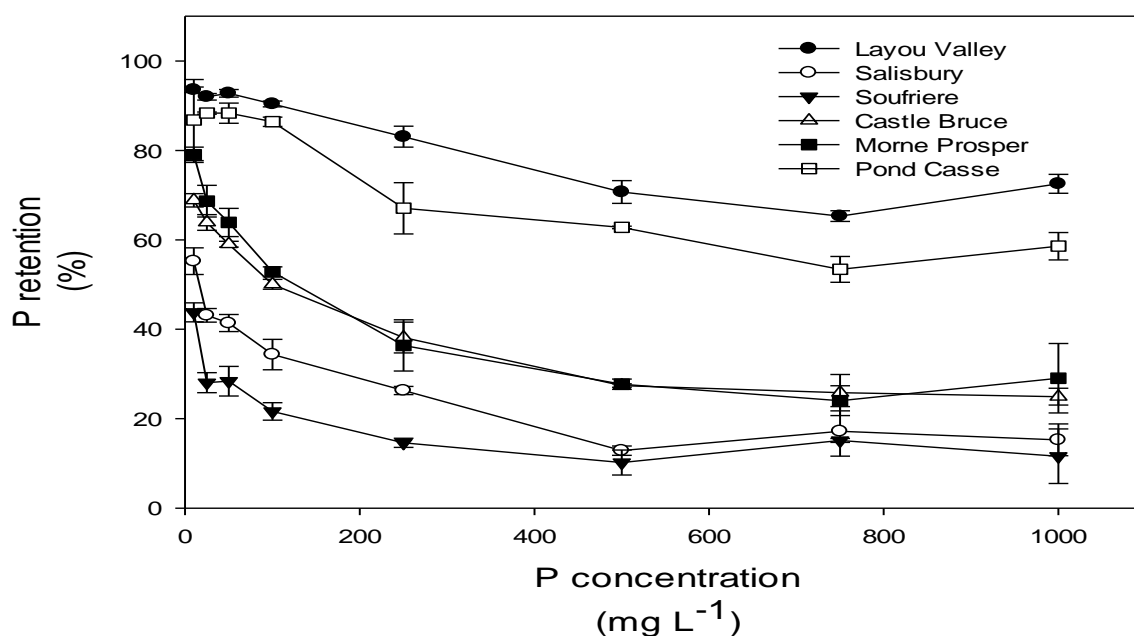


Fig. 7.4. P retention (%) at different total P concentrations (mg L⁻¹) across six contrasting volcanic soils from the Commonwealth of Dominica. Values represent means and error bars SEM. n = 36.

In the soil plant environment, these results suggest that added phosphate would be most available to roots when small amounts are supplied frequently as required by the plant particularly for soils from Soufriere and Salisbury. Larger amounts may be easily lost through surface runoff and by subsurface drainage or could rapidly become fixed and permanently unavailable to plants (MacDonald et al., 2011). However, P sorption is known to decrease as pH increases (Barrow, 1984) thus the potential importance of liming (Yuan et al., 2000; Yatno and Zauyah, 2008; Auxtero et al., 2012), which has the effect on the rate at which the electrostatic potential in the plane of adsorption varies.

Although this study concerns short-term adsorption of P, where most probably, only very accessible sites are involved in P-fixation, the present results indicate that a characteristic rate is established fairly quickly as was highlighted by Barrow (1980). Some authors (Quang et al., 1996) have suggested that long-term adsorption experiments would tend to explore occluded sites and added P could compete with native P, which may be occluded in oxihydroxides or precipitated with Al and Fe.

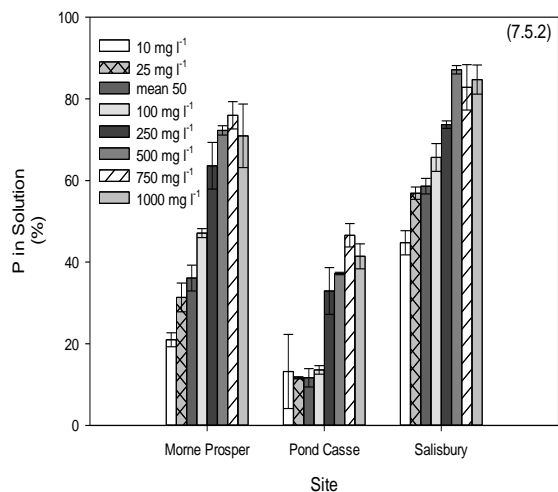
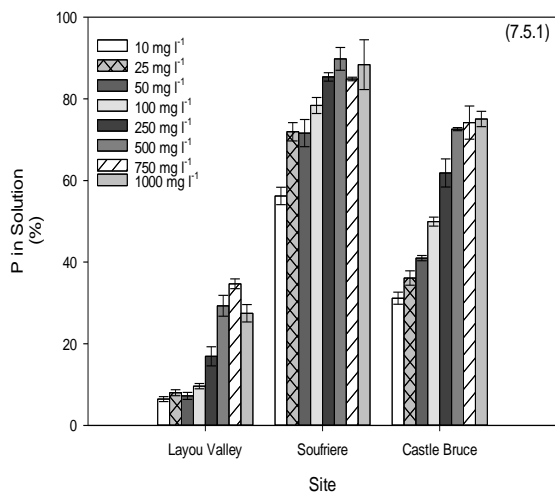


Fig. 7.5. Percentage P in solution at different P standard concentrations across six major agricultural soils from the Commonwealth of Dominica. Values represent means and error bars SEM. n = 36.

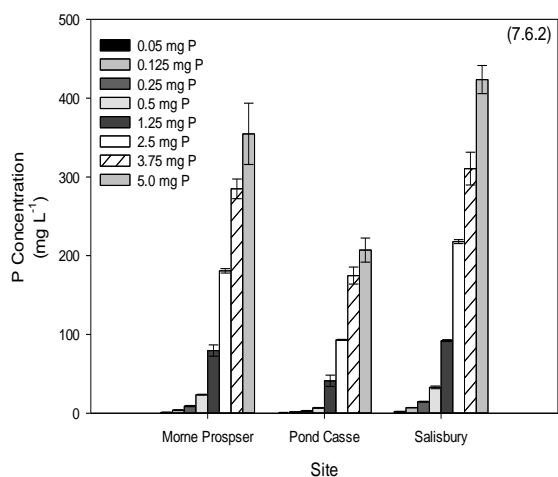
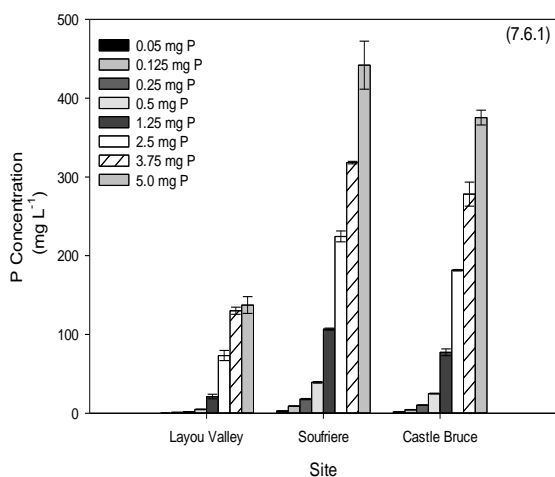


Fig. 7.6. P concentration (mg L^{-1}) at different total P content (mg) across six major agricultural soils from the Commonwealth of Dominica. Values represent means and error bars SEM. n = 36.

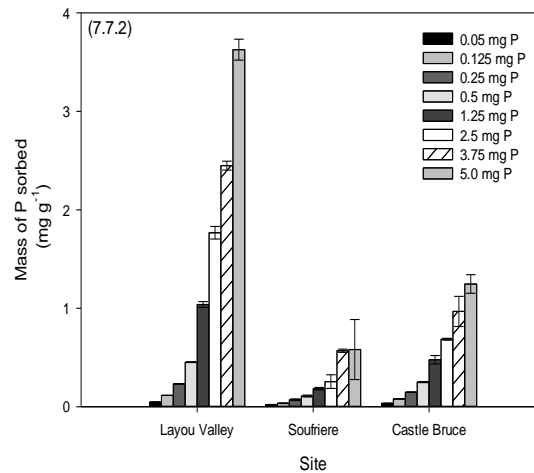
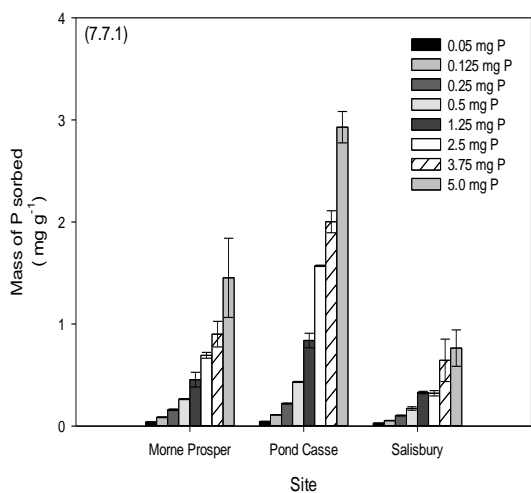


Fig. 7.7. Mass of P sorbed (mg g^{-1}) at different total P content (mg) across six major agricultural soils from the Commonwealth of Dominica. Values represent means and error bars SEM. n = 36.

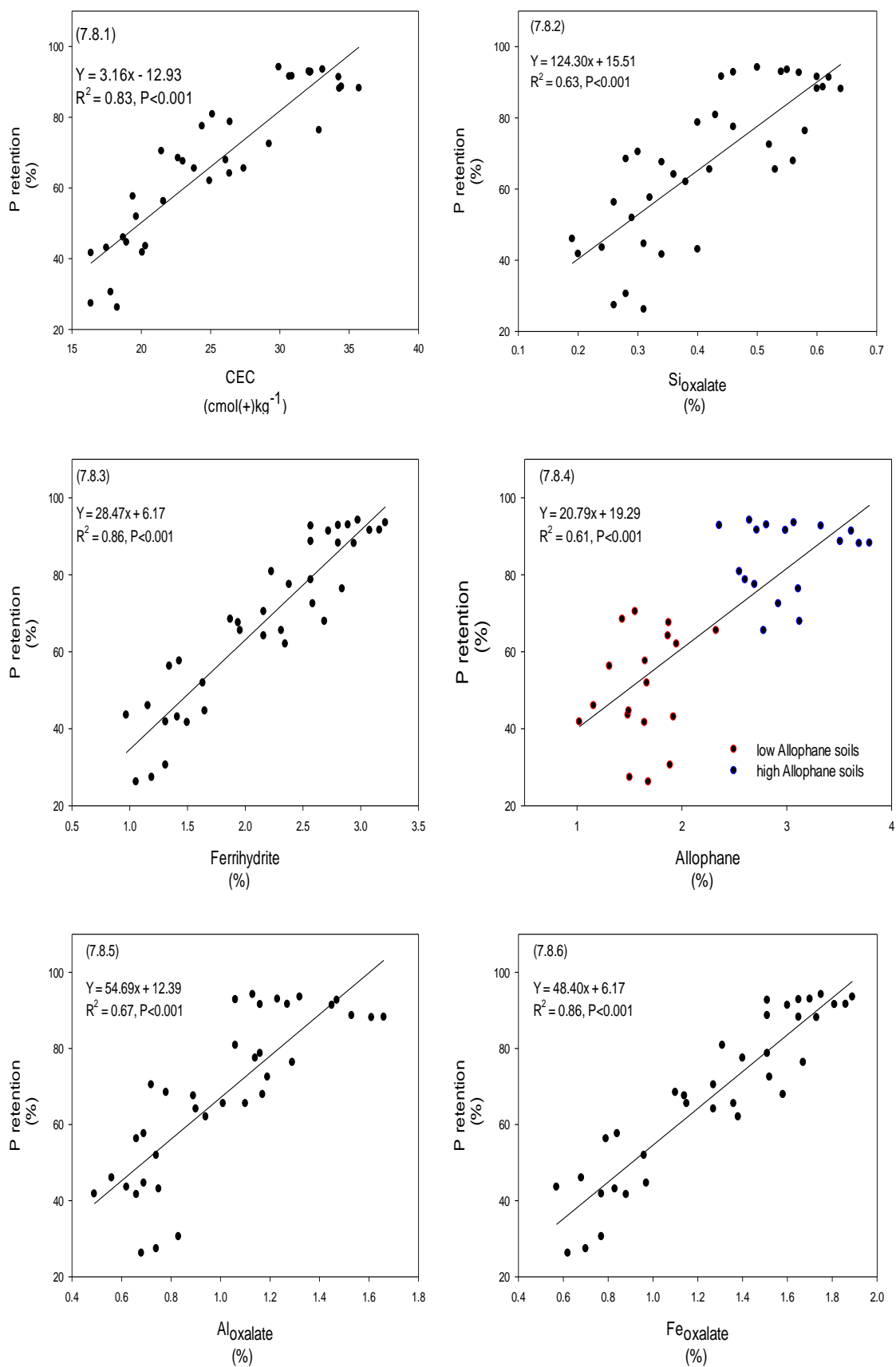


Fig. 7.8. Relationship between P retention and CEC, Si_o, ferrihydrate, allophane and oxalate extractable Al and Fe. Values represent means and error bars SEM. n = 36.

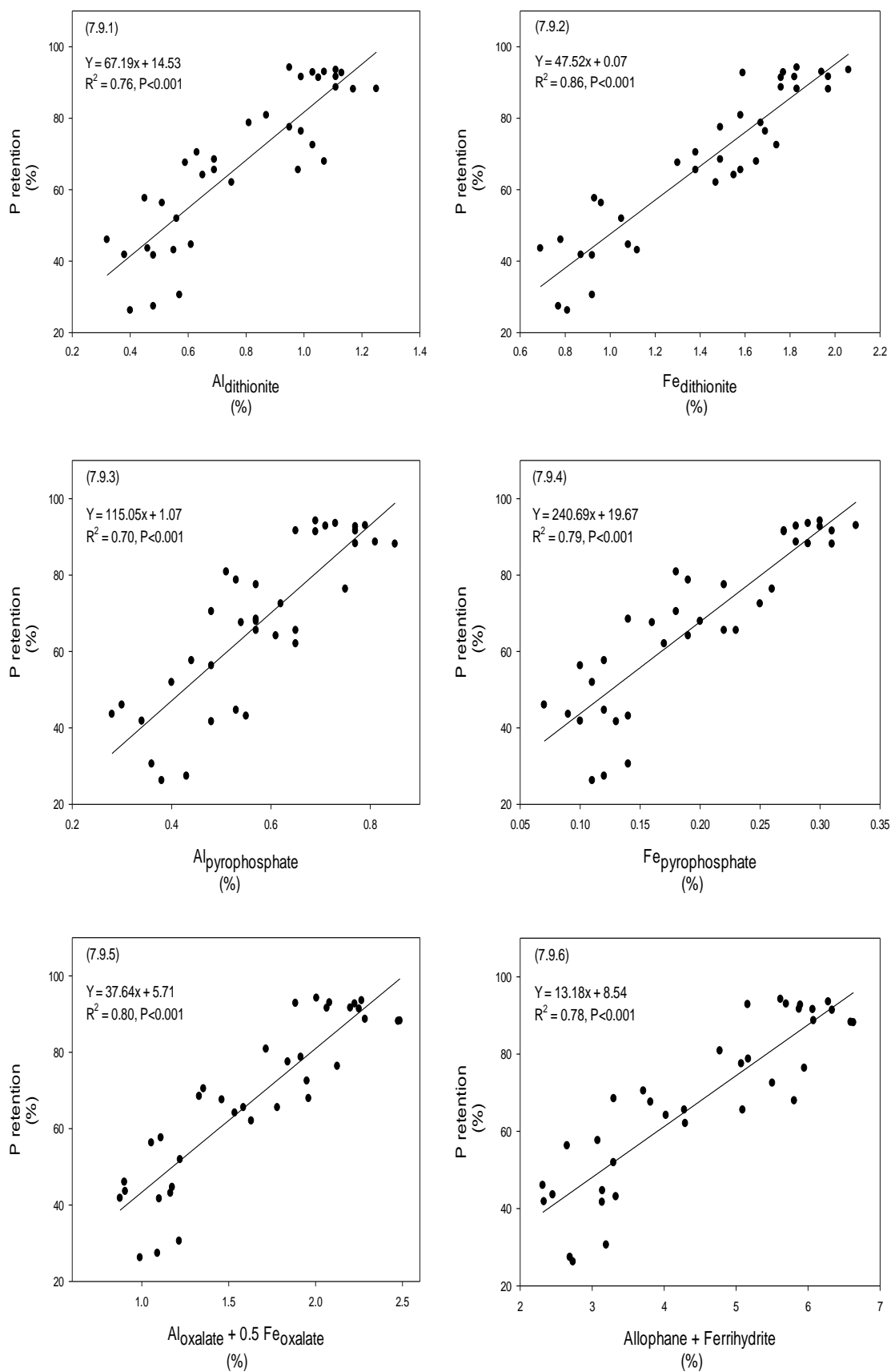


Fig 7.9. Relationship between P retention and various dissolution constituents of Al and Fe of the tropical volcanic soils of the Commonwealth of Dominica. n = 36.

All soil parameters considered were significantly ($P < 0.001$) correlated to P_{ret} (Fig. 7.8, 7.9) with the exception of the crystalline forms (Fe_{cry} and Al_{cry}) suggesting little importance in P retention for this set of data. P_{ret} had a significant correlation ($P < 0.001$) with pH NaF ($R^2 = 0.74$), clay content ($R^2 = 0.72$), and organic matter ($R^2 = 0.79$) but was negatively correlated with base saturation ($R^2 = 0.63$). In addition, the positive relationship was even stronger with regards to cation exchange capacity (Fig. 7.8.1). The slopes of the various Al forms in relationship to P_{ret} are generally steeper than the Fe forms, suggest that P retention was closely related to Al for this set of data. However the relationship of P_{ret} with ferrihydrite showed a steeper slope when compared to the relationship between P_{ret} and allophane (Fig. 7.8.3, 7.8.4). In addition, stepwise regression showed that Fe_d had a significant relationship with P_{ret} ($P < 0.001$) and singly accounted for more than 80% of explanatory power.

The relationship of P_{ret} with allophane was significant ($R^2 = 0.61$, $P < 0.001$) as well as with the ferrihydrite content ($R^2 = 0.86$, $P < 0.001$). Extractable oxalate behaved quite differently with regards to Al, Fe and Si. There was good agreement between P_{ret} and Si_o ($R^2 = 0.63$, $P < 0.001$) as well as between P_{ret} and Al_o ($R^2 = 0.67$, $P < 0.001$). However the slope of the curve for Si_o was steeper than the curves for Al_o as well as for Fe_o suggesting a stronger influence in P retention. With regards to Fe_d , P retention showed a very strong relationship ($R^2 = 0.86$), with Fe_o displaying a similar tendency ($R^2 = 0.86$).

The relationship with Fe_p was also strong ($R^2 = 0.79$). The relationship between P_{ret} and the various Al forms (Fig. 7.9) showed a weaker correlation although Al_d was the strongest ($R^2 = 0.76$) followed by Al_p ($R^2 = 0.70$) and finally Al_o ($R^2 = 0.67$). Nonetheless, a forward stepwise regression analysis with P_{ret} as the dependent variable and the various soil constituents as independent variables showed that P retention was best explained ($R^2 = 0.92$, $P < 0.001$) by: [$P_{\text{ret}} = 43.99 - (2.16 \text{ base saturation.}) + (1.43 \text{ organic matter}) + (27.13 \text{ Fe}_d)$]. The P values were: base saturation. (0.036), organic matter (< 0.001), and Fe_d (< 0.001).

These results tend to suggest that P was immobilized both on organic complexes and amorphous poorly crystalline Al/Fe colloids. The degree of slope for the various Fe and Al forms in the correlation equation are not similar, suggesting that P sorbed per unit element might be dependent of the form (Moody and Radcliffe, 1986; Geogoulis and Moustaka, 2010). However, the slope of the curves for dithionite and oxalate extractable Al and Fe are gentler than the pyrophosphate extractable Al and Fe slopes suggesting the role of organic complexes in P-sorption capacity (Uehara and Gillman, 1981; Quang et al., 1996). The data also tends to suggest that active Al in allophane, and Al-humus complexes is quite reactive with phosphate due to the very high specific surface of the allophane mineral (Theng et al., 1982; Yatno and Zauyah, 2008) irrespective of a low presence in soils from Pond Cassé as an example.

According to Bascomb (1968) and McKeague (1968) pyrophosphate is effective in extracting Al- and Fe- organic complexes from the soil, but is less effective in extracting Al and Fe from non-crystalline or crystalline hydrous oxides. Dithionite extracts free Fe oxides (Wada and Higashi, 1976; Singh and Gilkes, 1991) but does not dissolve allophane (Velescu et al., 2010). Oxalate extracts poorly ordered Fe compounds such as ferrihydrite (Velescu et al., 2010) and is also active in dissolving allophane and amorphous Al hydroxides (Parfitt and Henmi, 1982). McKeague and Day (1966) noted that dithionite extraction dissolves Al and Fe present in metal organic complexes and as well as Al and Fe from some non-crystalline or crystalline in organic as well as inorganic forms (Arshad et al., 1972). Pyrophosphate extracts Al and Fe associated with humus more specifically than dithionite.

For these Dominican soils, it is highly probable that most P-sorption is primarily due to amorphous and metal organic complexes of Fe/Al. Crystalline Al oxides, clay minerals and other soil constituents are likely to be of secondary importance in determining P-sorption at low energy sites. Furthermore Fe metal organic complexes and crystalline forms showed a better agreement with P_{ret} when compared to the poorly ordered Al minerals.

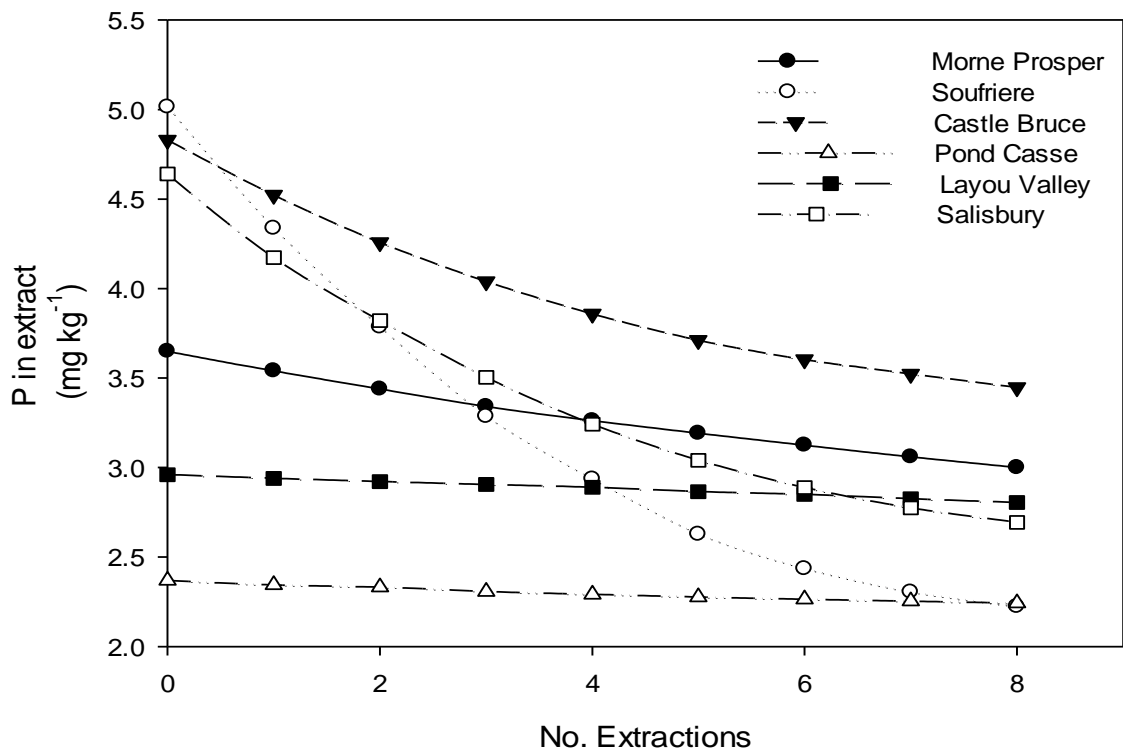


Fig. 7.10. Proportion of P remaining in the soil (mg kg^{-1}) following eight successive extractions with 0.01 M CaCl_2 of six major agricultural soils from the Commonwealth of Dominica.

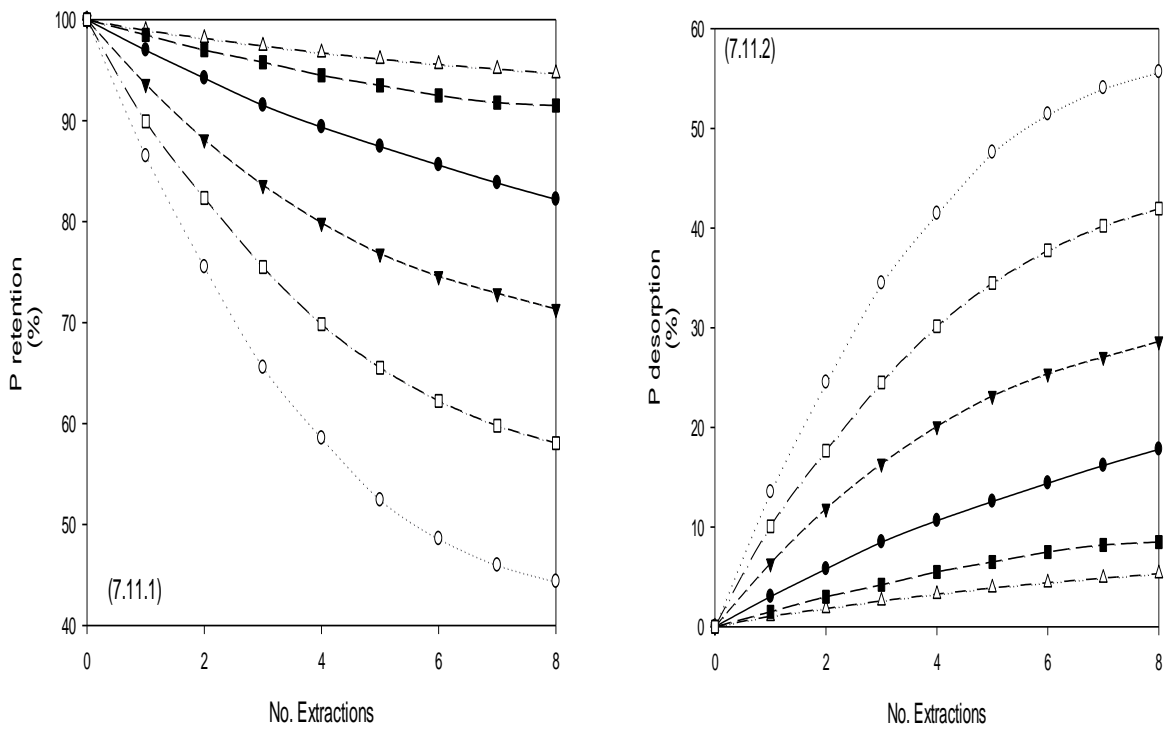


Fig. 7.11. Cumulative percentage P retention and desorption following eight successive extractions with 0.01 M CaCl_2 of six major agricultural soils from the Commonwealth of Dominica.

The results for the P desorption (P_{des}) studies highlighted that it was possible to desorb more P from soils with lower P_{ret} capacity (Fig. 7.11). The ANOVA for the proportions of P remaining in the soil following eight successive extractions with 0.01 M $CaCl_2$ (Fig.7.10) revealed significant differences ($P < 0.001$, $R^2 = 0.99$) between sites. The mean P content in the extract was 1.19 mg P kg^{-1} (0.23). Soils from Soufriere recorded the highest desorption, 2.80 mg kg^{-1} (0.04), followed by Salisbury, 1.95 mg kg^{-1} (0.04), Castle Bruce, 1.38 mg kg^{-1} (0.05), and Morne Prosper, 0.65 mg kg^{-1} (0.01). However soils from Pond Cassé, 0.13 mg kg^{-1} (0.00) and Layou Valley, 0.25 mg kg^{-1} (0.03), equally recorded the lowest values ($P = 0.224$). The proportions of extractable P remaining in the soil following eight successive extractions with 0.01 M $CaCl_2$ decreased (Fig. 7.10) with the percentage P_{des} gradually increasing.

In the Pond Cassé and Layou Valley soils for example, 5.49% and 8.47% respectively was desorbed after the eight extraction with $CaCl_2$ (Fig. 12). In contrast, after eight successive extractions with $CaCl_2$, 55.89% and 42.03% of added P in the Soufriere and Salisbury soils desorbed. Morne Prosper desorbed 17.81% and Castle Bruce desorbed 28.57%. The varied proportions of P_{des} observed for these soils suggest possibilities of P losses through soil erosion, sediment P loss, surface runoff and subsurface drainage. If not managed appropriately, P transfer may possibly be channelled to nearby water bodies and with intensified P input could potentially be problematic in the marine environment. However topography and precipitation are more than likely to heavily influence the susceptibility of these soils to P losses via erosion.

Soils from Soufriere and Salisbury containing low amounts of allophane, Al_d and Fe_o and Fe_d showed low values of P retention, but moderately high P desorption values. These results tend to suggest that phosphate ions applied as fertilizer on these soils are highly available for plant use, but may be easily lost through surface runoff and by subsurface drainage. Larger application rates could become fixed and permanently unavailable to plants (MacDonald et al., 2011), thus these soils may require restricted amounts of P fertilizer, and P

losses will have to be effectively controlled to minimize the potential of nutrient runoff. On the contrary, continuous cultivation with little or no P input not only decreases the amount, but would also influence the structural composition and bioavailability of P in these soils (Solomon et al., 2002), and the amount of P required at the root surface will depend on the depletion profile that develops with time (Gerke et al., 1994; Syers et al., 2008). This is evidently demonstrated by the acute decline of available P after the eight successive extractions with 0.01 M CaCl₂ where soils from Soufriere and Salisbury in particular have the highest P desorption rates (Fig. 7.10 and 7.11).

Moreover, due to its low solubility and mobility in soil and coupled with the fact that soluble P diffuses very slowly and only over short distances ($10^{-12} - 10^{-15}/\text{m}^2/\text{s}$, Marschner, 1995), P can be rapidly depleted in the rhizosphere by root uptake, resulting in a gradient of P concentration in a radial direction away from the root surface (Shen et al., 2011; Barrow, 2015) and hence soils from sites such as Soufriere will require restricted but regular P applications to maintain a favourable P concentration in the soil solution for plant uptake (Barrow, 1980; Borie and Zunino, 1983; Barrow and Debnath, 2014).

P desorption was negatively and significantly correlated ($P < 0.001$) with associated soil constituents, with the exception of base saturation ($R^2 = 0.56$). The negative relationship with organic matter was strong ($R^2 = 0.73$) as well as clay content ($R^2 = 0.78$) but even stronger for pH NaF ($R^2 = 0.81$) and CEC ($R^2 = 0.86$). The results also showed that allophane content was strongly correlated ($R^2 = 0.78$) as was the other soil constituents suggesting a significant role of these materials in P desorption. The ferrihydrite content was also strongly correlated, implying a highly appreciable role that it plays in P desorption ($R^2 = 0.92$). Oxalate extractable silica was also significantly correlated with P desorption ($R^2 = 0.82$) most probably attributed to moderate SiO₂ content (Shoji et al., 1975; Le Bas et al., 1986) influenced by parent material which is mainly andesitic rock (Lang, 1967; Le Bas et al., 1986), considered to be intermediate

rocks with SiO₂ content between 57-63%. However, Jones et al., (1982) and Sollins et al., (1996) have suggested that silica plays a negligible role in P desorption and tends to function more as a dilutant for goethite present. The relationship of P_{des} with the various Al forms showed significant (P<0.001) correlation with Al_d (R² = 0.89), Al_p (R² = 0.83) and Al_o (R² = 0.82). Likewise, P_{des} also showed a strong relationship (P<0.001) with the various Fe forms with Fe_o (R² = 0.92), Fe_d (R² = 0.92), and Fe_p (R² = 0.86) (Fig. 7.12).

With a number of significant relationships between soils constituents, a forward stepwise regression analysis with P_{des} as the dependent variable and the various soil constituents as independent variables showed that P desorption was best explained (R² = 0.95, P<0.001) by: [P_{des} = 84.81 – (5.51 allophane + ferrihydrite) - (19.37 Fe_d) - (0.59 organic matter)]. The P values were: organic matter (0.011), Fe_d (<0.001), and allophane + ferrihydrite (<0.001). In addition, the stepwise regression analysis also showed that the crystalline forms of Al (P = 0.058) and Fe (P = 0.324) were not significantly correlated to P desorption. However allophane + ferrihydrite accounted for 92% of the observed variance regarding P desorption.

Soils from Pond Cassé, Layou Valley, and to a lesser extent Morne Prosper showed strong P retention and low desorption capacity (Fig. 7.11). These soils would require an effective application of P fertilizer to help increase the supply of P for plant use. P release for crop use in these soils may be quite difficult and large amounts of P fertilizer using efficient application methods may be required through fast release applications for annual crops in addition to slow release P fertilizers for perennial crops. Thus it is evident that deeper in depth studies regarding behaviour of P in soil and crop response to different rates of fertilizer application on these tropical volcanic soils merits greater attention especially as it relates to P solubility in meeting crop requirements. This is particularly important because from this study the soils can be separated into two distinct groups. However, soil properties differ much more between these two groups of soils rather than within them (e.g. Fig. 7.8.4).

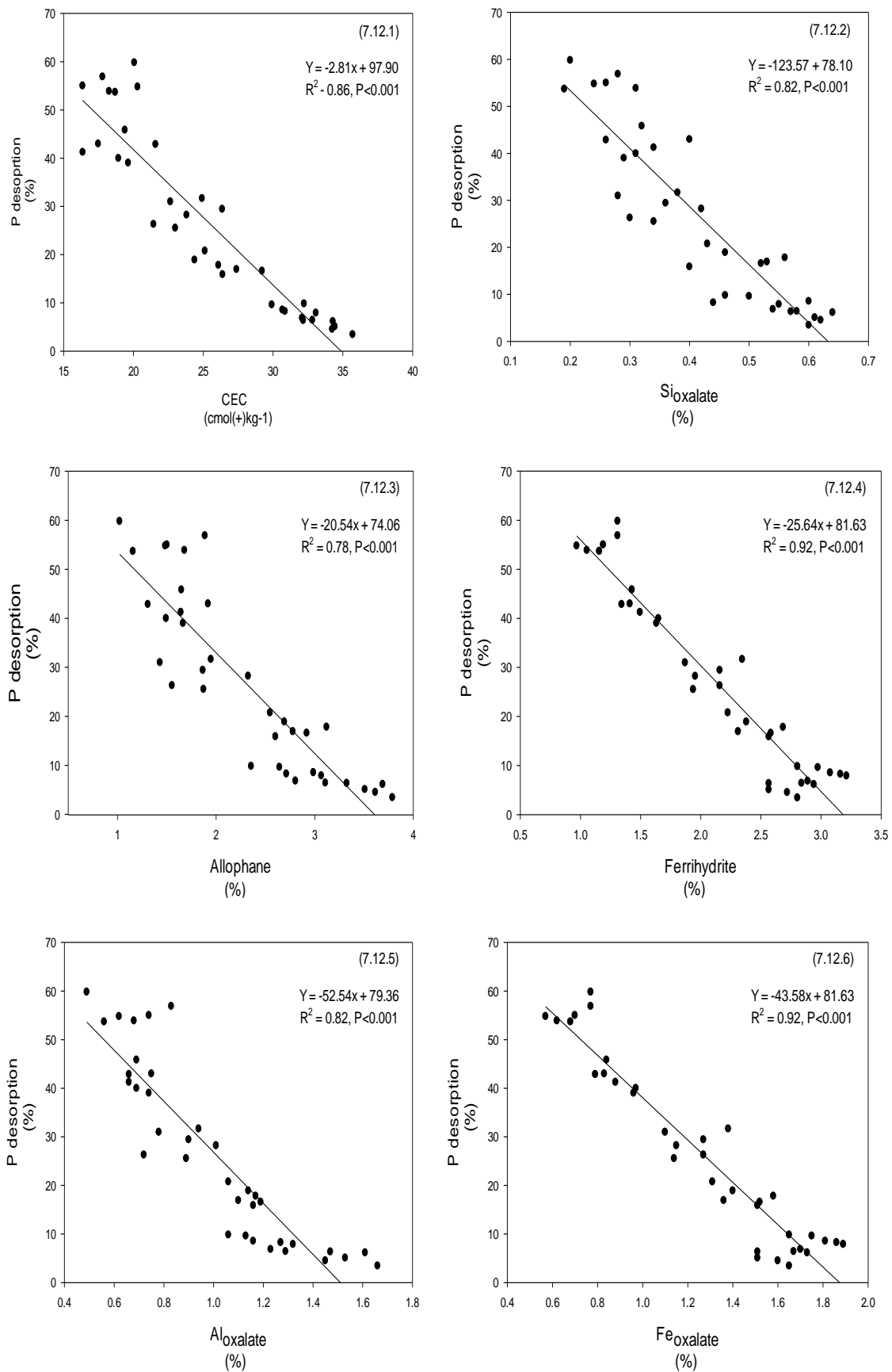


Fig. 7.12. Relationship between P desorption and various soil constituents of six major agricultural soils from the Commonwealth of Dominica. n = 36.

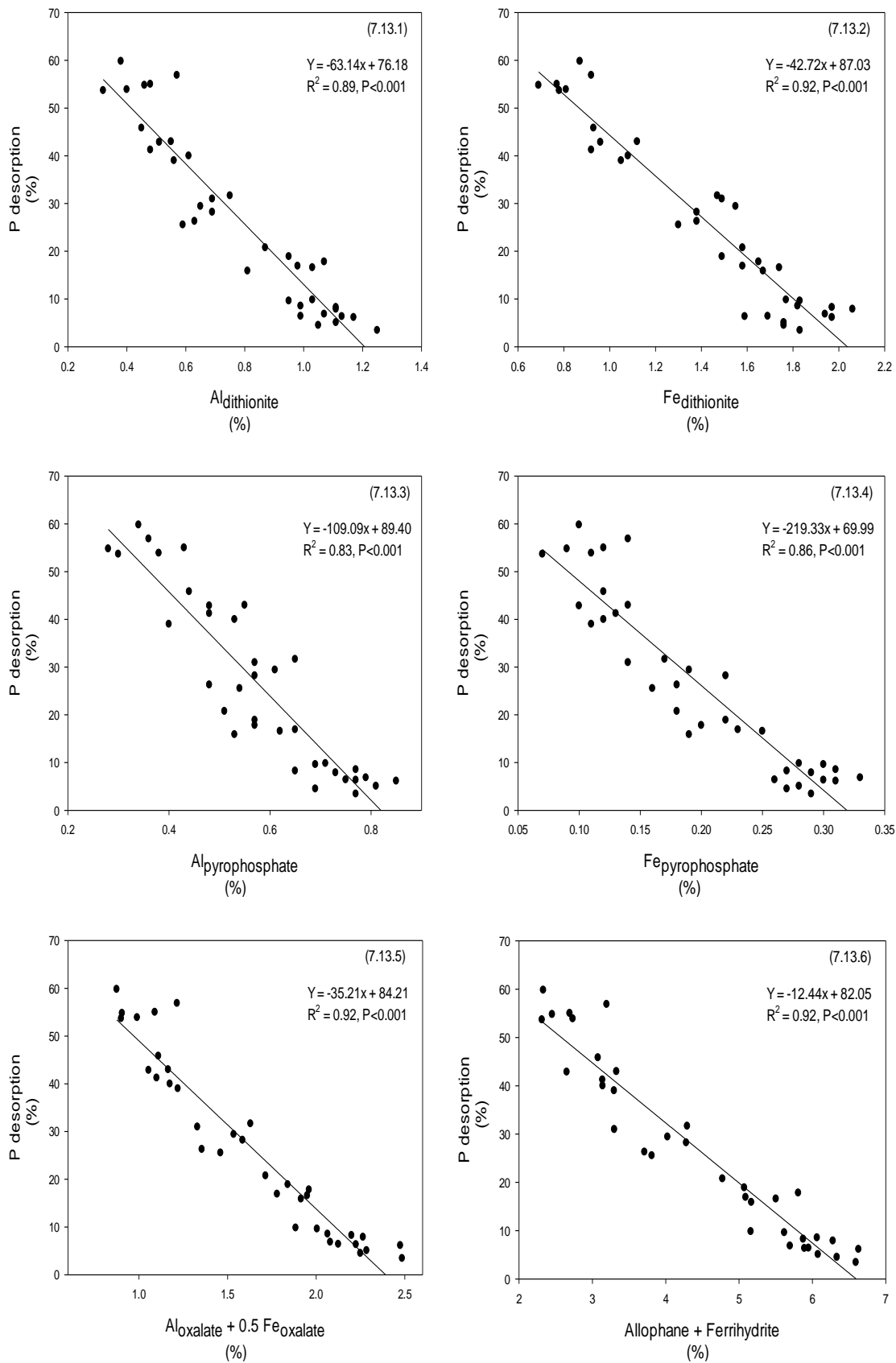


Fig 7.13. Relationship between P desorption and various dissolution constituents of Al and Fe of six major agricultural soils from the Commonwealth of Dominica. n = 36.

The significant explanatory power of allophane + ferrihydrite in controlling P desorption tends to suggest that the presence and dominance of Fe in P desorption at low energy sites may be based on the relative atomic weights of Al (26.982) and Fe (55.845). This is further supported by the relationship between $Al_o + 0.5 Fe_o$ and P desorption ($R^2 = 0.92$, $P < 0.001$). By using one-half the mass of Fe, a requirement of about the same amount of Fe and Al is needed for surface reactivity and exchange of OH^- groups (Van Ranst et al., 2004). As shown in this study, from the correlation coefficients, Fe constituents (Fe_d and Fe_o) had strong negative influences on P desorption as was Al constituents (Al_d and Al_o) suggesting the importance of small unit particle and extensive surface area with variable charge surfaces. However, the degree of the various slopes showcase that ferrihydrite had a steeper degree of slope when compared to allophane (Fig. 7.12.3, 7.12.4).

The results suggest that the kind of clay mineral is extremely important in determining P sorption. The data tends to suggest that Al-oxi-hydroxides may be involved in P desorption at high energy sites most probably via a weak ligand exchange (Parfitt, 1989a,b, Syers et al., 2008) or by solid-state diffusion (Bolan et al., 1985; Quang et al., 1996). Specifically, Fe_o gives a measure of the so-called “active” forms of free Fe (del Campillo and Torrent, 1992) which is essentially ferrihydrite (Parfitt et al., 1988) and small amounts of organic bound Fe.

Due to its hydroxylated surface and high specific surface ferrihydrite is highly influential in P sorption. Phosphate bound to ferruginous materials are more stable than those bound to Al, because they are less soluble than crystalline/amorphous Al materials (Fontes and Weed, 1996; Rengel, 1998). The lowest P desorption (5.49%) was observed in soils from Pond Cassé containing a high percentages of extractable Fe forms as well as ferrihydrite, suggesting that P is strongly held by this soil. Conversely, Soufriere and Salisbury containing low amounts of these constituents (Table 7.1), showed much greater amounts of desorb P than other soils. Hence from this study it was possible to separate these volcanic soils into two distinct groups.

The results tend to suggest that P desorption was influenced both by poorly crystalline amorphous Al/Fe colloids and by Al/Fe humic complexes (Fig. 7.13). However, it can be observed that oxalate and dithionite extractable Fe (Fig. 7.12.6, 7.13.2) had a relatively stronger correlation with P desorption when compared oxalate and dithionite extractable Al (Fig. 7.12.5, 7.13.1). In addition, the dithionite and oxalate extractable Fe had a stronger correlation coefficient when compared to pyrophosphate extractable Fe, suggesting that Fe_d was a better indicator in determining P desorption as was Fe_o when compared to Fe_p results which have been put forward by Uehara and Gillman (1981) and Quang et al., (1996).

Nonetheless, the data tends to suggest that active Al in allophane, and Al-humus complexes were reactive with phosphate due to the very high specific surface of the amorphous minerals (Theng et al., 1982; Allbrook, 1985; Creton et al., 2008; Yatno and Zauyah, 2008). However, it is noticeable that dithionite extractable Al had a relatively stronger relationship with P_{des} than oxalate and pyrophosphate extractable Al with P_{des} .

The dithionite extraction, which is known to dissolve amorphous as well as crystalline Fe (McKeague and Day 1966; Arshad et al., 1972; Parfitt and Childs, 1988), had a somewhat similar R^2 value to that of oxalate extractable Fe. A possible explanation has been made by Arshad et al., (1972) who suggested that in addition to the chelating power, oxalate extraction results in an appreciable dissolution of crystalline minerals. According to these authors, much greater dissolution of layer silicates by oxalate solution may be attributed to its low pH at which much of Fe (Fe^{2+}) in particular is soluble possibly due to the preferential dissolution of octahedral Fe^{2+} configuration as was highlighted by Loughnan (1969) and Al-Ani and Sarapää (2008).

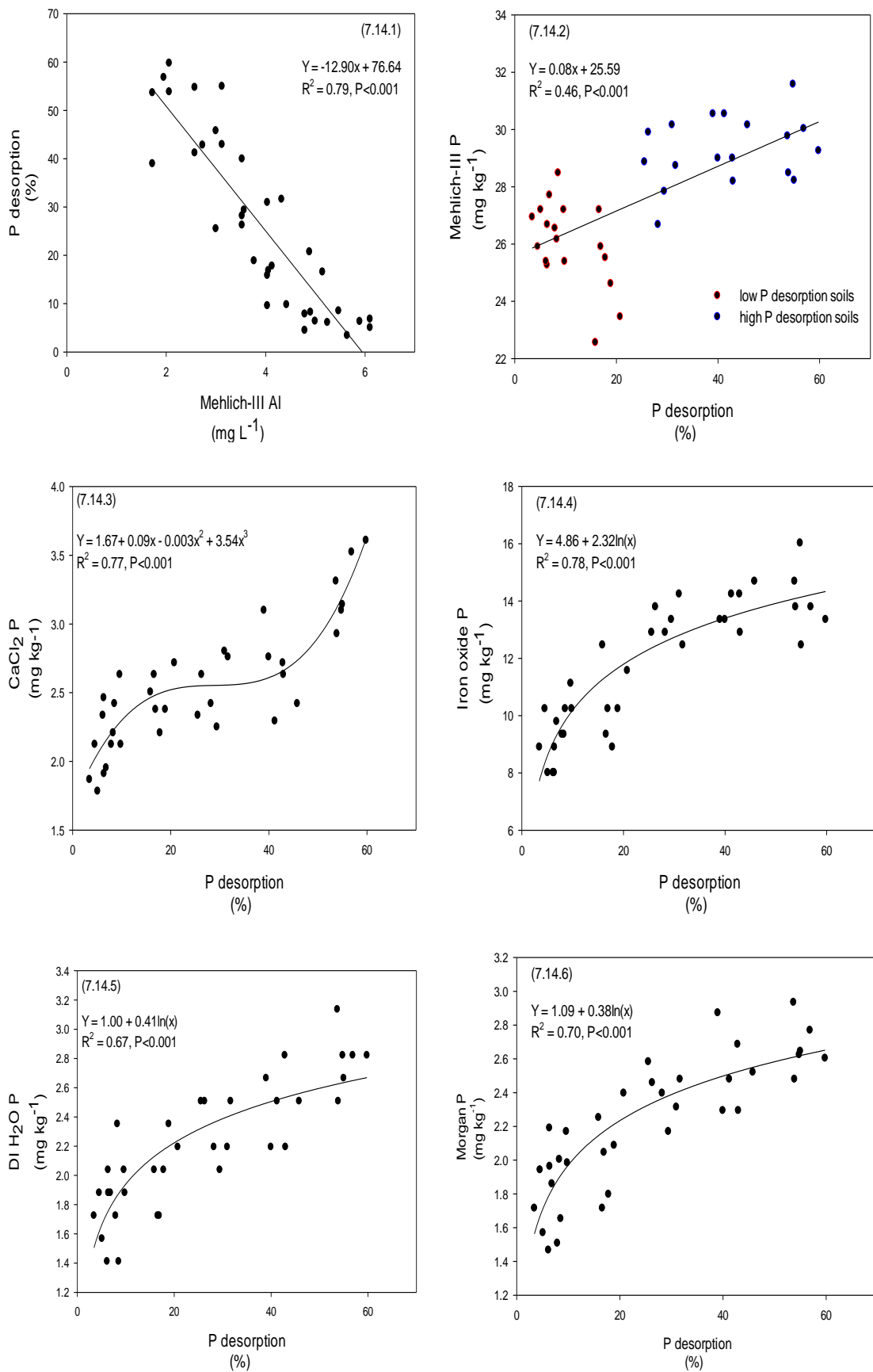


Fig. 7.14. Relationship between P desorption (%) and various P extraction methods of the tropical volcanic soils of the Commonwealth of Dominica. n = 36.

The percentage of P_{des} in 0.01M $CaCl_2$, has been reported to correspond to the P held in solution at field conditions (Beauchemin and Simard, 1999; Daly and Casey, 2003; McDowell and Sharpley, 2003; Nair et al., 2004). A wide variation in relation to plant available P is exhibited by these soils (Fig. 7.14). Following fertilizer application, we may expect much more of P release from Soufriere and Salisbury as the totality of P desorbed, 55.89% and 42.03% respectively can be partially equated to plant P availability (Fig. 7.11). The data shows that P in soils from Layou Valley, Pond Cassé, and Morne Prosper are strongly retained and not easily released (Fig. 7.14.2). These soils as well as reducing P loss through surface runoff and subsurface drainage, will also induce negative effects on P availability to plants to the extent that large application of P is needed to maintain an optimum level of P in soil solution due to the abundance of binding sites unoccupied by P.

P desorption was positively and significantly ($P < 0.001$) correlated to the Mehlich-III extractable P ($R^2 = 0.46$), $CaCl_2$ extractable P ($R^2 = 0.77$), iron oxide extractable P ($R^2 = 0.78$), deionized water extractable P ($R^2 = 0.67$), and Morgan extractable P ($R^2 = 0.70$), but was negatively and significantly ($P < 0.001$) correlated to Mehlich-III extractable Al ($R^2 = 0.79$). Effectively, a multiple linear regression analysis showed that amongst the various soil P test methods employed the strongest predictors were $CaCl_2$ extractable P ($P < 0.001$), iron oxide extractable P ($P = 0.006$) and deionized water extractable P ($P = 0.05$). In addition, the Mehlich-III extractable Al ($P < 0.001$) was also a good indicator of P desorption but was negatively correlated.

The relationship of P desorption with $CaCl_2$ extractable P showed a strong cubic relationship (Fig. 7.14.3). A plausible explanation is that initially as P was partially dissolved it was desorbed and held in soil solution, readily available for plant uptake. Significant increases in desorption might have initiated some re-adsorption and/or re-precipitation reaction on the surfaces of Fe- and Al-oxides thus lowering the concentration in soil solution. It may

also be plausible that some level of immobilization of P was occurring causing a decrease in plant available P. Immobilization occurs when these plant available P forms are consumed by microbes to raise the level of P_o contained in microbial tissues, turning the P into organic P forms that are not available to plants (Anderson, 1975). The microbial P will become available over time as the microbes die increasing the accessibility of plant available P. In addition, as desorption progressively continued more P became into solution than was being possibly re-absorbed or precipitated and as a result an increase in the availability of extractable CaCl_2 P.

The results between P_{des} and Mehlich-III extractable P tends to suggest that the acidic nature of the extractants (based on the use of a solution containing ammonium fluoride at pH 2.5) does reflect P held in solution at field conditions. It is known that fluoride serves to complex Al cations that potentially bind with phosphates thereby increasing the quantity of orthophosphate in solution (Zhang et al., 2008; Schroder et al., 2009). Furthermore acetic acid which contributes to the release of available P in most soils would not readily discharge in the soil complex under natural field conditions in concentrations sufficiently high enough to prevent aluminium and iron fluoride from precipitating, albeit from an anthropogenic source. In addition, the acidity of the nitric reagent which increases the solubility of Fe and Al phosphates (Zhang et al., 2008) may also not be present in high concentrations under natural field conditions, notwithstanding prolonged and indiscriminate use of N fertilizers (NH_4^+) can cause a build-up of soil acidity and hence the removal of soil nutrients.

In general most of the methods tested (Chapter 6) showed good agreement to P desorption. More interestingly, the results strongly suggest that most of the method tested can be used for predicting parameters such as dissolved reactive phosphorus and biologically active phosphorus concentrations in runoff (Pote et al., 1996; Maguire and Sims, 2002a,b; Sharpley et al., 2003), thematic areas of growing concern to agrarian based economies, especially to the Commonwealth of Dominica given its susceptibility to soil loss via erosion.

4 Discussion

4.1 P retention and Fe and Al forms

Phosphate retention in most tropical soils is usually attributed to Fe and Al oxides, hydroxides and oxyhydroxides (Barrow, 1984; Allbrook, 1985; Singh and Gilkes, 1991), accredited to the presence of Fe-OH and Al-OH groups at the mineral surface (Borggaard, 1983, 1986; Fontes and Weed, 1996) which releases considerable amounts of OH⁻ to NaF solutions (Perrott et al., 1976a,b; Singh and Gilkes, 1991; Gilkes and Hughes, 1994). Phosphate is largely retained by reacting with variable-charge materials in soil (Barrow, 1978; Barrow et al., 1980; Bowden et al., 1980; Barrow, 1984; Bolan et al., 1985; Barrow and Ellis, 1986; Pardo and Guadalix, 1990; Quang et al., 1996). P sorption of volcanic soils is known to be related to soil constituents such as Al_o and Al_o + 0.5 Fe_o (Moody and Radcliffe, 1986; Quang et al., 1996; Auxtero et al., 2008). From this study it is quite evident that other forms of these aluminosilicates (Fe_d in particular) are very much involved in the sorption of added P, results which are in agreement with the findings of Uehara and Gillman (1981).

From the results, all forms of extractable Al were significantly and positively correlated to P retention but values were lower than those for Fe forms. Dithionite Al had the highest correlation ($R^2 = 0.76$, $P < 0.001$). This comparatively weaker correlation tends to suggest that at least some of the Al dissolved from these volcanic soils is not at low energy phosphate adsorption sites (Imai et al., 1981; Barrow, 1983; Allbrook, 1985; Parfitt, 1989a; Madeira et al., 2007b). Moreover, the relatively weaker correlation of Al as compared to Fe with phosphate sorption is believed to be due to the dissolution of aluminium in hydrous oxides, organic complexes, as well as in allophane (Allbrook, 1985), all of which have differing capabilities to retain P. Indeed these volcanic soils showed a tendency to be separated into two distinct groups with soil properties differing much more between these two groups of soils (e.g. Fig. 7.8.4 & Fig. 7.14.2) rather than within them and hence their distinctive P_{ret} characteristics.

Furthermore, it is apparent that a sharp difference of reactivity exists between the various classes of Fe-oxihydroxides to an extent that the correlation coefficient between P-sorption and organically bound Fe-oxides was appreciable weaker when compared to crystalline and poorly crystalline Fe-minerals (Fig. 7.8, 7.9). Fontes and Weed (1996) and Quang et al., (1996) have underscored that P sorption positively correlates to the specific surface area of Fe oxides. This suggest that besides the quantity, the kind of clay mineral is extremely important in determining P sorption (Perrott et al., 1976b). The positive correlation of Fe and Al with dithionite and oxalate suggest that poorly crystalline amorphous Fe- and Al-oxides are important drivers in P sorption in these Dominican volcanic soils. Crystalline Fe and Al constituents may be important at high energy sites, but plausibly not at the same intensity.

Generally Fe has a stronger organic complexation in comparison to Al, and Fe is preferentially removed upon dissolution, resulting in the accumulation of Al at the expense of Fe (Farmer et al., 1984; Buurman and van Reeuwijk, 1984). Hence the presence of secondary ferruginous compounds will tend to reflect the availability of P for plant uptake (Bascomb, 1968; Peretyazhko and Sposito, 2005). Ferrihydrite is typically found as the dominant iron oxyhydroxide in volcanic soils (Ugolini and Dahlgren, 2002), related to the combination of high and constant humidity conditions and factors disturbing Fe crystallization such as high organic matter content and high Al activity in acid conditions (Malucelli et al., 1999).

Because Fe has a greater stability in oxyhydroxides as compared to humus complexes, concentrations of Fe-humus complexes are typically low (Wada and Higashi, 1976). On the contrary, Al-humus complexes form preferentially in pedogenic environments that are rich in organic matter and have pH values of less than five (Shoji and Fujiwara, 1984). In this pH range, organic acids are the dominant proton donor, lowering pH and aqueous Al activities through the formation of Al-humus complexes (Ugolini and Dahlgren, 2002; Rutkowska et al., 2015). Under these conditions, humus effectively competes for dissolved Al, leaving little Al

available for co-precipitation with silica to form aluminosilicate material. More interestingly, the amount of ferrihydrite will partly control the amount of phosphate adsorbed by a soil during the slow reaction phase of P adsorption (Parfitt, 1989a).

Indeed the relationship between P retention and ferrihydrite (Fig. 7.8) showed a highly significant positive relationship ($R^2 = 0.86$, $P < 0.01$), whilst that for allophane was somewhat weaker ($R^2 = 0.61$) and for silica was $R^2 = 0.63$. Hence, phosphate sorption by poorly crystalline alumina-silicates, such as allophane, tends to occur at hydroxyl-aluminium sites (Rajan and Perrott, 1975). Significantly, the adsorption capacity of allophane at higher phosphate levels is directly related to the aluminium content (Theng et al., 1982) and P-retention is decreased by the part of the binding sites that is already occupied by P (Madeira et al., 2007b). It has also been noted that the poor relationship of allophane with phosphate retention may be due to the varying contributions of hydrous aluminium oxide and organic aluminium complexes and allophane to phosphate retention (Borggaard, 1983, 1986; Allbrook, 1985) and varying Al/Si ratios of allophane may also contribute to variation of P retained by allophane (Parfitt and Henmi, 1980), thus the separation of these soils into two distinct groups.

Within these Dominican volcanic soils, P buffering capacity is lower in soils from Soufriere, Salisbury and Castle Bruce, most probably due to the relatively low allophane content (Table 7.1). Furthermore, the climatic environment of Pond Cassé, Layou Valley and Morne Prosper with high rainfall should favour the development of active forms of Al and Fe in the weathering of volcanic material thus increasing the soil's P adsorption potential (van Hees et al., 2006). Wada (1980) and Van Ranst et al., (2004) have reported that the presence of active Al and Fe compounds, associated with a rise in pH (pH NaF) results in a concomitant formation of more allophane. As a consequence the occurrence of a distinct dry season on the leeward side of the island has most probably impeded the intensity of chemical weathering in catchments such as Salisbury and Soufriere hence low allophane content.

This climatic environment may have enhanced the formation of crystalline layer silicate minerals at the expense of poorly crystalline amorphous materials, understanding that climatic conditions also play an important role in the formation of crystalline minerals as crystallization is promoted as the soil climate becomes warmer and dryer (Ugolini and Dahlgren, 2002). Hence it is plausible that these soils display less desilication and consequently less enrichment of Al and Fe with layered silicates prevailing over allophane and Fe oxides. Therefore, as volcanic soils become progressively more weathered, metastable non-crystalline materials are transformed to more thermodynamically stable mineral phases (Ugolini and Dahlgren, 2002). This transformation results in loss of andic soil properties and the conversion of many tropical Andosols to Inceptisols (Cross and Schlesinger, 1995; Chen et al., 2001).

4.2 P adsorption and organic matter

Several workers have noted contradicting relationships between soil organic matter and phosphate adsorption (Saunders, 1965; Perrott, 1978; Sibanda and Young, 1986; Yuan et al., 2000; Guppy et al., 2005). Reports have shown an increase, decrease and no effect on P sorption as influenced by SOM. However, competition between organic matter and phosphate for adsorption sites on soils is thought to be due to the chelating ability of hydroxyl-carboxyl ligands found in soil organic matter (Parfitt, 1979; Reddy et al., 1980). Furthermore, it has been reported that when soils contain high organic matter, Al released from volcanic ash by weathering is primarily retained by humus, whereas when the supply of organic matter is limited, Al tends to transform into some inorganic forms, which may be allophane, imogolite, and allophane-like constituents (Wada and Higashi, 1976).

In this study, organic matter was positively correlated with P retention. This observation suggests that the dominant effect of organic matter in the soils studied was probably to favour the formation of poorly ordered oxihydroxides. This conclusion is supported by significant correlations between organic matter and Fe_o , ($R^2 = 0.61$, $P < 0.001$) and between organic matter

and Al_o , ($R^2 = 0.56$, $P < 0.001$). When the data for organic carbon was substituted for organic matter, the relationship with Fe_o marginally increased ($R^2 = 0.65$, $P < 0.001$) but decreased markedly with Al_o ($R^2 = 0.42$, $P < 0.001$).

From a nutritional standpoint, as applied OM decomposes in the soil, carbon compounds are produced through microbial action that may react directly with P sorption sites in soil, potentially increasing the solution P concentration and hence plant-available P (Guppy et al., 2005). Humified soil organic matter can significantly reduce the amount of phosphate required to maintain a solution concentration necessary for crop growth, with this effect more pronounced in acidic soils. An increase in soil organic matter, usually associated with an increase in the amount of humic acids, reduces the amount of phosphate adsorbed on the oxide surface (Parfitt, 1979; Sibanda and Young, 1986) most probably associated with the nature of the adsorption energy of both phosphate and humic acids (HA), and the occupation of adsorption sites by carboxyl groups. However, Sibanda and Young (1986) noted that it may also be that the unfavourable electrostatic field generated around an adsorbed HA molecule is more important in preventing phosphate adsorption.

According to Sibanda and Young (1986), only a small proportion of organic matter added to soil will remain as HA and although adding fresh HA will reduce phosphate fixation it may be that with time this becomes occluded and ineffective as regards surface reactions. Therefore, the creation of surface negative charges on allophane interaction with humic substances through the incorporation of fresh organic matter has implications for the management of allophanic soils (Shoji et al., 1993). This management challenge is further augmented by the evidence that carrying only a small negative charge at $pH < 6$, allophane by itself would be ineffective in retaining nutrient cations in the pH range of most soils (Yuan et al., 2000).

By developing an excess of surface negative charge, the formation of complexes with organic matter would substantially increase the capacity of soil to retain and immobilize positively charged species (Bowden et al., 1980; Barrow, 1984, Barrow and Ellis, 1986). Hence, one of the direct effects of SOM addition on plant available P includes increase formation of metal bridges within a rather broad P concentration range by replacing two singly coordinated hydroxyl groups on the oxide surface per molecule of phosphate, leading to an increased sorption of P (Wada and Higashi, 1976; Parfitt, 1979; Borie and Zunino, 1983). However, it should be noted that when the P concentration in solution is high as a result of added P through fertilizer application, ionic phosphate is able to replace organic matter from new high energy surfaces after saturating external surface sites resulting in an overall increase in the number of adsorption sites (Imai et al., 1981).

4.3 P adsorption described by the Langmuir and Freundlich equation

It has been noted that the adsorption of phosphate occurs on low energy surfaces and also on high energy surfaces (Holford et al., 1974; Rajan and Perrott, 1975; Iñiguez and Val, 1984; Parfitt, 1989a,b) with the adsorption capacity of the low-energy surface usually at least double that of the high-energy surface (Holford et al., 1974). With high concentrations of P, phosphate is adsorbed on high energy sites arising from the disruption of hydroxy aluminium (Rajan and Perrott, 1975; Theng et al., 1982; Quang et al., 1996), as well as by the displacement of structural silicate (Rajan and Perrott, 1975). The fast adsorption which does not last more than a few hours is usually attributed to adsorption on very accessible external surfaces (Parfitt, 1989b; Pardo and Guadalix, 1990; Quang et al., 1996; Madeira et al., 2007b), whereas the slower part of sorption would be due to solid-state diffusion and precipitation processes associated with adsorption on internal surfaces and with new reactive areas, exposed increasingly with time, to phosphate ions in solution (Parfitt and Henmi, 1980; Imai et al., 1981; Bolan et al., 1985; Parfitt, 1989b; Barrow, 2015).

In comparing the P sorption isotherms using the Freundlich and Langmuir equation, it is noticed that the relationship of P adsorption using the Freundlich equation gave a higher correlation coefficient than for the linearized and modified Langmuir equation (Fig.7.4). It has been reported (Fitter and Sutton, 1975; Mead, 1981; Holford, 1982) that the Freundlich isotherm has two parameters while Langmuir's equations has only one, and fits the data on defect sites better than the Langmuir's equations. The data shows an apparent systematic deviation away from the linearized form of the Langmuir equation which is indicated by the apparent linear distribution of the data values in the Freundlich plots. According to Holford et al., (1974) and Singh and Gilkes (1991), these deviations can be most probably attributed to the presence of P sorption sites with different bonding energies. Adsorption occurs simultaneously on all surfaces, although in direct proportion to the bonding energy of the unoccupied sites (Holford et al., 1974). Nonetheless, the P sorption data for these volcanic soils was also well described by the linear forms of these equations as is highlighted by the strong positive correlation coefficient (Fig. 7.1, 7.2, 7.3). However, Holford et al., (1974) were instrumental in suggesting that if consideration is only given to the detection of high energy surfaces by omitting sufficiently low concentrations as might have been the case of Olsen and Watanabe (1957) then the goodness of fit might well favour the Langmuir equation as opposed to the Freundlich.

The goodness of fit of the equations to the data may be partly due to the limited range of equilibrium P concentrations considered ($0.01 - 1.0 \text{ g P L}^{-1}$) and to the generally very low native P content of these soils, as was suggested by Barrow (1978). In addition, the goodness of fit of the Langmuir linearized equation depends largely on the number and distribution of points on the isotherm (Holford et al., 1974). In this case study, all the measured adsorption must have apparently occurred on low energy surfaces given the concentration range, so that a realistic estimate of the k value is questionable in terms of validity (Bolan et al., 1985). In this

regard, both equations and their coefficients may be regarded as being strictly empirical and their use in this study has been essentially to derive P sorption coefficients for comparison purposes and to study the relationship of P retention with other soil properties.

The differences in the slope of the response, i.e. mass of P sorbed plotted against P concentration with regards to the Freundlich when compared to the modified Langmuir equation (Fig. 7.1, 7.2) are most noticeable between soils from Morne Prosper and Castle Bruce, albeit soils from Layou Valley and Pond Cassé showed steeper slopes and as such higher P retention capacity. The restriction in concentration range has the disadvantage that results are limited to a given range of concentrations, but it has the compensating advantage that the behaviour of the soils within this range is summarized easily and provides a useful index of the amount of adsorption under standard conditions (Barrow and Shaw, 1979).

Interactions of anions such as phosphate with allophane involves three different reactions which can be summarized as non-specific adsorption of anions by simple Coulombic interaction with positive charges on Al-OH or Fe-OH groups, specific adsorption and incorporation of the anion as a ligand in the coordination shell of an Al or Fe atom (Wada, 1978), and decomposition of allophane induced specifically by adsorbed anions and precipitation of Al or Fe compounds (Iñiguez and Val, 1984).

In variable charge systems, the balance between these possible mechanisms depends on the charge on the surface, the amount of P sorbed, and time (Barrow et al., 1980; Bowden et al., 1980; Barrow, 1984; Barrow and Ellis, 1986). Reaction with the negatively charged phosphate ions makes the surface more negative and each increment of P reacts with a surface with different charge and different potential from that of the previous increment (Pardo and Guadalix, 1990; Barrow, 2015). It has been reported that the simple kinetic equations fail to describe the effect of time on sorption partly because the mechanism of P adsorption is different

from that postulated and partly because they do not consider electrostatic effects when phosphate ions react with a charged surface (Bolan et al., 1985; Barrow, 2015).

Work by Holford et al., (1974) using a two-surface Langmuir equation suggests that phosphate is adsorbed on two types of surface of contrasting bonding energy so that the two surface approach is more applicable when high-energy surfaces are fully saturated with P. The P sorption capacity of low energy sites is mainly related to clay content as influenced by mineralogy, and P sorption increases as pH decreases (acid effect). These low energy sites are positively correlated with organic carbon and poorly crystalline Fe-oxihydroxides (Fig. 7.9). It has been reported that as these two variables are closely correlated, organic matter is likely to be considered as an indirect factor of P fixation through its association with Fe-oxihydroxides and not as an important source of P adsorption sites (Quang et al., 1996), however the present study found organic matter in these soils to be a direct factor in P fixation.

An important characteristic of the adsorption of phosphate is that the process increases the negative charge on the surface of the soil and thus lowers the point of zero charge (Bowden et al., 1980) and as such it becomes increasingly difficult for each additional increment of phosphate to adsorb and hence the affinity of the surface decreases as adsorption increases (Barrow, 1984; Barrow and Ellis, 1986). The specific adsorption of phosphate refers to the incorporation of anions as ligands in the coordination shell of Fe or Al atoms and as highlighted by Shoji et al., (1993) differs from the ion exchange reaction in a number of ways. One such difference is that sorption reactions of these anions are not completely reversible making the sorbed anions difficult to be desorbed (Shoji et al., 1993, Van Ranst et al., 2004).

According to Parfitt (1979), phosphate is most likely adsorbed on the oxide surfaces as binuclear bridging complexes within a rather broad P concentration range by replacing two singly coordinated hydroxyl groups on the oxide surface per molecule of phosphate. When phosphate is adsorbed by soil, or by soil constituents, the extent of adsorption and the charge

on the surface depends on several factors including pH, the concentration of adsorbing ion, the concentration and properties of the electrolyte, and the nature of the adsorbent (Bowden et al., 1980; Barrow, 2015). Parfitt and Henmi (1980) suggested that only 10% of aluminium in allophane can accommodate phosphate which may be present as hydrous aluminium oxides and or organic aluminium complexes. The adsorption of allophane by phosphate occurs at defect sites where broken bonds are exposed, giving rise to such groups as Al-OH and because these groups are protonated at low pH, they act as sites for anion adsorption. The availability of P thus depends to a large extent on interactions with constituents carrying a variable charge (Barrow et al., 1980; Bowden et al., 1980; Barrow, 1984; Bolan et al., 1985; Barrow and Ellis, 1986; Pardo and Guadalix, 1990; Quang et al., 1996) which involves changes in surface charge.

Notwithstanding the above mentioned, from this study it can be observed that P sorption capacity was generally enhanced by the presence of non-crystalline amorphous Fe oxihydroxides as well as Al/Fe humic complexes. However it is plausible that crystalline Fe oxihydroxides together with Al soil colloids play an important role in P sorption at high energy sites to the extent that P-sorption capacity is generally enhanced in the most of acidic soils, and in those containing much poorly crystalline amorphous Fe- and Al-oxihydroxides and high contents of organic carbon (Quang et al., 1996).

5 Conclusion

Phosphorus deficiency is very common in volcanic soils showing andic properties and in the case of the Commonwealth of Dominica may be even more acute than may have been previously thought given the paucity of data with regards to P behaviour in these soils, as well as being chronic given the limited access and conservative use of P fertilizers within the last two decades, partially attributed to the country's weak purchasing power on the international market. This is despite the growing trends in compost and animal manure application primarily as an economic substitute, and a source of nutrients for organic producers.

From an agronomic standpoint, we can simplify two forms of soil P, one tightly held with a low dissociation constant and a low adsorption index, and one relatively loosely held with a high dissociation constant and a high adsorption index. Based on these characteristics, these Dominican soils can tentatively be differentiated between moderately weak and strong buffer capacity. Hence, it can be concluded that the soils of this present study can be divided into separate groups displaying different P fertilizer requirements based on their P sorption characteristics which ultimately determines the availability of P in soil solution.

These differences potentially have significant effects on the residual value of phosphate fertilizer to include the agronomic efficiency of P fertilizer applications. However, this study did not include P-bonding energy measurements needed for recommendations on P-fertilizer requirements and as such the discussion is limited to the potential efficiency of P fertilizer utilization. Nonetheless in most soils on which little P fertilizer has been used, there is a large unfilled capacity for P adsorption on high-energy surfaces (Pardo and Guadalix, 1990; Madeira et al., 2007b). Much P fertilizer can, therefore, be added to them before significant adsorption will occur on the low-energy surface in soil types such as Layou Valley, Pond Cassé and Morne Prosper. In these soils once the high energy surface is saturated through the incorporation of P fertilizer, supplementary additions of P will be adsorbed very weakly on the low-energy surface and, because of the rapid increase in solution P concentration (Fig. 7.5, 7.6), is more likely to be precipitated as insoluble mineral phosphates (Parfitt, 1989a).

However, some P which remains labile in solution and on low-energy surfaces, may potentially leach further down the soil profile. One of the practical mitigating approaches to these challenges lies in the management of soil organic matter in preventing the depletion of organic carbon which can result from soil erosion associated with poor husbandry practices. By promoting the interaction between minerals and humic materials the addition of lime (CaCO_3) would help stabilize OM in these allophanic soils, although considerable controversy

exists in the literature regarding whether or not liming decreases P fixation (Barrow, 1984). However, as most plant residues are not incorporated at the end of the cropping season, as is evident in the Morne Prosper farming region in particular, this results in a non-renewal of the organic matter pool and as such the organic horizon is being lost thereby decreasing fertility over the cropping years in addition to when land clearing activities are being performed.

Nonetheless, it is also generally accepted that repeated application of inorganic P results in an organic P build up and that this form of phosphorus participates via mineralization in the P-cycle and may contribute to the pool of available P (Anderson, 1975). With further field work, it should be possible to specify characteristic rates of reaction for particular regions or particular soil types. Currently a constant rate of reaction is assumed in fertilizer application as is evident in the broad spectrum recommendations made with regards to N-P-K and triple super phosphate (TSP) use. However, given the varying P sorption characteristics of these tropical volcanic soils, Holford et al., (1974) and Barrow and Debnath (2014) recommended that the objective in using P fertilizers, in excess of immediate crop requirements, should be to perhaps saturate no more than the high-energy surfaces, which in most soils will be less than 30% of their total adsorption capacity.

For annual crops, fertilisers with high P solubility are essential in meeting the crops P requirement. On the other hand, a slow release P fertiliser will be more suitable for slow growth perennial species. Furthermore, slow release P fertilisers may improve P use efficiency in high-rainfall areas and/or on coarse-textured soils where dissolved P can be possibly be lost via leaching. Equally important would be the identification of soil P levels that exceed crop P requirements and have the potential for P enrichment by means of runoff. However, amounts of P lost in runoff are not related solely to soil test P, but also due to variable site runoff and erosion potentials (Sharpley et al., 1996; 2008). Thus, methods which incorporates site specific P test with assessments of potential runoff and erosion losses merit greater attention.

CHAPTER 8

EFFECTS OF LOW MOLECULAR WEIGHT ORGANIC ACIDS (LMWOAs) ON PHOSPHORUS RELEASE AND AVAILABILITY IN VOLCANIC SOILS FROM THE COMMONWEALTH OF DOMINICA.

Abstract: There is shared agreement within the scientific literature that organic ligands generally enhance both the solubility and dissolution of aluminosilicate minerals. This is characterized by decreasing the free metal concentrations in hydrolysis, by forming surface complexes with Al, Fe and Si, affecting both metal solubility and speciation. All LMWOAs have a high carboxyl group content and many can form strong complexes with Al and Fe affecting the dissolution and transport of these secondary oxyhydroxides. However, because of their heterogeneous nature, each of these organic acid classes may contain molecules with varying affinities for oxide surfaces.

Notwithstanding the significant amount of work that has been researched into the use of organic acids derived from biological origin for the dissolution of Al and Fe species, little attention has been given to the potential use of other LMWOAs particularly pyroligneous acid derived from the pyrolysis of ligneous/hemicellulolytic material. The objective of this study is to gain new knowledge of this LMWOA and its Al and Fe complexing ability by (1) comparing the impact of citric, oxalic, pyroligneous and acetic acids on P accumulation in plant tissue and (2) assessing P availability by use of the Hedley P sequential extraction, Olsen P, Bray & Kurtz and Mehlich-III P (Pm3) with an aim of understanding the P dynamics within the different nutrient pools.

The results show plant-available P is poor [Pm3 = 37.1 mg kg⁻¹ (4.96)] but shoot PO₄ content is highly correlated (P<0.001) to resin and bicarbonate P and showed little to no correlation with the refractory P forms. The results also highlight that citric acid + oxalic acid yielded the highest P content in plant tissue. Pyroligneous acid showed good promise as a LMWOA but further work is required to assess its full potential as an on-farm derived soil amendment.

Key words: Organic Acid, P accumulation, Allophane, Dominica

1. Introduction

Tropical soils are generally depleted in primary minerals and contain large amounts of secondary minerals, Al- and Fe-oxides, as well as amorphous minerals (Jackson and Sherman, 1953; Stallard, 1988; Theng and Yuan, 2008). Within the last two decades a significant number of studies have shown that organic ligands can implicitly influence the kinetics and reaction mechanisms of mineral dissolution through surface complexation with metal ions (Gerke et al., 1994; Varadachari et al., 1994; Jones, 1998; Huang et al., 2003; van Hees et al., 2005; Ström et al., 2005; Li et al., 2008; Wang et al., 2012a) as well as through direct acid attack (Barman et al., 1992; Jones and Kochian, 1996).

The solubility and dissolution of aluminosilicate minerals is generally enhanced by decreasing the activation energy for the rate-limiting steps in hydrolysis (Furrer and Stumm, 1986; Bennett and Casey, 1994; Welch and Ullman, 1996; Blake and Walter, 1999; Yuan et al., 2000), affecting metal solubility and speciation (Fox and Comerford, 1990). In these models, an organic ligand replaces a hydroxyl group, which is coordinated to the metal ion on the surface of the oxide, to form a surface complex (McKnight et al., 1992). These free metal ions could then be immobilised in secondary mineral phases or the exchangeable pool, thus increasing the solubility of minerals (Gerke, 1992; Welch and Ullman, 1993; Shao et al., 2011).

Low molecular weight organic acids (LMWOAs) are generally produced during the decomposition of organic material in the soil, for example leaf litter and dead roots by fungi and bacteria (Bolan et al., 1994; van Hees et al., 2000). Furthermore, root exudates and leaf washing may contain acids of this kind (McKeague et al., 1986; Jones, 1998; Ryan et al., 2009). However, many organic acid species are very short-lived in the soil environment due to rapid mineralization via thermal degradation or biodegradation reactions (Lundström and Øhman, 1990; Jones, 1998; Blake and Walter, 1999; Jones et al., 2003; van Hees et al., 2005).

The degree of complexation depends on the particular organic acid involved to include the number and proximity of carboxyl groups, the concentration and type of metal, and the pH of the soil solution (Pohlman and McColl, 1986; Hue et al., 1986; Barman et al., 1992; Varadachari et al., 1994; Bolan et al., 1994; Jones, 1998). To this extent, it has been suggested that organic acids with only one carboxyl group (i.e. malate, lactate, formate and acetate) have very little metal-complexing ability (Jones and Darrah, 1994; Jones, 1998; Goynes et al., 2006).

It has also been suggested that the effects of organic acids on aluminosilicate mineral dissolution would be most pronounced in the near-neutral pH region (Blake and Walter, 1999). However inhibition may also be observed (Welch and Ullman, 1996) caused by competition for adsorption sites at the mineral surface. Likewise, Jones and Brassington (1998) reported that when organic acids enter solution, within the first ten minutes, more than 80% quickly become sorbed onto the soil exchange complex and they postulated that this sorption capacity would greatly diminish their effectiveness to mobilize nutrients from the rhizosphere.

All LMWOAs have a high carboxyl group content and many can form strong complexes with Al and Fe which clearly affects the dissolution and transport of these secondary oxyhydroxides (Hue et al., 1986; Drever and Stilings, 1997; Jones et al., 1996; Jones, 1998). Depending on the dissociation properties and number of these carboxylic groups, organic acids can carry varying negative charge, thereby allowing the complexation of metal cations in solution and the displacement of anions from the soil matrix (Jones, 1998). Because of their heterogeneity, each of these organic acid classes may contain molecules with varying affinities for oxide surfaces (Pohlman and McColl, 1986; McKnight et al., 1992; Barman et al., 1992). Furthermore, there exist modelling results as well as experimental work which support the theory that LMWOAs contribute to the translocation of Al and Fe in the podsolization process (Kodama and Schnitzer, 1976; Buurman and Van Reeuwijk, 1984; van Hees and Lundström, 2000; van Hees et al., 2005).

It has been shown that around 28-37% of Al in soil solution in the O horizon is bound to this kind of organic solute (van Hees et al., 1996, 2000) thus migration of Al and Fe metals can be assisted by LMWOAs. One possible mechanism put forward of immobilisation of Fe and Al bound to these organic acids is bio-degradation of the organic part of the complex (Lundström et al., 1995). Although they are generally weak acids, several researchers have reported that these compounds produce protons which attach to oxygen sites at the mineral surface, weakening the metal-oxygen bond and catalysing a dissolution reaction (Terry, 1983; Barman et al., 1992; Welch and Ullman, 1993).

Notwithstanding the significant amount of work that has been researched with regards to the use of organic acids derived from biological origin for the dissolution of Al and Fe species, little attention has been given to the potential use of other LMWOAs particularly pyroligneous acid derived from the pyrolysis of ligneous/hemicellulolytic material. From a clearly analytical point of view, the condensate of smoke has been reported to be rich in low-molecular weight acids (formic and acetic), alcohols (methanol) and aldehydes (formaldehyde and acetaldehyde) (Focht, 1999; Diebold, 2000; Yang et al., 2014b; Matthew and Zakaria, 2015). Some of the largest constituents are acetic acid (0.5–12.0% by weight of total condensate), formic acid (0.3–9.1%), methanol (0.4–2.4%), formaldehyde (0.1–3.3%), acetaldehyde (0.1–8.5%), and hydroxyacetaldehyde (0.9–13.0%) (Diebold, 2000).

Various studies have shown the beneficial effects of pyroligneous extract applied to soil as an organic “fertilizer” and a bio-pesticide for the growing of food crops to increase crop productivity and quality (Yoshimura et al., 1995; Mu et al., 2003, 2006; Rico et al, 2007; Steiner et al., 2008; Schnitzer et al., 2010; Zulkarami et al., 2011; Payamara, 2011; Mmojieje and Hornung, 2015). However, based on the current literature, it appears that there is limited documented evidence to support the hypothesis which identifies the complexation of metal cations in solution and the displacement of anions from the soil matrix by pyroligneous acid

(Lashari et al., 2013; Togoro et al., 2014; Benzon et al., 2015). Nonetheless, with an ever increasing understanding and knowledge of these soil processes, it is now possible to determine the potential importance of such an organic acid in a complex soil environment.

Given the finite resource base of phosphorus, primarily derived from rock phosphate and the growing concern with regards to phosphorus security, the objective of this study is to gain new knowledge of the effects of pyroligneous acid (PLA) on P availability through its ability to dissolve Al and Fe complexes by (1) assessing the impact of pyroligneous acid in comparison to citric, oxalic, and acetic acids on $\text{KH}_2^{33}\text{PO}_4$ accumulation in plant tissue grown in tropical volcanic soils, (2) assessing P availability and distribution throughout the various P pools by use of the Hedley P sequential extraction, (3) evaluate the relationship between plant P uptake and the various forms of P, and (4) assessing the P nutrient status in relation to the requirements for optimum crop growth and development by the use of the Olsen, Bray & Kurtz, and Mehlich-III P extraction methods. Hence the ultimate aim is to understand how native P stocks from the various P pools in the soil environment as well as applied fertilizer can potentially become more plant available through the use of these LMWOAs and thus reduce P fertilizer applications to an absolute required minimum, paying attention to economic and environmental concerns.

2. Materials and Methods

2.1 Description of Extraction Methods

The methods chosen had a few similarities and further mention, where appropriate, will not be made. The similarities included: dry weight of soil (2 g), volume of extracting solution (20 ml), filtration (Whatman No. 42), centrifugation (3184 RCF for 10 minutes), and colorimetry analysis (Murphy and Riley, 1962).

2.1.1 Olsen P

The Olsen P or sodium bicarbonate phosphorus soil test method is based on the use of HCO_3^- , CO_3^{2-} and OH^- in the presence of 0.5 M NaHCO_3 (pH 8.5) solution to decrease the solution concentrations of soluble Ca^{2+} by precipitation as CaCO_3 and soluble Al^{3+} and Fe^{3+} by formation of Al and Fe oxyhydroxides, thus increasing P solubility (Olsen et al., 1954). The increased surface negative charges and/or decreased number of sorption sites on Fe and Al oxides surfaces at high pH levels is reported to enhance desorption of available P into solution (Fixen and Grove, 1990; Schoenau and Karamanos, 1993; Kuo, 1996).

Procedurally 2 g soil was weighed into a 50 ml centrifuge tube and 20 ml of 0.5 M NaHCO_3 (pH 8.5) extracting solution added. Tubes were shaken end-over-end at 200 rpm for 30 minutes. Samples were further centrifuged at 3184 RCF for 10 minutes. The extract was then filtered through Whatman No. 42 in the presence of 200 mg activated charcoal (Darco™® G60, Sigma Aldrich, UK) to obtain a colourless filtrate.

To reduce the interference of carbonates, 5 ml of sample and a range of P standards (0 - 25 mg L⁻¹ P) were then decanted into 20 ml scint vials and 1 ml of 1.5 M H_2SO_4 added to allow for the release of CO_2 by permitting samples and standards to degas for 10 minutes. P content was then analysed by colorimetry using the Murphy and Riley (1962) molybdate blue method on a Biotek™® Powerwave XS microplate spectrophotometer. An Olsen P value of 10 mg P kg⁻¹ soil is generally considered to be optimum for plant growth (Sims, 2000b).

2.1.2 Bray & Kurtz P-I

The Bray & Kurtz phosphorus soil test method is based on the use of NH_4F , 0.025 M HCl in 0.03 M NH_4F solution (pH 2.6) to enhance P release from aluminium phosphate by decreasing Al activity in solution through the formation of various Al-F complexes (Bray and Kurtz, 1945; Sims, 2000b).

For acidic soils, the fluoride in the extractant enhances P release from Al phosphates by decreasing Al activity in solution through the formation of various Al-F complexes (Sims, 2000b) as well as suppressing the re-adsorption of solubilized P by soil colloids (Holford, 1980). It is reported that the acidic nature of the extractant (pH 2.6) also contributes to dissolution of available P from Al, Ca, and Fe-bound forms in most soils.

Procedurally the same extraction method as for Olsen P was followed except that 20 ml 0.025 M HCl in 0.03 M NH_4F (pH 2.6) extracting solution was used. A Bray & Kurtz P-1 value of 25 to 30 mg P kg^{-1} soil is often considered optimum for plant growth (Sims, 2000b).

2.1.3 Mehlich-III

The Mehlich-III phosphorus soil test method is based on the use of an acidic solution that contains acetic acid (0.2 M CH_3COOH), ammonium nitrate (0.25 M NH_4NO_3), ammonium fluoride (0.015 M NH_4F), nitric acid (0.013 M HNO_3), and 0.001 M EDTA ($[(\text{HOOCCH}_2)_2\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_2\text{COOH})_2]$) at pH 2.5 (Mehlich, 1984; Tucker, 1992). Acetic acid in the extractant contributes to the release of available P in most soils by keeping the solution buffered below pH 2.9 to prevent calcium fluoride from precipitating. Ammonium exchanges with K, Ca and Mg and EDTA chelates Fe, Mn, Zn, and Cu (Sims, 1989; Tran and Simard, 1993). It is reported that the acidity of the nitric and acetic reagents, increases the solubility of Fe and Al phosphates and extracts a portion of Ca phosphates if present (Zhang et al., 2008). Fluoride serves to complex Al cations that potentially bind with phosphates thereby increasing the quantity of orthophosphate in solution (Zhang et al., 2008; Schroder et al., 2009).

Procedurally the same extraction method as for Olsen P was followed except that a total volume of 20 ml extracting solution which consisted of 0.2 M acetic, 0.25 M ammonium nitrate, 0.015 M ammonium fluoride, 0.013 M nitric acid, and 0.001 M EDTA (pH 2.5) was used. A Mehlich-III value of 45 to 50 mg P kg⁻¹ soil is generally considered to be optimum for plant growth and crop yields (Sims, 2000b).

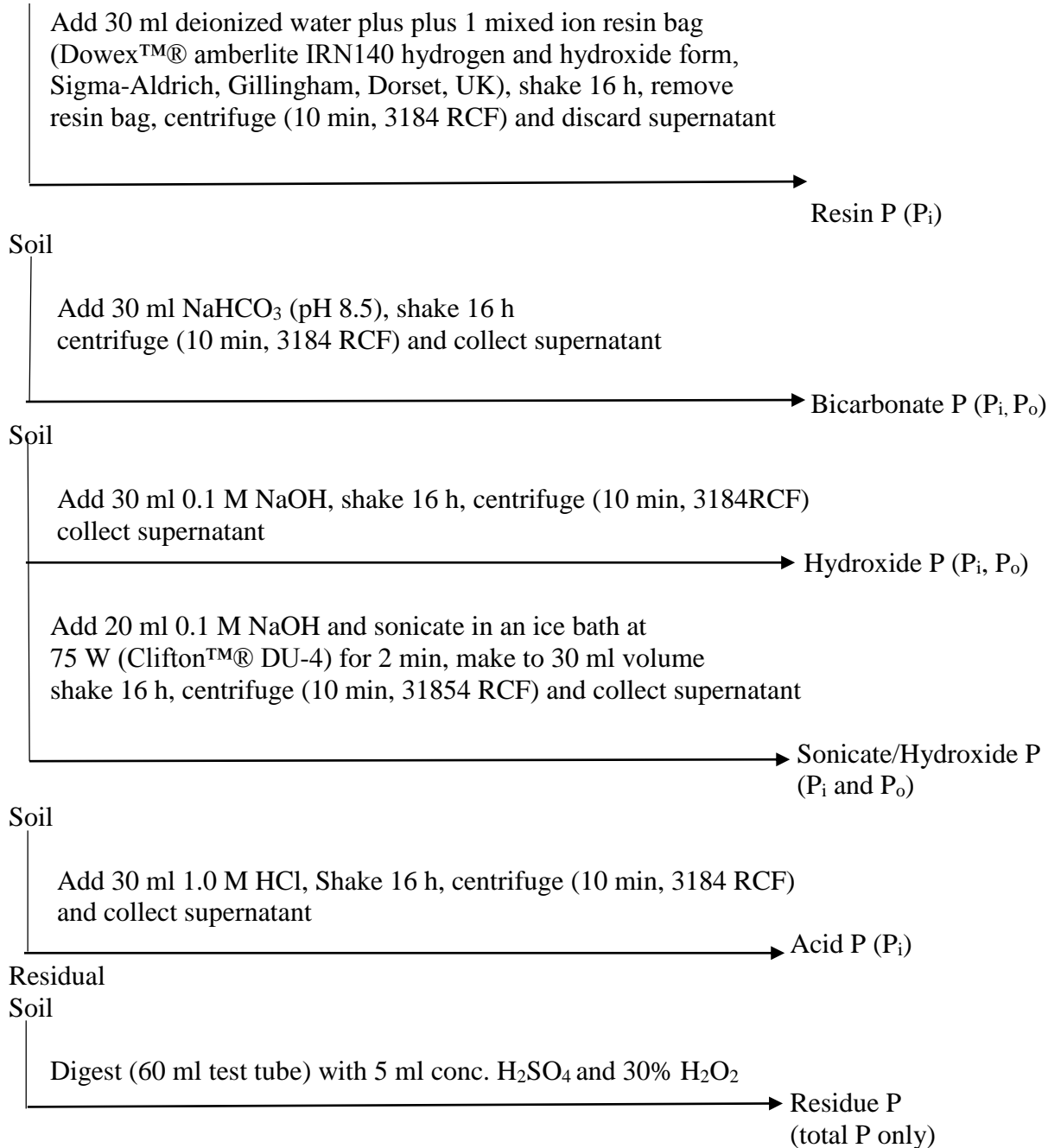
2.1.4 Hedley Sequential P Fractionation

The Hedley sequential phosphorus (P) fractionation method is based on the ability to successively extract several soil phosphorus compounds from the same soil sample by using extractants with increasing strength (Hedley et al., 1982). It recognizes plant-available forms (Resin P_i, Bicarbonate P_i and P_o) and refractory forms (NaOH P_i, and P_o, Sonic P_i, and P_o, HCl P_i, Residual P) of soil phosphorus (Cross and Schlesinger, 1995). The fractions that are extracted first have high plant availability; whereas the fractions that are extracted last have very low plant availability (Tiessen et al., 1984; Tiessen and Moir, 1993).

The method consist of several steps which are highlighted in a schematic diagram (refer to diagram 8.1). As stated, the method is sequential in that it utilizes the same 0.5 g of soil throughout the six extraction steps. At the end of each step, P content was analysed by colorimetry using the Murphy and Riley (1962) molybdate blue method on a Biotek™® Powerwave XS microplate spectrophotometer. It should be noted that the organic fractions were not determined and as such the cumulative total of extractable P represents the inorganic fractions only. As a result the values reported tend to be overestimated with regards to the inorganic P fractions.

Diagram 8.1: Hedley sequential phosphorus fractionation method for soils

0.5 g soil samples in 50 ml screw cap centrifuge tubes



1. Resin bags were removed and washed in deionized water. Phosphate was eluted by shaking with 50 ml 0.5 M HCl for 2 hours. This step was further repeated and supernatant collected. Resin P content was analysed by colorimetry using the Murphy and Riley (1962) molybdate blue method on a Biotek™[®] Powerwave XS microplate spectrophotometer.
2. 5 ml concentrated H₂SO₄ was added to evaporate water which was used to transfer soil from the previous HCl fraction. Samples were allowed to cool and 30% H₂O₂ added at a rate of 0.5 ml and reheated for 30 minutes. Additional volumes of 0.5 ml of 30% H₂O₂ were added until liquid was clear (10x). Samples were then cooled and made to 20 ml volume with deionized water. Residue P was determined by colorimetry using the Murphy and Riley (1962) molybdate blue method on a Biotek™[®] Powerwave XS microplate spectrophotometer.

NB: organic fractions (P_o) were not determined and as such the cumulative total of extractable P represents the inorganic fractions only. As a result the values reported tend to be overestimated with regards to the inorganic P fractions.

2.2 ³³P mobilization in Dominican volcanic soils influenced by LMWOAs

³³P mobilization studies were conducted by weighing 1 g of soil into 50 ml centrifuge tubes. 10 ml of KH₂PO₄ labelled as ³³P was added (0.17 kBq). The initial activity of the ³³P was selected on the basis of a back calculation allowing for decay to achieve a sample with sufficient activity to be in the optimal range for accurate scintillation counting (P. Tallboy, personal communication). 10 ml of 10 mM oxalic acid (pH 2.15), citric acid (pH 2.66), acetic acid (pH 3.35), buffered to pH 3.69 (equivalent to pH of pyroligneous acid) was added.

A positive and negative control using HCl (pH 2.10 buffered to 3.69) and H₂O respectively were also applied. Samples were placed to shake end-over end for 30 minutes at 200 rpm. Samples were then centrifuged for 10 minutes at 3184 RCF. One (1) ml of the supernatant was further centrifuged at high speed (20,817 RCF) for 5 minutes. An aliquot of 0.5 ml was then mixed with 4 ml scintillation fluid (Wallace™® optiphase 3 liquid). ³³P activity was measured by Cerenkov counting using a Wallace™® 1404 liquid scintillation counter (EG&G Ltd., Milton Keynes, UK). Percentage P sorbed, percentage P in solution, P concentration (mg L⁻¹) and mass of P sorbed (mg g⁻¹) were calculated. Bar charts were subsequently constructed by plotting organic acids versus %P sorbed for the suite of soils studied.

2.3 Maize pot trial: Effect of organic acids on the release of P from phosphate rocks added to soil.

The pot trial consisted of growing maize (*Zea mays* L.) in a Sanyo Fitotron™® growth cabinet in a randomized complete block design with 3 replicates over a period of 8 weeks. The growth conditions were set at 16 hours light at 27 °C and 8 hours dark at 21 °C, relative humidity of 65-70% and a light intensity of 300 μmol m⁻².

Soils from four contrasting sites were used due to reason of space within the growth cabinet. 425 g of soil was packed into 785 cm³ pots and originally planted with 3 maize seedlings per pot. Seeds of maize were previously soaked for 24 hours in aerated, deionized

water and then allowed to pre-germinate on moistened filter paper for 48 hours at room temperature (~25°C).

Rock phosphate (30% P₂O₅) was applied at 165 kg ha⁻¹ of P (0.45 g/pot), equivalent to 550 kg ha⁻¹ of 30% P₂O₅. Rock phosphate was incorporated 3-5 cm deep, on the day of thinning seedlings to 1 plant per pot. Additionally, 50 ml of 50 mM organic acid was applied as a soil amendment (drench) in weeks 1, 3, and 5. The rock phosphate was further analysed by total x-ray fluorescence and a suite of native element concentrations (mg kg⁻¹) obtained.

The properties of the pyroligneous acid sourced from Dominica were not known, and the chemical constituents were only referenced from the cited literature and hence analytical characterization was conducted. A batch sample was characterized by gas chromatography-mass spectrometry using a Varian™® GC-MS system comprising of a CP-3900 gas chromatograph (Walnut Creek, USA) with a 1177 injector, CP-8410 auto-sampler and an ion-trap mass spectrometry (Varian™® Saturn 2100T) following which the composition of the sample was established (Fig. 8.2).

For the growing of maize, a Hoagland nutrient solution (Hoagland and Arnon, 1950) was formulated to supply macro and micro nutrients. Individual nutrient stocks for making up the Hoagland solution were prepared and stored in separate bottles with appropriate labels. Phosphate as 1.0 M KH₂PO₄ was omitted and rock phosphate (30% P₂O₅) was utilized as the P source. Plants were watered with deionized water 2-3 times per week, with nutrient solution being applied once per week. On the day of application, each component was then added to 800 ml deionized water and made up to 1 L volume. After the solution was mixed, plants were watered with 50 ml of nutrient solution per pot. The nutrient application was ceased one week prior to harvesting of plants. The following components were used in the Hoagland nutrient solution.

Component	Stock Solution	ml Stock solution / 1L H ₂ O
Macronutrients		
2 M KNO ₃	202 g l ⁻¹	2.5
1 M Ca(NO ₃) ₂ ·4H ₂ O	472 g l ⁻¹	2.5
Iron	15 g l ⁻¹	1.5
2 M MgSO ₄ ·7H ₂ O	493 g l ⁻¹	1.0
1 M NH ₄ NO ₃	80 g l ⁻¹	1.0
Micronutrients		
H ₃ BO ₃	2.86 g l ⁻¹	1.0
MnCl ₂ ·4H ₂ O	1.81 g l ⁻¹	1.0
ZnSO ₄ ·7H ₂ O	0.22 g l ⁻¹	1.0
CuSO ₄ ·5H ₂ O	0.051 g l ⁻¹	1.0
H ₃ MoO ₄ ·H ₂ O	0.09 g l ⁻¹	1.0

NB: Phosphate as 1 M KH₂PO₄ (136 g l⁻¹) usually added at a rate of 0.5 ml stock solution to 1 l distilled water was not added and phosphate rock (30% P₂O₅) substituted.

Growth parameters included stem diameter (mm), height of plant (cm), and number of leaves were recorded in weeks, 1, 2, 4, 6, 7, and 8. At the end of the growing period, plants were harvest, fresh weight for root and shoots recorded and then set to oven dry at 80°C until constant weight (~3 days) and ground in a ball mill. 0.2 g of dried, ground plant tissue was then placed in a 20 ml glass vial and was ashed in a muffle furnace at 500°C for 16 hours (Nathan and Sun, 2006). Total P in plant material was determined by dissolving ash material with 1 ml 20% v:v HCl and 9 ml of deionized water (Adrian, 1973). The solution was then filtered through Whatman No. 42 into a new 20 ml polypropylene vial. The filter paper was washed with 5 ml deionized water to collect any residual material. The P content in the plant tissue was then analysed by colorimetry using the Murphy and Riley (1962) molybdate blue method on a Biotek™® Powerwave XS microplate spectrophotometer.

The Hedley sequential P extraction in the pot trial experiment was performed before the sowing of maize seedlings and after the harvest of maize plants. However due to technical difficulties encountered, the P fractionation data obtained before the plants were established was compromised and as such the data presented only reflects the P fractionation at the end of the pot trial.

2.3 Maize rhizotube trial: Low molecular weight organic acid (LMWOAs) and ³³P mobilization in the rhizosphere and uptake by maize plants.

The rhizotube trial consisted of constructing a microcosm from a nylon tube, which comprised a 220 mm long, 9 mm diameter main “rhizotube” section attached to a 50 mm long, 20 mm diameter section which was used to hold the seedling (Ström et al., 2002). Pin holes were pierced at 10 mm intervals down the length of the main rhizotube to ensure aeration. Before the addition of the maize seedling, the microcosms were filled with 20.42 g of soil to a bulk density of $\sim 1.02 \text{ g cm}^{-3}$ (Fig. 8.1g).

After adding plants, the microcosms were placed in a growth room (Sanyo Fitotron™®) with a day/night rhythm of 18/22°C and a 16 hour photoperiod with a light intensity of $300 \mu\text{mol m}^{-2}$. Microcosms were kept moist by placing rhizotubes into a 500 ml glass beaker with ~ 50 ml of deionized water and through the addition of deionized water via the soil surface (1 ml day^{-1} equivalent to 10 mm day^{-1}). The microcosms were enclosed within a large plastic bag to maintain a high relative humidity (Fig 8.1c,e).

Two and four days after transplanting, 400 μl of a $5 \mu\text{M KH}_2^{33}\text{PO}_4$ solution (60 kBq) were injected into the microcosms at the same location (Fig. 8.1a). Three and five days later, the microcosms were injected with 0.40 ml of solution containing (1) pyroligneous acid (50 mM), (2) oxalic + citric acid (25 mM + 25 mM), and (3) acetic acid (50 mM) buffered to the pH of PLA (pH 3.69). Deionized water was used as a control. Effectively, the P source was added to the various soils before the addition of the organic acids. After 8 days from transplanting, the shoots, roots and ³³P labelled root zone were harvested, dried (80°C), ashed (500°C) and ³³P content determined by Cerenkov scintillation counting (Wallace™® 1404 liquid scintillation counter and optiphase 3 scintillation fluid; EG&G Ltd, Milton Keynes, UK).

2.4 Analysis of Phosphate Rock by total reflection X-ray fluorescence (TXRF)

20 mg of ground phosphate rock was weighed into a 1.5 ml Eppendorf tube. 1 ml of triton X100 solution was added. 10 µl of 1000 mg l⁻¹ Se internal standard was added. The solution was homogenized using a vortex (~10 seconds). 10 µl of suspension was transferred to a pre-siliconized disc and dried for 10 minutes on a hot plate set at 50°C with a glass lid. The disc was placed on disc cassette and introduced into S2 Picofox Bruker®™ TXRF spectrometer for analysis.

Table 8.1. Summary of total reflection X-ray fluorescence analysis of the 30% P₂O₅ phosphate rock. n = 8

g kg ⁻¹						
Al	P	K	Ca	S	Mn	Fe
13.04 (1.62)	13.52 (0.56)	11.54 (0.29)	105.40 (9.55)	9.24 (2.28)	0.10 (0.03)	3.31 (0.94)
Cu	Zn	Cl	As	Hg	Ce	Ti
0.06 (0.01)	0.06 (0.003)	2.93 (0.14)	0.003 (4.48e ⁻⁴)	0.01 (0.003)	0.10 (0.01)	0.23 (0.05)

2.5 Calculations used in radioisotope studies

$$\text{Total P content} = \text{Volume of PO}_4 \text{ added (L)} \times \text{Concentration Blank (mg L}^{-1}\text{)} \quad [1]$$

$$\% \text{ P in solution} = \frac{\text{CPM}}{\text{CPM Blank}} \quad [2]$$

$$\text{Mass of P} = \text{Total P content (mg)} \times \% \text{ P in solution} \quad [3]$$

$$\text{P concentration (mg L}^{-1}\text{)} = \frac{\text{Mass of P}}{\text{Total volume}} \quad [4]$$

$$\% \text{ P sorbed} = (1 - \% \text{ P in solution}) \times 100 \quad [5]$$

$$\text{Mass of P sorbed} = \frac{(\% \text{ P sorbed} \times \text{Total P content (mg)})}{100} \quad [6]$$

2.6 Statistical analysis

Sample analysis was done in triplicate and quadruplicate (rhizotube experiment) with mean and standard error of the mean (SEM) calculated. Statistical analyses were performed using the SPSS version 20.0 for Windows program (SPSS Inc., Chicago, IL). Significant differences between groups means was determined by analysis of variance (t-test and ANOVA) and Tukey's test was used for multiple comparison between the sample means where the ANOVA F statistics was significant at P<0.05 unless otherwise stated.

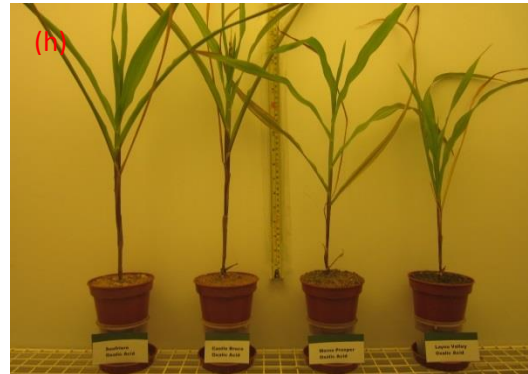
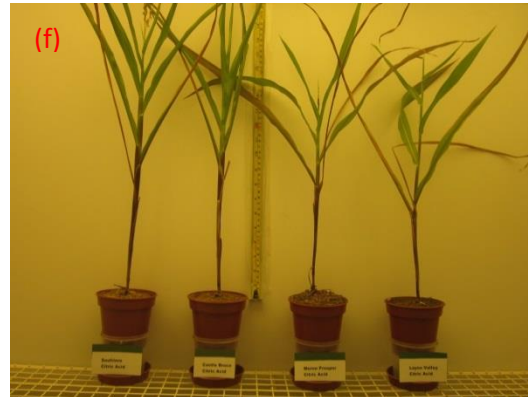
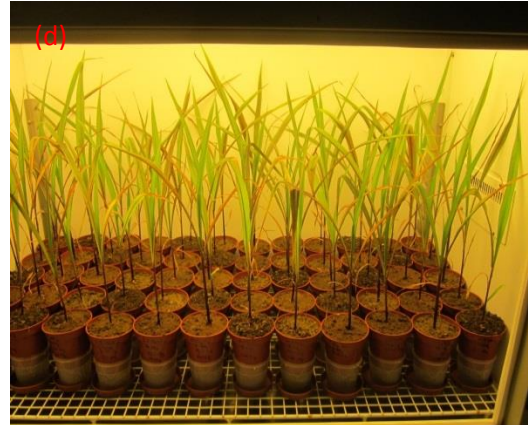
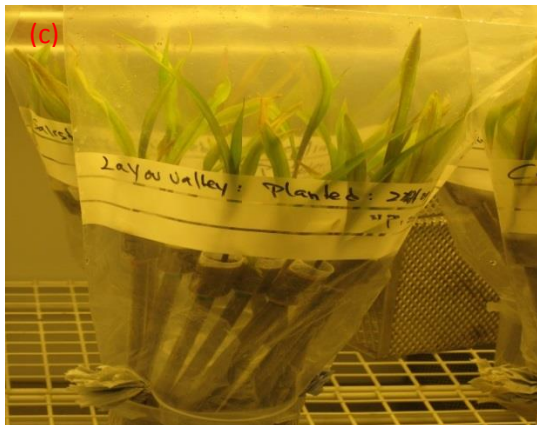


Fig. 8.1. Pictorial representation of the maize rhizotube trial (left) and the maize pot trial (right) looking at effects of LMWOA on phosphate mobilization in volcanic soils of the Commonwealth of Dominica. Note the P-deficiency symptoms of anthocyanin production of the leaf sheath in fig. 8.1b and 8.1d.

3. Results

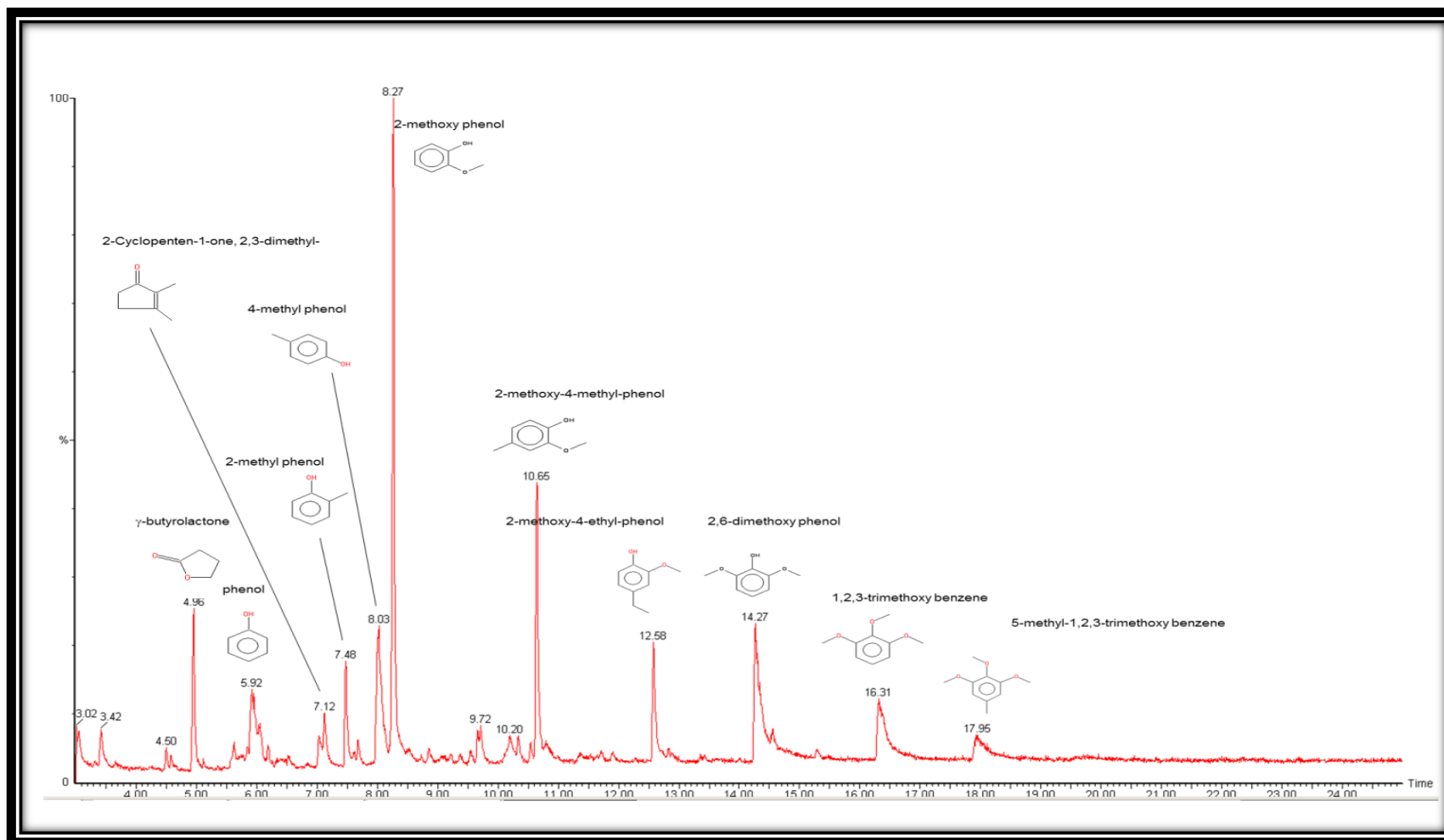


Fig. 8.2. Chromatogram obtained of Pyroigneous acid (PLA) by Gas Chromatography- Mass Spectrometry

3.1 Pyroligneous Acid GC-MS

Pyroligneous acid is a complex mixture of oxygenated aliphatic and aromatic compounds (Balat, 2011), and compounds such as carboxylic acids and phenols are formed by pyrolysis in the process of carbonization (Bilehal et al., 2012). To produce PLA, gases from a charcoal kiln are channelled in such a way as to allow condensation of the vapour. In this exploratory study, the pyroligneous acid was moderately acidic, having a pH of 3.69 well within the range of PLA produced from different plant sources (; Haller and Jonsson, 2014; Matthew and Zakaria, 2015), and an electric conductivity of $2.67\mu\text{s cm}^{-1}$. The identified organic substances are shown in Fig. 8.2 with their GC retention indices. In this study, more than 16 substances were fully identified. The major substances were 2-cyclopenten-1-one, 2,3-dimethyl, γ -butyrolactone, phenol, 2-methyl phenol, 4-methyl phenol, 2-methoxy phenol, 2-methoxy-4-methyl-phenol, 2-methoxy-4-ethyl-phenol, 2,6 dimethoxy phenol, 1,2,3-trimethoxy benzene, and 5, methyl-1,2,3-trimethoxy benzene.

It can be observed that phenols and methoxyphenols, products of the thermal degradation of lignin, (Fischer and Bienkowski, 1999; Steiner et al., 2008; Souza et al., 2012) represents a significant percentage of the identified substances (Fig. 8.2). The chromatogram is in agreement to a number of reports made concerning the basic constituent of PLA (Mu et al., 2004; Nakai et al., 2007; Mun and Ku, 2010; Kim et al., 2011; Jung et al., 2012; Yang et al., 2014b; Papenfus et al., 2015). Some compounds, present in small quantities in the PLA are not highlighted because they could not be readily identified, most probably due to insufficient mass spectrum quality (Souza et al., 2012) and/or their relative concentrations could not be adequately evaluated. In addition it is more than likely that some of the PLA compounds partially or completely decompose thermally before they reached their retention time and as such peaks with low retention times could not be detected as has been reported by Steiner and co-workers (2008).

3.2 Hedley Sequential Fraction

The analysis for the Hedley sequential P fractionation was approached in two ways. The first approach was to analyse the data where the sources of variation ($n = 60$) included site, organic acid and the interactions. The results from this approach revealed varying trends. The resin P fraction (Fig. 8.3) highlighted significant differences ($P < 0.001$, $R^2 = 0.93$) between the various organic acids ($F(4, 59) = 88.34$, $PESq = 0.903$) as well as between sites ($F(3, 59) = 34.86$, $PESq = 0.734$). There were significant differences ($P < 0.01$) between the interaction of organic acid and site ($F(5, 59) = 3.005$, $PESq = 0.487$). The mean was $7.47 \mu\text{g P g}^{-1}$ soil (0.18). The water control recorded the lowest P content, $5.31 \mu\text{g P g}^{-1}$ soil (0.19). PLA, $7.46 \mu\text{g P g}^{-1}$ soil (0.36) and acetic acid, $7.81 \mu\text{g P g}^{-1}$ soil (0.15) were not significantly different from each other ($P = 0.377$). Furthermore, oxalic acid, $8.21 \mu\text{g P g}^{-1}$ soil (0.22) and acetic acid did not differ at ($P = 0.25$). However, citric acid, $8.57 \mu\text{g P g}^{-1}$ soil (0.25) and oxalic acid yielded the highest resin P content, without differing from each other ($P = 0.35$). Soils from Soufriere, $8.28 \mu\text{g P g}^{-1}$ soil (0.34) recorded the highest resin P content, followed by Castle Bruce, $7.81 \mu\text{g P g}^{-1}$ soil (0.33), Morne Prosper, $7.16 \mu\text{g P g}^{-1}$ soil (0.31) and Layou Valley, $6.64 \mu\text{g P g}^{-1}$ soil (0.36) recording the lowest resin P content. Tukey HSD multiple comparison showed significant differences between sites ($P < 0.05$) and significant differences between all organic acids ($P < 0.001$) in comparison to the H_2O control.

The bicarbonate fraction also showed significant differences ($P < 0.001$, $R^2 = 0.99$) between organic acids ($F(4, 59) = 709.95$, $PESq = 0.987$) and site ($F(3, 59) = 1186.27$, $PESq = 0.989$). The mean was $7.27 \mu\text{g P g}^{-1}$ soil (0.22). The water control, $5.12 \mu\text{g P g}^{-1}$ soil (0.26) recorded the lowest bicarbonate P content, while acetic acid, $7.53 \mu\text{g P g}^{-1}$ soil (0.50) and PLA, $7.71 \mu\text{g P g}^{-1}$ soil (0.35) constituted a separate homogenous subset ($P = 0.062$). On the contrary, citric acid, $7.92 \mu\text{g P g}^{-1}$ soil (0.37) and oxalic acid, $8.05 \mu\text{g P g}^{-1}$ soil (0.43) recorded the highest bicarbonate P content at ($P = 0.213$). Soils from Soufriere, $8.63 \mu\text{g P g}^{-1}$ soil (0.36)

recorded the highest bicarbonate P content and soils from Layou Valley, 5.50 $\mu\text{g P g}^{-1}$ soil (0.21) recording the lowest bicarbonate P content. Tukey HSD multiple comparison showed significant differences between all sites, and organic acids versus H₂O control ($P < 0.001$).

The sodium hydroxide (NaOH) fraction showed significant differences ($P < 0.001$, $R^2 = 0.81$) between organic acids ($F(4, 59) = 6.415$, $\text{PESq} = 0.403$), as well as site ($F(3, 59) = 41.496$, $\text{PESq} = 0.767$). The mean was 205.8 $\mu\text{g P g}^{-1}$ soil (3.41). The water control, 187.67 $\mu\text{g P g}^{-1}$ soil (6.55) extracted the least amount of NaOH P. PLA, 206.37 $\mu\text{g P g}^{-1}$ soil (7.01), oxalic, 210.19 $\mu\text{g P g}^{-1}$ soil (7.97), citric, 212.04 $\mu\text{g P g}^{-1}$ soil (7.09), and acetic acid, 212.72 $\mu\text{g P g}^{-1}$ soil (8.16) were not significantly different from each other recording the highest NaOH values. Soils from Soufriere, 184.32 $\mu\text{g P g}^{-1}$ soil (3.90) and Castle Bruce, 186.96 $\mu\text{g P g}^{-1}$ soil (2.89) equal at $P = 0.957$ recorded the lowest NaOH values. Morne Prosper, 220.29 $\mu\text{g P g}^{-1}$ soil (5.73) and Layou valley, 231.63 $\mu\text{g P g}^{-1}$ soil (4.35), equal at $P = 0.148$ recorded the highest NaOH values. Tukey HSD multiple comparison showed a suite of varied differences between sites and significant differences between the H₂O control and citric, oxalic and acetic acid ($P < 0.001$) as well as between the H₂O control and PLA ($P < 0.05$).

The sonic NaOH fraction showed significant differences ($P < 0.001$, $R^2 = 0.71$) between organic acids ($F(4, 59) = 14.148$, $\text{PESq} = 0.598$) and site ($F(3, 59) = 11.24$, $\text{PESq} = 0.470$). The mean was 36.96 $\mu\text{g P g}^{-1}$ soil (0.65). PLA, 35.94 $\mu\text{g P g}^{-1}$ soil (1.02), acetic, 38.35 $\mu\text{g P g}^{-1}$ soil (1.07), and oxalic acid, 38.96 $\mu\text{g P g}^{-1}$ soil (1.17) did not differ from each other at $P = 0.203$. However, citric, 40.47 $\mu\text{g P g}^{-1}$ soil (1.43), oxalic and acetic acid did not differ significantly at $P = 0.546$. Soils from Castle Bruce, 33.82 $\mu\text{g P g}^{-1}$ soil (1.03) and Soufriere, 35.39 $\mu\text{g P g}^{-1}$ soil (1.06) at $P = 0.583$ recorded the lowest values. Furthermore, soils from Morne Prosper, 38.29 $\mu\text{g P g}^{-1}$ soil (1.24) and Soufriere did not differ significantly at $P = 0.103$. However soils from Layou Valley, 40.34 $\mu\text{g P g}^{-1}$ soil (1.28) and Morne Prosper recorded the highest sonic NaOH values being equal at $P = 0.354$. The HCl fraction showed significant

differences ($P < 0.001$) between organic acid ($R^2 = 0.652$, $PESq = 0.483$) and site ($R^2 = 0.652$, $PESq = 0.431$). Tukey HSD multiple comparison revealed significant differences between the H₂O control and citric and oxalic acid ($P < 0.001$), and H₂O control and acetic acid and PLA ($P < 0.01$). The residue fraction also showed significant differences ($P < 0.001$) between organic acid ($R^2 = 0.889$, $PESq = 0.643$) and site ($R^2 = 0.889$, $PESq = 0.852$). Tukey HSD multiple comparison also showed significant differences between the H₂O control and all the organic acids ($P < 0.001$) with regards to the residue fraction.

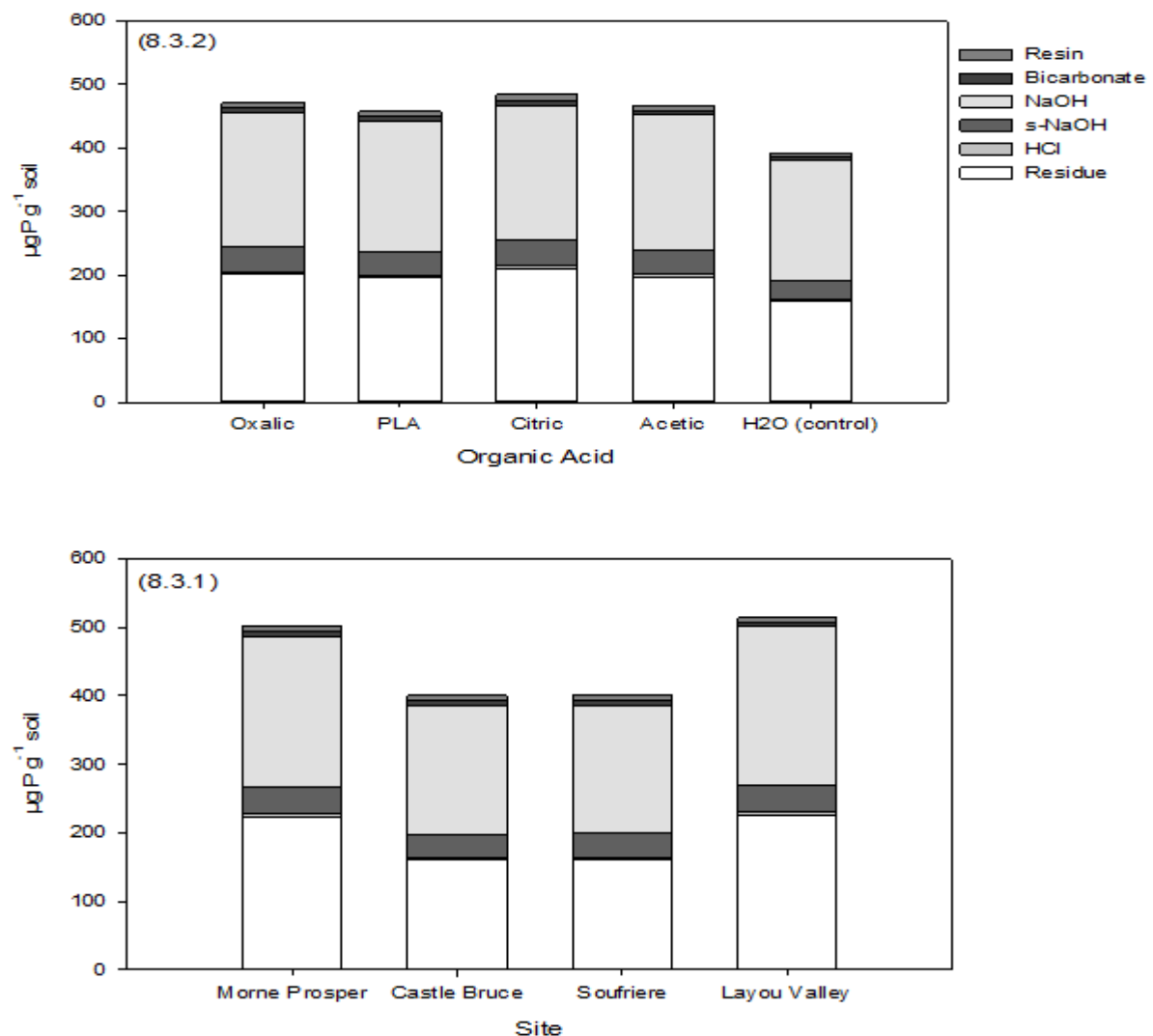


Fig. 8.3. Phosphorus content ($\mu\text{g g}^{-1}$) as extracted by the Hedley sequential extraction of four agricultural soil from the Commonwealth of Dominica used for the growing of maize, fertilized with phosphate rock and amended with LMWOA's. Values represent means. $n = 60$. NB: Organic P fractions were not determined and total inorganic P (P_i) tends to be overestimated in the absence of organic (P_o) fractions.

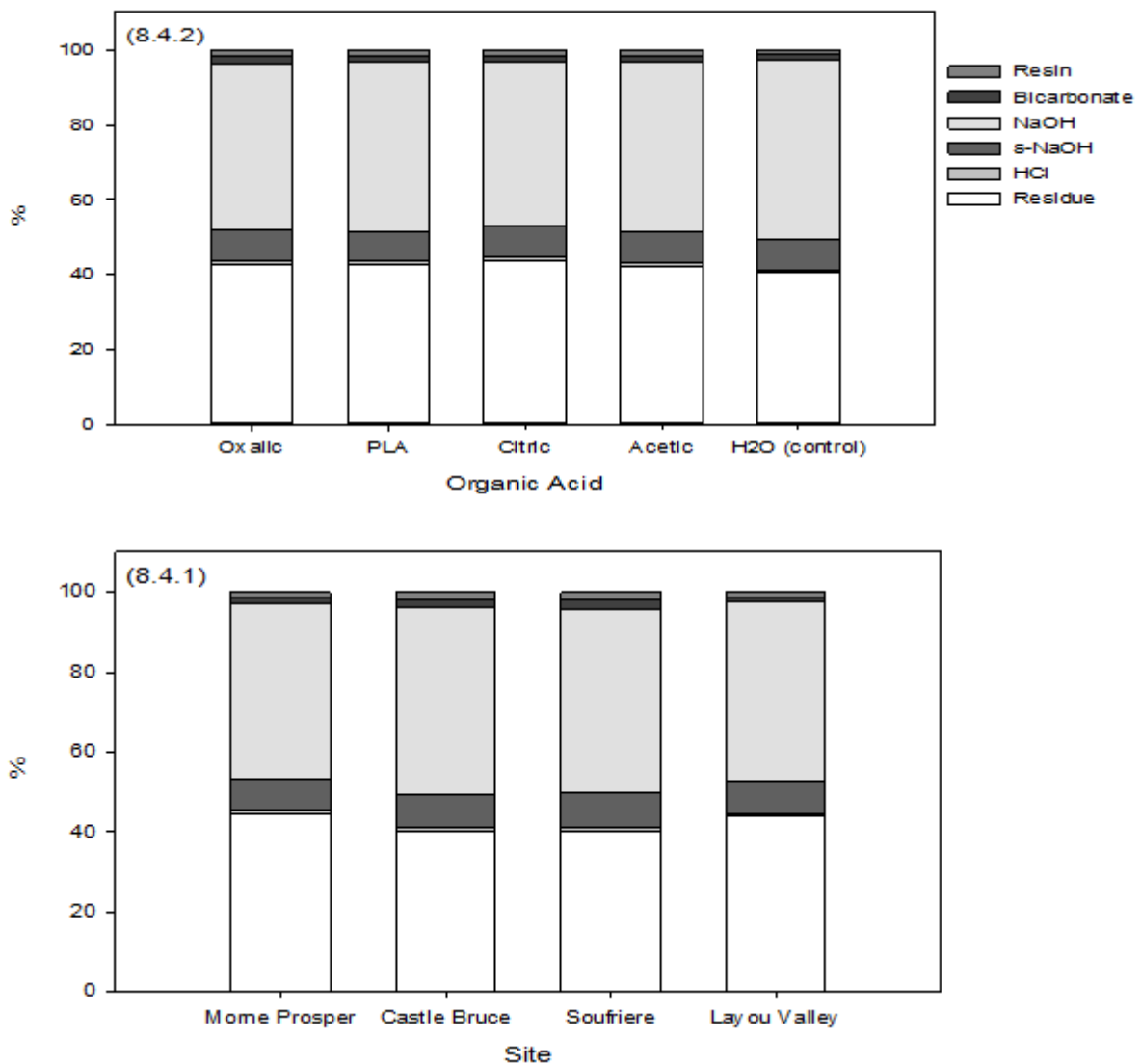


Fig. 8.4. Percentage of P extracted by the Hedley sequential extraction of four agricultural soils from the Commonwealth of Dominica fertilized with phosphate rock and amended with LMWOA's. n = 60.

The total amount of P extracted as a cumulative sum of all the fractions for soils from Layou Valley was, $513.65 \mu\text{g g}^{-1}$ (19.34), followed by Morne Prosper, $500.72 \mu\text{g g}^{-1}$ (25.14), Castle Bruce, $400.61 \mu\text{g g}^{-1}$ (10.81), and finally Soufriere, $401.34 \mu\text{g g}^{-1}$ (11.07) (Fig. 8.3). From detailed observation, it was noticed that the amount of resin and bicarbonate P, considered to be the fractions most available for plant uptake (Amer et al., 1955; Tiessen et al., 1984; Tiessen and Moir, 1993; Cross and Schlesinger, 1995; Boschetti et al., 2009; Dieter et al., 2010) extracted from the Soufriere soils, $8.28 \mu\text{g P g}^{-1}$ soil (0.34) and $8.63 \mu\text{g P g}^{-1}$ soil (0.36); and Castle Bruce, $7.81 \mu\text{g P g}^{-1}$ (0.33) and $8.12 \mu\text{g P g}^{-1}$ (0.30) is significantly different

($P < 0.001$) in comparison to soils from Morne Prosper, $7.15 \mu\text{g P g}^{-1}$ (0.31) and $6.81 \mu\text{g P g}^{-1}$ (0.35); and soils from Layou Valley, $6.64 \mu\text{g P g}^{-1}$ soil (0.36) and $5.55 \mu\text{g P g}^{-1}$ soil (0.21).

The mean HCl P extracted across all sites was $3.96 \mu\text{g P g}^{-1}$ soil (0.13). Citric acid, $4.42 \mu\text{g P g}^{-1}$ soil (0.26) and oxalic acid, $4.38 \mu\text{g P g}^{-1}$ soil (0.27) extracted the highest P, with acetic acid, $4.15 \mu\text{g P g}^{-1}$ soil (0.26) and PLA, $4.02 \mu\text{g P g}^{-1}$ soil (0.27), followed by H₂O control, $2.85 \mu\text{g P g}^{-1}$ soil (0.18). Soils from Layou Valley, $4.55 \mu\text{g P g}^{-1}$ soil (0.25) and Morne Prosper, $4.40 \mu\text{g P g}^{-1}$ soil (0.26) recorded the highest P values whilst soils from Soufriere, $3.36 \mu\text{g P g}^{-1}$ soil (0.22), and Castle Bruce, $3.54 \mu\text{g P g}^{-1}$ soil (0.20) recorded the lowest P extractable values. The mean residue P extracted across all sites was $192.62 \mu\text{g P g}^{-1}$ soil (5.17) and was highest in soils from Layou Valley, $224.99 \mu\text{g P g}^{-1}$ soil (7.49) and lowest in soils from Castle Bruce, $160.35 \mu\text{g P g}^{-1}$ soil (4.95).

As a percentage of total P extracted (Fig. 8.4), the resin and bicarbonate fractions accounted for a mean percentage of 2.77% in soils from Morne Prosper, 3.98% in the case of Castle Bruce, 4.21% in soils from Soufriere, and a mere 2.36% in soils from Layou Valley. The NaOH fraction with a mean of 45.51% (0.42) across sites showed significant differences ($P < 0.001$). The sonic NaOH, 8.18% (0.12) and HCl fraction, 0.87% (0.02) had significant differences ($P < 0.001$), however the residue fraction behaved differently in that it accounted for a mean 42.12% (0.55) across all sites with significant differences between sites ($P < 0.001$) being highest in the Morne Prosper (44.62% (0.39) and Layou Valley (43.80% (0.84) equal at ($P = 0.997$) and lowest at Castle Bruce 40.03 (0.71) and Soufriere, 40.20% (0.36) ($P = 0.998$).

With regards to the organic acids, there were significant differences ($P < 0.001$) when compared to the water control (Fig. 8.3.2). PLA extracted a mean of $457.32 \mu\text{g P g}^{-1}$ soil (31.73) across all sites. Oxalic acid, $470.80 \mu\text{g P g}^{-1}$ soil (36.29), citric acid, $484.11 \mu\text{g P g}^{-1}$ soil (34.0), acetic acid, $467.46 \mu\text{g P g}^{-1}$ soil (34.13) and the H₂O control extracted a mean of $390.71 \mu\text{g P g}^{-1}$ soil (19.26) across all sites. However, it can be noticed that soils from Layou

Valley and Morne Prosper consistently extracted more P than did soils from Castle Bruce and Soufriere; and this tends to suggest it is partly related to the total bulk soil phosphorus content which was 257.09 mg P kg⁻¹ soil (7.13) for Morne Prosper, 131.12 mg P kg⁻¹ soil (3.75) for Soufriere, 176.83 mg P kg⁻¹ soil (6.21) for Castle Bruce, and 259.07 mg P kg⁻¹ soil (7.61) for soils from Layou Valley as was determined by TXRF analysis.

These results tend to suggest that while the pool of primary phosphate will ultimately decline; the NaOH, sonicated NaOH, HCl and residue phosphorus should eventually increase as P becomes geochemically fixed to Fe and Al oxides, especially in soils with higher P sorption capacity (Cross and Schlesinger, 1995). All the same, the data also tends to suggest that in the long term P availability will be more than likely linked to geochemical processes whereby the refractory forms of P in due course should become more sparingly available, as the proportion of total P held in various forms changes. However, in the short term, it can be deduced that biological processes influences P distribution most significantly as can be observed from the resin and bicarbonate P pools (Tiessen et al., 1983). The agronomic implication is that plant available P in these volcanic soils will more than likely be derived from labile, non-occluded, or inorganic forms notwithstanding organic P recycling becomes critically important to the availability of soil P and hence the importance of SOM conservation.

On the other hand, when the variable of site is removed from the analysis (n = 60) and the effect of the various organic acids on P fractionation is specifically analysed within individual sites (n = 15), different trends are observed between the P fractions from site to site (Table 8.2). However there was a general trend with regards to the resin and bicarbonate fractions across all individual sites. Citric acid showed a general tendency to be significant in comparison to the H₂O control (P<0.001) across all sites with the exception of the bicarbonate fraction in soils from Soufriere (P<0.01). The organic acids were not significantly different from the H₂O control in the NaOH fraction across all sites with the sole exception of soils from

Morne Prosper ($P < 0.05$). The sonic NaOH fraction showed significant differences between citric acid and the H₂O control ($P < 0.05$) for soils from Morne Prosper.

Oxalic and citric acid showed significant differences ($P < 0.05$) from the H₂O control in soils from Layou Valley and Soufriere, with no significant difference observed for soils from Castle Bruce for the sonic NaOH fraction. The HCl fraction only showed significant differences ($P < 0.01$) in soils from Morne Prosper. The residue fraction showed significant differences between the H₂O control and citric, oxalic and acetic acid for soils from Morne Prosper ($P < 0.01$). There were no significant differences between the H₂O control and the organic acids for soils from Soufriere, while soils from Castle Bruce only showed significant differences between the H₂O control and citric acid ($P < 0.05$). In the case of soils from Layou Valley, oxalic, PLA, and acetic acid showed significant differences in comparison to the H₂O control ($P < 0.05$), while citric acid showed significant differences ($P < 0.01$) to the H₂O control.

Table 8.2. Tukey HSD multiple comparison of the different P fractions as extracted by the Hedley P sequential extraction of soils from the Commonwealth of Dominica. Values represent means. n = 15.

Site	Organic Acid	Hedley P Sequential Extraction ($\mu\text{g P g}^{-1}$ soil)					
		Resin	Bicarbonate	NaOH	S-NaOH	HCl	Residue
Morne Prosper	H ₂ O (control)	4.98	4.61	184.13	32.01	2.89	173.28
	Oxalic acid	7.87***	8.07***	233.22*	40.47 NS	4.87**	238.36**
	PLA	7.07***	7.43***	227.87*	36.84 NS	4.51**	231.35 NS
	Citric acid	8.02***	7.87***	230.16*	43.49*	5.05**	243.76**
	Acetic acid	7.85***	6.06***	226.04*	38.65 NS	4.69**	232.11**
	SEM	0.569	0.651	9.117	1.916	0.388	12.823
	P value	0.001	0.001	0.05	0.05	0.01	0.01
Soufriere	H ₂ O (control)	6.16	6.00	170.67	30.2	2.53	143.72
	Oxalic acid	8.69 **	9.59**	185.63	37.45*	3.61	168.26
	PLA	8.84 **	8.80**	186.8	34.42 NS	3.43	160.49
	Citric acid	9.70***	9.17**	193.39	38.05*	3.79	169.58
	Acetic acid	7.96*	9.59**	185.1	36.84 NS	3.43	164.74
	SEM	0.595	0.674	3.722	1.437	0.217	4.683
	P value	0.001	0.001	NS	0.05	NS	NS
Castle Bruce	H ₂ O (control)	5.53	5.90	179.88	28.99	2.71	138.22
	Oxalic acid	8.90***	8.76***	187.33	35.03	3.79	159.67 NS
	PLA	8.12**	8.66***	185.24	33.22	3.43	163.33 NS
	Citric acid	8.66***	8.63***	189.09	35.63	3.97	180.95*
	Acetic acid	7.83**	8.66***	193.27	36.23	3.79	160.20 NS
	SEM	0.600	0.556	2.209	1.308	0.224	6.794
	P value	0.001	0.001	NS	NS	NS	0.05
Layou Valley	H ₂ O (control)	4.57	3.97	215.99	33.22	3.25	179.44
	Oxalic acid	7.36**	5.79***	234.60	42.88*	5.23	238.36*
	PLA	5.8 NS	5.95***	225.59	39.26 NS	4.69	228.13*
	Citric acid	7.89***	5.98***	235.51	44.69 *	4.87	248.5**
	Acetic acid	7.58**	5.81***	246.48	41.67 NS	4.69	230.5*
	SEM	0.631	0.384	5.126	1.988	0.339	11.930
	P value	0.001	0.001	NS	0.05	NS	0.01

Key: * = significant at $P < 0.05$; ** = significant at $P < 0.01$; *** = significant at $P < 0.001$

3.3 Maize Pot Trial

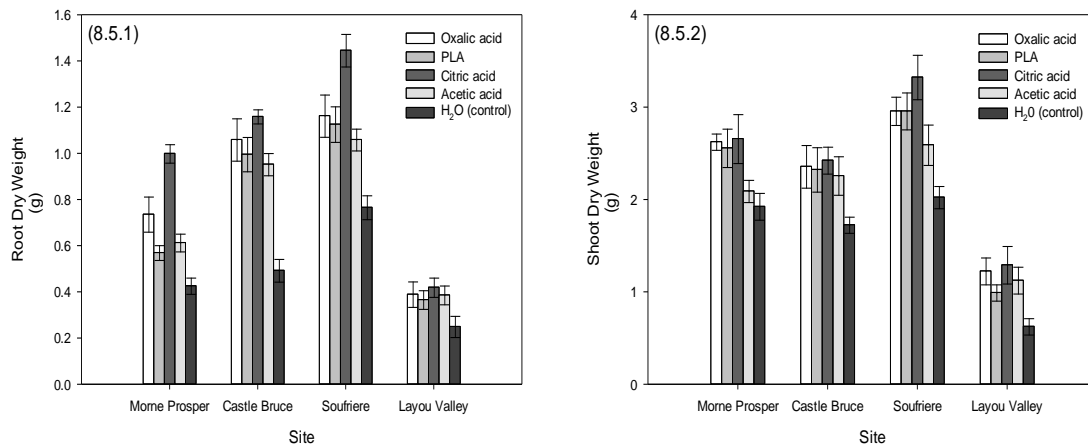


Fig. 8.5. Dry weight (g) of root (8.5.1) and shoot (8.5.2) of maize grown with rock phosphate amended with different LMWOA's on four agricultural soils of the Commonwealth of Dominica. Values represent means and error bars represent SEM. n = 60.

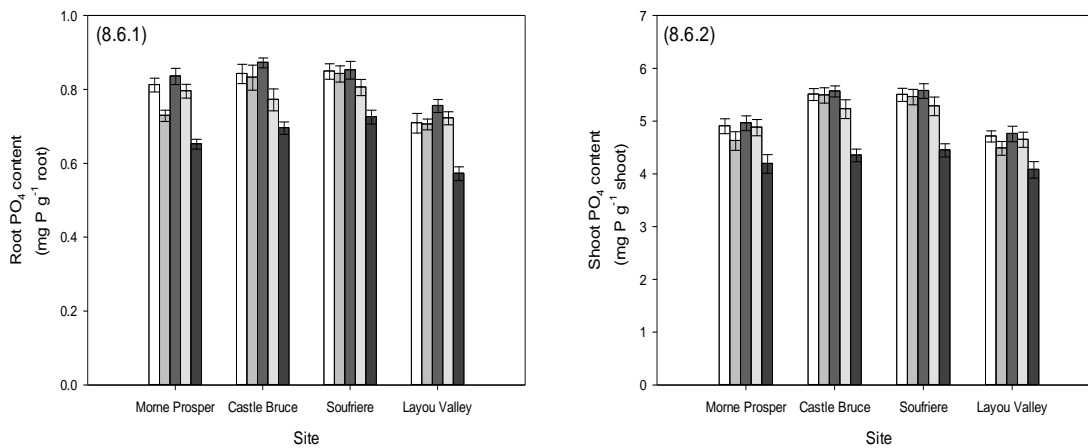


Fig. 8.6. P content (mg P g⁻¹) of root (8.6.1) and shoot (8.6.2) of maize grown with rock phosphate amended with different LMWOA's on four agricultural soils of the Commonwealth of Dominica. Values represent means and error bars represent SEM. n = 60.

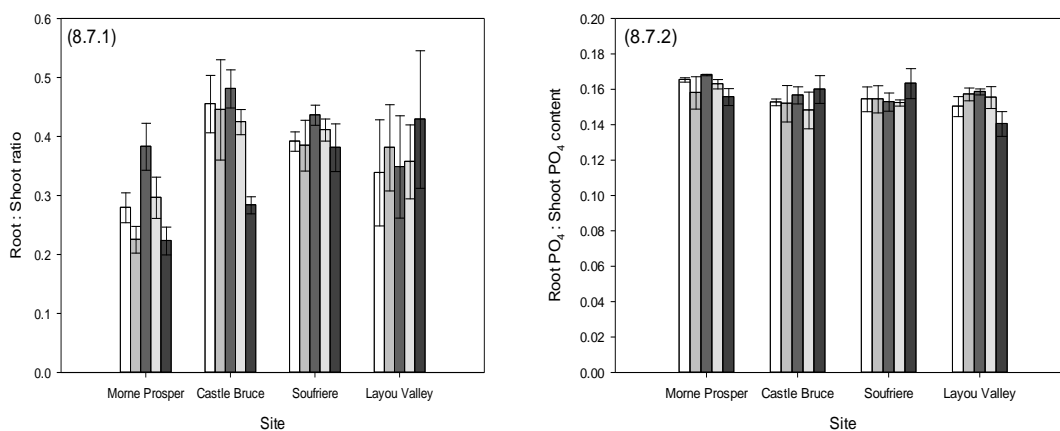


Fig. 8.7. Root: shoot ratio of dry weight (8.7.1) and PO₄ content (8.7.2) of maize grown with rock phosphate amended with different LMWOA's on four agricultural soils of the Commonwealth of Dominica. Values represent means and error bars represent SEM. n = 60.

Results for the root dry weight (Fig. 8.5.1) revealed significant differences ($P < 0.001$) between organic acids ($F(4, 59) = 42.569$, $PESq = 0.818$, $R^2 = 0.948$) as well as between sites ($F(3, 59) = 159.214$, $PESq = 0.926$, $R^2 = 0.948$). The mean dry weight was 0.77 g (0.05). Plants grown in soils amended with citric acid recorded the highest root dry weight with a mean of 1.01 g (0.10), followed by oxalic acid, 0.84 g (0.10), PLA, 0.77 g (0.10) and acetic acid, 0.75 g (0.09), which did not differ significantly among each other ($P = 0.260$). The water control recorded the lowest mean root dry weight, 0.48 g (0.06). Plants grown on soils from Soufriere had the highest mean root dry weight, 1.11 g (0.06), followed by Castle Bruce, 0.93 g (0.07), Morne Prosper, 0.67 g (0.05), and finally Layou Valley, 0.36 g (0.02).

The results for the shoot dry weight (Fig. 8.5.2) showed similar trends with significant differences ($P < 0.001$) between organic acids ($F(4, 59) = 13.561$, $PESq = 0.588$, $R^2 = 0.893$) as well as between sites ($F(4, 59) = 84.788$, $PESq = 0.870$, $R^2 = 0.893$). The mean dry weight was 2.11 g (0.10). Plants grown with the water control recorded the lowest shoot dry weight, 1.58 g (0.18). Plants grown in soils amended with acetic acid, 2.02 g (0.18), PLA, 2.21 g (0.24), oxalic acid, 2.29 g (0.21) did not significantly differ from each other ($P = 0.214$). However soils amended with citric acid, 2.43 g (0.24), not significantly differing from PLA and oxalic acid ($P = 0.442$), recorded the highest mean shoot dry weight. The results for site showed that plants grown on soils from Soufriere recorded the highest mean shoot dry weight, 2.77 g (0.14), followed by soils from Morne Prosper, 2.37 g (0.10) and Castle Bruce, 2.22 g (0.10) which did not significantly differ from each other ($P = 0.537$), with plants grown on soils from Layou Valley, 1.05 g (0.08) performing the poorest.

The results for the mean phosphate content in plant roots (Fig. 8.6.1) revealed that there was significant differences ($P < 0.001$) between organic acids ($F(4, 59) = 35.102$, $PESq = 0.789$, $R^2 = 0.871$) as well as between sites ($F(3, 59) = 32.764$, $PESq = 0.721$, $R^2 = 0.871$). The mean was 0.77 mg P g⁻¹ root (0.01). Plants grown with the water control recorded the lowest P

content, 0.66 mg P g⁻¹ root (0.02). Plants grown on soils amended with acetic acid, 0.78 mg P g⁻¹ root (0.01), PLA, 0.78 mg P g⁻¹ root (0.02), oxalic acid, 0.81 mg P g⁻¹ root (0.02), and citric acid, 0.82 mg P g⁻¹ root (0.02) did not significantly differ from each other (P = 0.166). However, plants grown on soils amended with citric acid and oxalic acid, which also did not significantly differ from each other (P = 0.882) recorded the highest root PO₄ content. Plants grown on soils from Layou Valley, 0.69 mg P g⁻¹ root (0.02) recorded the lowest P content. Plants grown on soils from Morne Prosper, 0.77 mg P g⁻¹ root (0.02) formed an independent group. Plants grown on soils from Soufriere, 0.82 mg P g⁻¹ root (0.02) and Castle Bruce which were not significantly different from each other (P = 0.813) recorded the highest P root content.

Mean phosphate in shoots (Fig. 8.6.2) displayed similar trends at the same order of magnitude (0.0065 x 10³). The results indicate that there was more accumulation of P in the shoots when compared to the roots. These results gives an indication of P use efficiency (PUE) in terms of the plants' ability to utilize soil and fertilizer P (Hedley et al., 1994; Rao et al., 1997; Horst et al., 2001; Grant at al., 2005). Nonetheless, there were significant differences (P<0.001) between organic acids (F (4, 59) = 28.257, PESq = 0.748, R² = 0.854) as well as between sites (F (4, 59) = 31.827, PESq = 0.715, R² = 0.851). The mean shoot P content was 4.94 mg P g⁻¹ shoot (0.07). Plants grown in soils with the water control had the lowest P shoot content, 4.28 mg P g⁻¹ shoot (0.08). Plants grown in soils amended with PLA, 5.02 mg P g⁻¹ shoot (0.15), acetic acid, 5.02 mg P g⁻¹ shoot (0.10), oxalic acid, 5.16 mg P g⁻¹ shoot (0.12) and citric acid, 5.22 mg P g⁻¹ shoot (0.12) were not significantly different (P = 0.277) recording the highest shoot P content. Plants grown in soils from Layou Valley, 4.54 mg P g⁻¹ shoot (0.08) and Morne Prosper, 4.72 mg P g⁻¹ shoot (0.10) were not significantly different from each other (P = 0.230) recorded the lowest shoot PO₄ content; and plants grown in soils from Soufriere, 5.26 mg P g⁻¹ shoot (0.12) and Castle Bruce, 5.24 mg P g⁻¹ shoot (0.13) recorded the highest shoot PO₄ content at a value (P = 0.993). Tukey HSD multiple comparison showed that there

were significant differences ($P < 0.001$) between the H₂O control and all the organic acids with respect to root and shoot dry weight as well as the root and shoot PO₄ accumulation.

The ANOVA for the root-to-shoot ratio (Fig. 8.7) showed a significant difference ($P < 0.01$) between sites ($PESq = 0.322$, $R^2 = 0.474$) but failed to detect any significant difference between organic acids. The root-to-shoot ratio for plants grown on soils amended with oxalic acid, 0.37 (0.03), PLA, 0.36 (0.04), citric acid, 0.41 (0.02), acetic acid, 0.37 (0.02) and the H₂O control, 0.33 (0.04) were all equal at ($P = 0.235$). However, the root-to-shoot ratio for plants grown on soils from Morne Prosper, 0.28 (0.02) and Layou Valley, 0.37 (0.03) were equal ($P = 0.067$) and recorded the lowest root-to-shoot ratios. The root-to-shoot ratio for plants grown on soils from Layou Valley were also equal to plants grown on soils from Soufriere, 0.40 (0.01), and Castle Bruce, 0.42 (0.03) at a P value ($P = 0.542$).

Tukey HSD multiple comparison showed a varied suite of relationships. The root-to-shoot ratio for plants grown on soils from Morne Prosper were significantly different from plants grown on soils from all other sites ($P < 0.01$). The root-to-shoot ratio for plants grown on soils from Castle Bruce was equal to plants grown on soils from Soufriere ($P = 0.962$) and Layou Valley ($P = 0.542$). Similar trends were observed for the root-to-shoot ratio for plants grown on soils from Soufriere being equal to plants grown on soils from Castle Bruce ($P = 0.962$) and Layou Valley ($P = 0.826$).

The results show that the root-to-shoot ratio for maize plants grown in soils with more plant available P generally had an increase in the ratio. Additionally, ANOVA failed to detect significant differences between sites as well as between organic acids in terms of the root-to-shoot PO₄ ratio (Fig. 8.7.2) and tends to suggest that PO₄ accumulation was also hindered most likely due to the low PO₄ availability/access in these soils leading to severe P starvation.

The results for the growth patterns generally show that plants grown on soils with low P adsorption capacity (Soufriere) performed better than plants grown on soils with high P

adsorption capacity (Layou Valley), notwithstanding the performance of plants grown on soils from Morne Prosper which showed promising responses. In addition, the effects of the LMWOAs showed that from the first week up till harvest, leaf emergence, stem diameter engorgement, and plant height elongation varied significantly across sites, as well as across organic acids in relation to the water control. At 7 days after transplanting, leaf emergence (Fig. 8.8) was not significantly different with a mean of 2.17 (0.06).

Plant height (Fig. 8.9) showed significant differences ($P < 0.001$, $R^2 = 0.862$) between sites ($F(3, 59) = 69.241$, $PESq = 0.845$) and significant differences ($P < 0.01$, $R^2 = 0.862$) between organic acids ($F(4, 59) = 4.677$, $PESq = 0.330$). The mean plant height was 13.62 cm (0.47). Plants grown on soils from Layou Valley, 8.23 cm (0.44) recorded the lowest height and plants grown on soils from Soufriere, 15.15 cm (0.47), Morne Prosper, 15.38 cm (0.41) and Castle Bruce, 15.72 (0.57) recorded the highest plant height without differing significantly from each other ($P = 0.791$). Very interestingly, plant height in the water control, 11.88 cm (1.11) and oxalic acid, 13.40 cm (0.84) did not differ statistically ($P = 0.196$). However, citric acid, 14.17 cm (0.97), PLA, 14.21 cm (1.14) and acetic acid, 14.44 cm (1.14) recorded the highest plant height values at ($P = 0.555$). Tukey HSD multiple comparison showed PLA and citric acid were significantly different from the water control ($P < 0.05$) while acetic acid was different from the water control at a value ($P < 0.01$).

With regards to stem diameter (Fig. 8.10), the mean was 1.58 mm (0.02). There were significant differences between plants grown in soils from the four sites ($P < 0.001$, $R^2 = 0.592$) but no observed differences between organic acids. Plants grown on soils from Morne Prosper, 1.49 mm (0.04) and Layou Valley, 1.53 mm (0.03) recorded the lowest diameter values without differing significantly from each other ($P = 0.812$) whilst plants grown on soils from Castle Bruce, 1.65 mm (0.02) and Soufriere, 1.66 mm (0.01) had the highest diameter values without differing significantly from each other ($P = 0.992$).

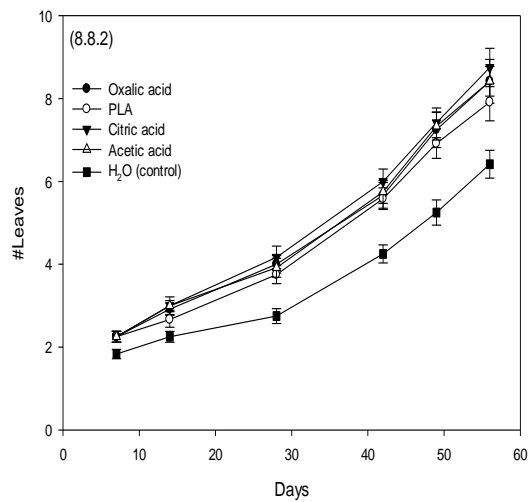
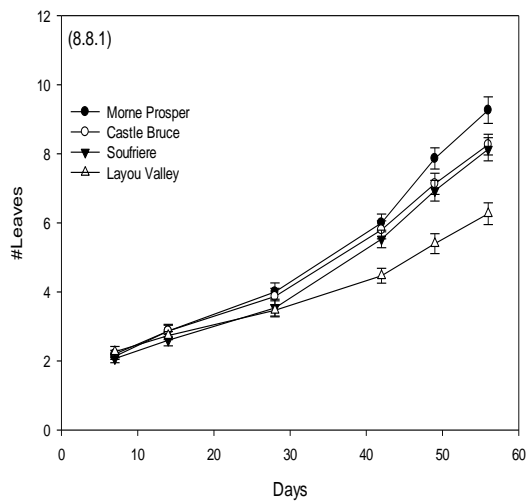


Fig. 8.8. Number of leaves of maize grown with phosphate rock amended with organic acids in four agricultural soils from the Commonwealth of Dominica. Values represent means and error bars represent SEM. n = 60.

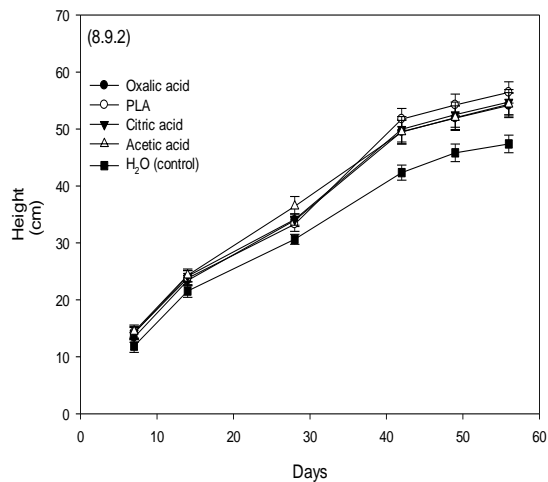
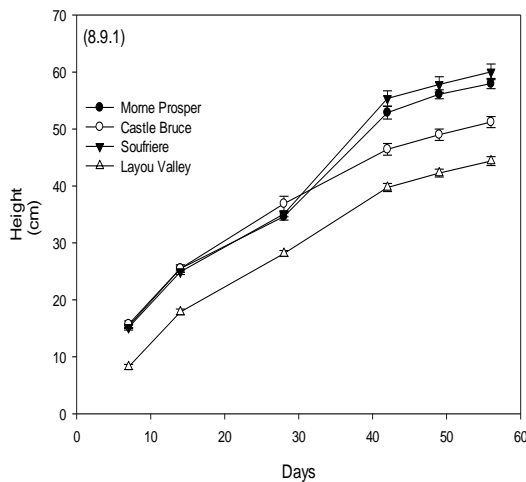


Fig. 8.9. Height (cm) of maize grown with phosphate rock amended with organic acids in four agricultural soils from the Commonwealth of Dominica. Values represent means and error bars represent SEM. n = 60.

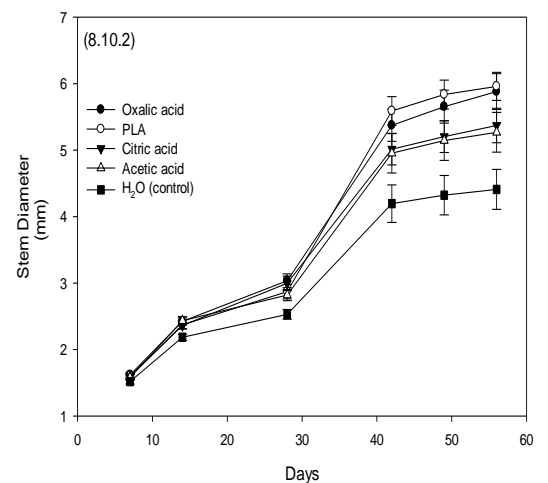
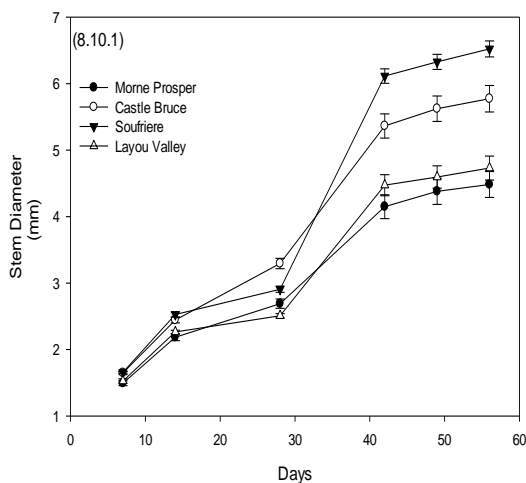


Fig. 8.10. Stem diameter (mm) of maize grown with phosphate rock amended with organic acids on four agricultural soils from the Commonwealth of Dominica. Values represent means and error bars represent SEM. n = 60.

At 14 days after transplanting, leaf emergence is non-significant between sites. There were significant differences between organic acids ($P < 0.05$, $R^2 = 0.383$, $PESq = 0.259$). The mean was 2.76 (0.08) with plants grown on soils from Soufriere, 2.60 (0.16), Morne Prosper, 2.87 (0.19), and Castle Bruce, 2.87 (0.17), and Layou Valley, 2.73 (0.12) equal. Plants grown on soils with the H₂O control, 2.25 (0.13), and plants grown on soils amended with PLA, 2.67 (0.19), and oxalic acid, 2.91 (0.15) were equal ($P = 0.075$). However plants grown on soils amended with citric acid, 3.00 (0.21) and acetic acid, 3.00 (0.12) were equal to plants grown on soils amended with PLA and oxalic acid ($P = 0.666$). Furthermore, Tukey HSD multiple comparison showed that the water control was different from oxalic and acetic acid ($P = 0.05$) but not significantly different from citric and PLA.

Plant height was significant between sites ($P < 0.001$, $R^2 = 0.859$, $PESq = 0.838$) and between organic acids ($P < 0.01$, $R^2 = 0.859$, $PESq = 0.331$). The mean was 23.44 cm (0.49). Plants grown on soils from Layou Valley were significantly different ($P < 0.001$) from plants grown on soils from the other sites. Likewise, Tukey HSD multiple comparison showed that the water control was not significantly different from oxalic acid, but significantly different from PLA ($P < 0.05$), citric and acetic acid ($P < 0.01$).

With regards to plant diameter, there were significant differences ($R^2 = 0.769$, $P < 0.001$) between sites ($PESq = 0.662$) and organic acids ($PESq = 0.457$). Plants grown on soils from Morne Prosper, 2.18 mm (0.05) and Layou Valley, 2.26 mm (0.03) were equal ($P = 0.296$), likewise plants grown on soils from Soufriere, 2.53 mm (0.04) and Castle Bruce, 2.44 mm (0.04) were equal ($P = 0.269$). More interestingly, Tukey HSD multiple comparison showed that the water control was significantly different from oxalic and acetic acid ($P < 0.001$) and also PLA and citric acid ($P < 0.01$).

Notably, at 28 days it becomes evident that organic acids had significant differences ($P < 0.001$, $R^2 = 0.518$, $PESq = 0.394$) with a stronger influence on leaf emergence when compared to site (Not Significant). The overall mean was 3.72 (0.12). The results show leaf emergence for plants grown on soils from Soufriere, 3.53 (0.26), Castle Bruce, 3.87 (0.24), Morne Prosper, 4.00 (0.26), and Layou Valley, 3.47 (0.17) were equal at ($P = 0.259$). Plants grown on soils with the H₂O control, 2.75 (0.18) were significantly different from plants grown on soils amended with PLA, 3.75 (0.22), acetic acid, 3.92 (0.23), oxalic acid, 4.00 (0.21), and citric acid, 4.20 (0.27) all being equal at a P value ($P = 0.690$). However Tukey HSD multiple comparison showed that the H₂O control was significantly different from PLA ($P < 0.05$), and from oxalic and acetic acid ($P < 0.01$) and as well from citric acid ($P < 0.001$).

Plant height (Fig. 8.9) was significant ($P < 0.001$, $R^2 = 0.879$) between sites ($PESq = 0.819$) and organic acid ($PESq = 0.587$). The overall mean was 33.70 cm (0.58). Tukey HSD multiple comparison showed that the water control was significantly different from oxalic and citric acid ($P < 0.01$), and from PLA ($P < 0.05$) and surprisingly from acetic acid ($P < 0.001$). The results for the stem diameter (Fig. 8.10) with an overall mean of 2.85 mm (0.05) showed similar trends in that there were significant differences ($P < 0.001$, $R^2 = 0.932$) between sites ($PESq = 0.904$), and organic acids ($PESq = 0.777$). Tukey HSD multiple comparison showed significant differences ($P < 0.001$) between all sites and all organic acids in comparison to the H₂O control.

At 56 days after transplanting (harvest), with a mean of 7.98 (0.22), there were significant differences ($P < 0.001$, $R^2 = 0.784$) for leaf emergence between sites ($PESq = 0.664$) and organic acids ($PESq = 0.535$). Plants grown on soils from Layou Valley, 6.27 (0.32) recorded the lowest number of leaves whilst plants grown on soils from Morne Prosper, 9.27 (0.38) recorded the highest number of leaves. Plants grown on the water control, 6.42 (0.34) recorded the lowest number of leaves; and plants grown on soils treated with PLA, 7.91 (0.45), oxalic acid, 8.42 (0.53), acetic acid, 8.42 (0.36), and citric acid, 8.75 (0.46) recorded the highest

number of leaves at a P value ($P = 0.238$). Tukey HSD multiple comparison showed that the water control was significantly different from PLA ($P < 0.01$) and significantly different from acetic, citric, and oxalic acid ($P < 0.001$).

There were also significant differences ($P < 0.001$, $R^2 = 0.920$) between sites (PESq = 0.884) and organic acids (PESq = 0.749) with regards to stem diameter, with a mean of 5.38 mm (0.14). Plants grown on soils from Morne Prosper, 4.48 mm (0.19) and Layou Valley, 4.73 mm (0.18) recorded the lowest values at ($P = 0.282$), with plants grown on soils from Soufriere, 6.52 mm (0.12) recording the highest stem diameter. The results for the organic acids show that plants grown in the water control, 4.41 mm (0.30) recorded the lowest stem diameter values, whilst acetic acid, 5.27 mm (0.30) and citric acid, 5.37 mm (0.26) constituted an independent homogeneous group ($P = 0.961$). Plants grown in soils amended with oxalic acid, 5.88 mm (0.27) and PLA, 5.96 mm (0.21) recorded the highest stem diameter values at ($P = 0.985$). However Tukey HSD multiple comparison showed that all the organic acids were significantly different from the water control ($P < 0.001$).

Results for plant height were significantly different ($P < 0.001$, $R^2 = 0.938$) between sites (PESq = 0.921) and organic acid (PESq = 0.749). Plants grown in soils from Morne Prosper, 58.0 cm (0.89) and Soufriere, 60.04 cm (1.37) recorded the highest plant height ($P = 0.080$). Plants grown on soils from Layou Valley recorded the lowest plant height, 44.38 cm (0.78). The overall mean was 53.41 cm (0.94). Plants grown in soils amended with oxalic acid, 54.14 cm (2.13), acetic acid, 54.34 cm (2.05), citric acid, 54.73 cm (2.21), and PLA, 56.43 cm (1.87) were equal ($P = 0.118$) but different from the water control, 47.38 cm (1.54). In effect, the Tukey HSD multiple comparison showed that all the organic acids were significantly different from the water control ($P < 0.001$).

3.3.1 Determination of plant available P

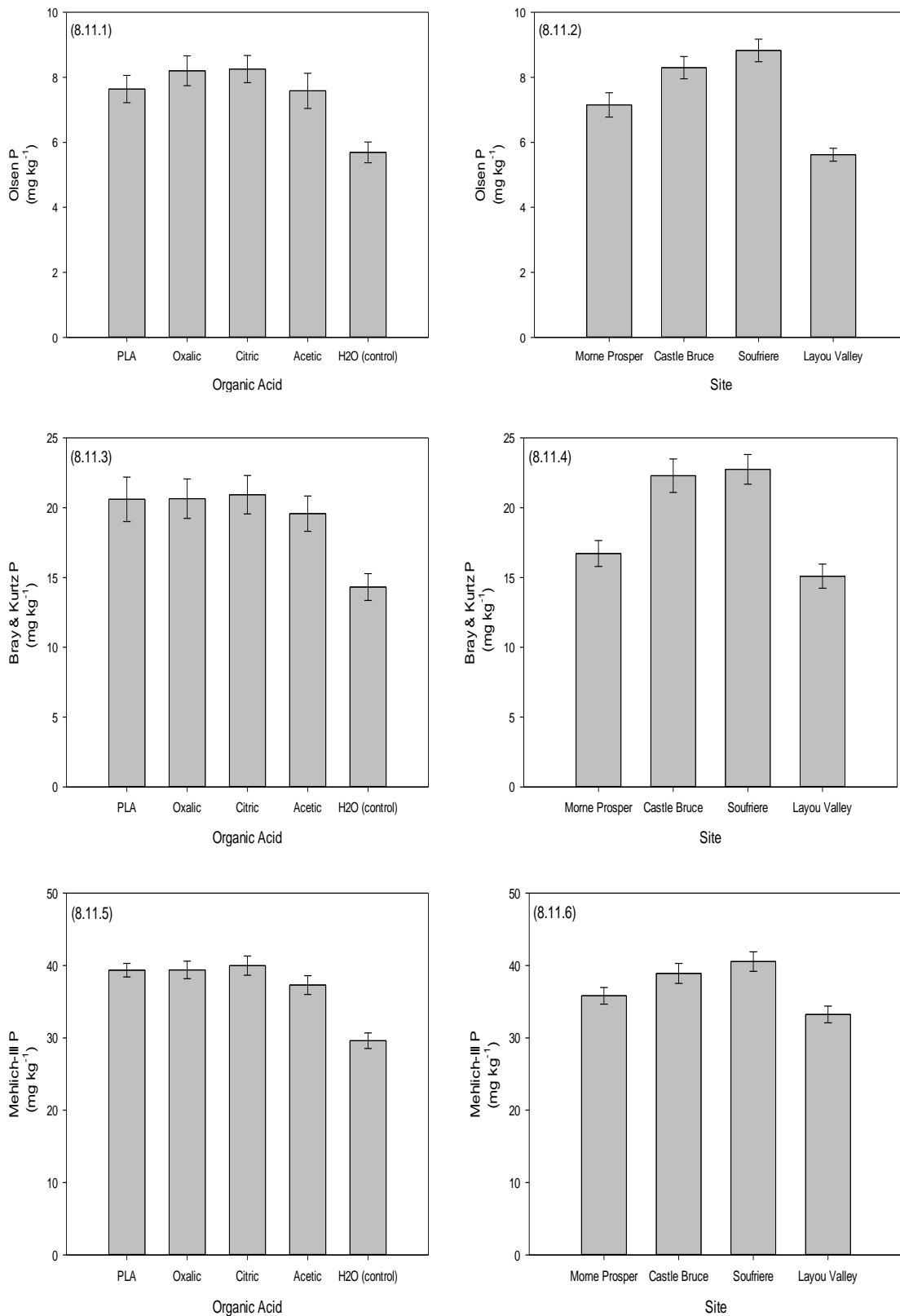


Fig. 8.11. Olsen, Bray & Kurtz and Mehlich-III extractable P (mg kg⁻¹) P of four agricultural soils from the Commonwealth of Dominica fertilized with rock phosphate and amended with organic acids used for the growing of maize. Values represent means and error bars represent SEM. n = 60.

The various P extraction methods show that the Olsen P method extracted the least amount of available P whilst the Mehlich-III method extracted the most (Fig. 8.11). The ANOVA showed significant differences ($P < 0.001$, $R^2 = 0.854$) between sites ($PESq = 0.777$) and organic acids ($PESq = 0.668$) with regards to Olsen extractable P. The mean was $7.47 \text{ mg P kg}^{-1}$ (0.22). Soils from Layou Valley, $5.62 \text{ mg P kg}^{-1}$ soil (0.20) extracted the least amount of P while soils from Castle Bruce, $8.30 \text{ mg P kg}^{-1}$ soil (0.34), and Soufriere, $8.83 \text{ mg P kg}^{-1}$ soil (0.35) equal at ($P = 0.313$) extracted the most amount of P. Soils from Morne Prosper, $7.15 \text{ mg P kg}^{-1}$ soil (0.37) formed an independent subset. The H_2O control extracted the least amount of P, $5.69 \text{ mg P kg}^{-1}$ soil (0.32) with acetic acid, $7.59 \text{ mg P kg}^{-1}$ soil (0.54), PLA, $7.64 \text{ mg P kg}^{-1}$ soil (0.42), oxalic acid, $8.20 \text{ mg P kg}^{-1}$ soil (0.46), and citric acid, $8.26 \text{ mg P kg}^{-1}$ soil (0.42) all being equal at ($P = 0.292$). Tukey HSD multiple comparison showed significant differences between the H_2O control and all the organic acids ($P < 0.001$).

Similar trends were observed for Bray & Kurtz extractable P, with a mean of $19.22 \text{ mg P kg}^{-1}$ soil (0.66), ANOVA showed significant differences ($P < 0.001$) between sites ($PESq = 0.612$, $R^2 = 0.724$) and organic acids ($PESq = 0.465$, $R^2 = 0.724$). Soils from Layou Valley, $15.09 \text{ mg P kg}^{-1}$ soil (0.87) and Morne Prosper, $16.72 \text{ mg P kg}^{-1}$ soil (0.93) extracted the least amount of P, being equal at ($P = 0.554$). Soils from Castle Bruce, $22.40 \text{ mg P kg}^{-1}$ soil (1.20) and Soufriere, $22.75 \text{ mg P kg}^{-1}$ soil (1.06) recorded the highest P extraction values being equal at ($P = 0.982$). However, the Tukey HSD multiple comparison between the H_2O control and acetic acid showed a significant difference ($P < 0.01$) and the H_2O control and oxalic, PLA and citric acid ($P < 0.001$). Likewise, for the Mehlich-III extractable P, there were significant differences ($P < 0.001$, $R^2 = 0.778$) between sites ($PESq = 0.541$) and organic acids ($PESq = 0.690$). It can be noted that for the Olsen, and Bray & Kurtz extractable P, site was a significant driver. Conversely for the Mehlich-III extractable P, the influence of organic acid was more a driver as can be appreciated from the respective partial eta square ($PESq$) values.

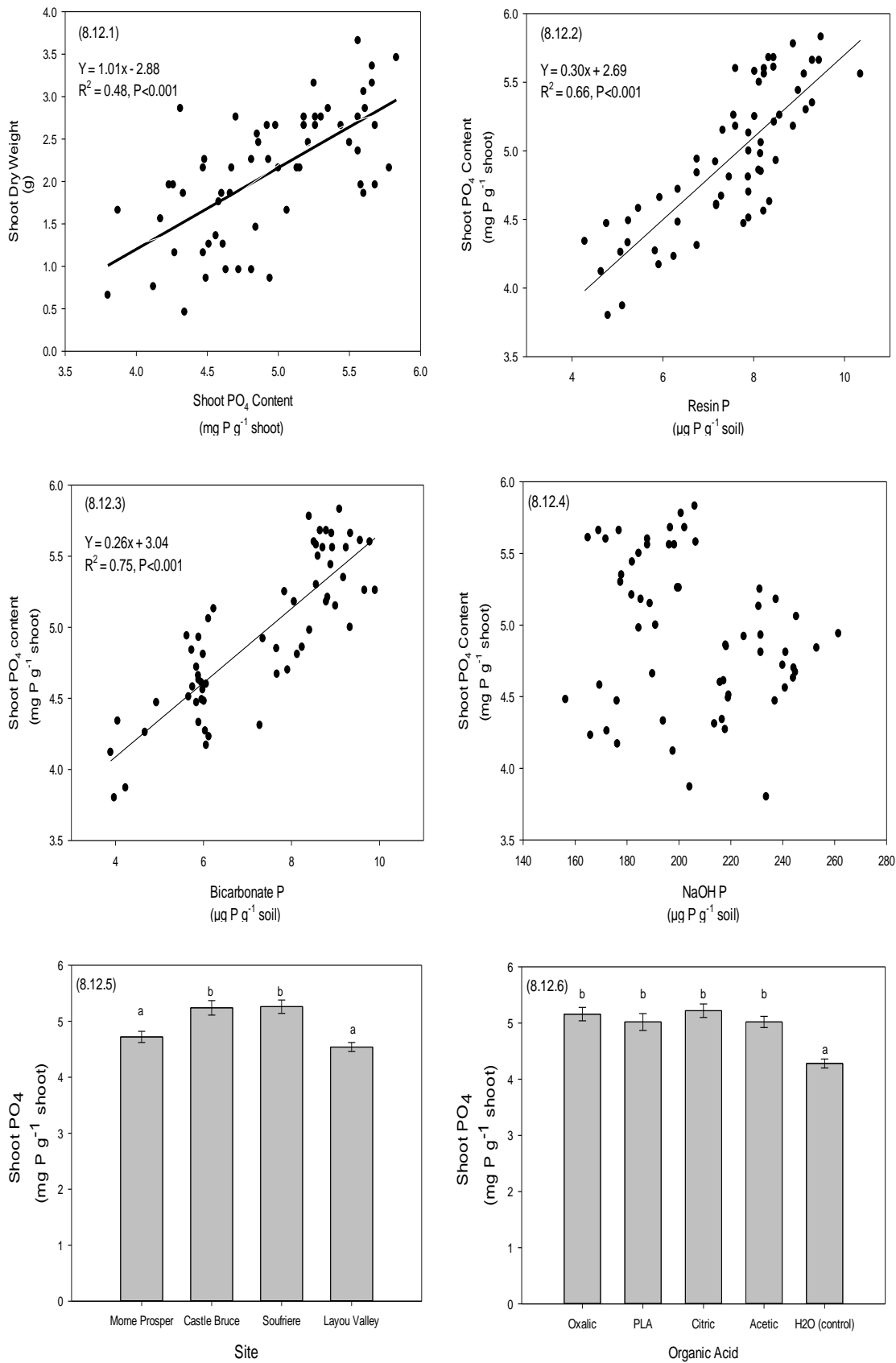


Fig. 8.12. Relationship between shoot PO₄ content and shoot dry weight; shoot PO₄ content in function of selected fractions of the Hedley sequential P extraction; and effect of organic acids on P uptake by maize. Correlation significant at $P < 0.001$, $n = 60$.

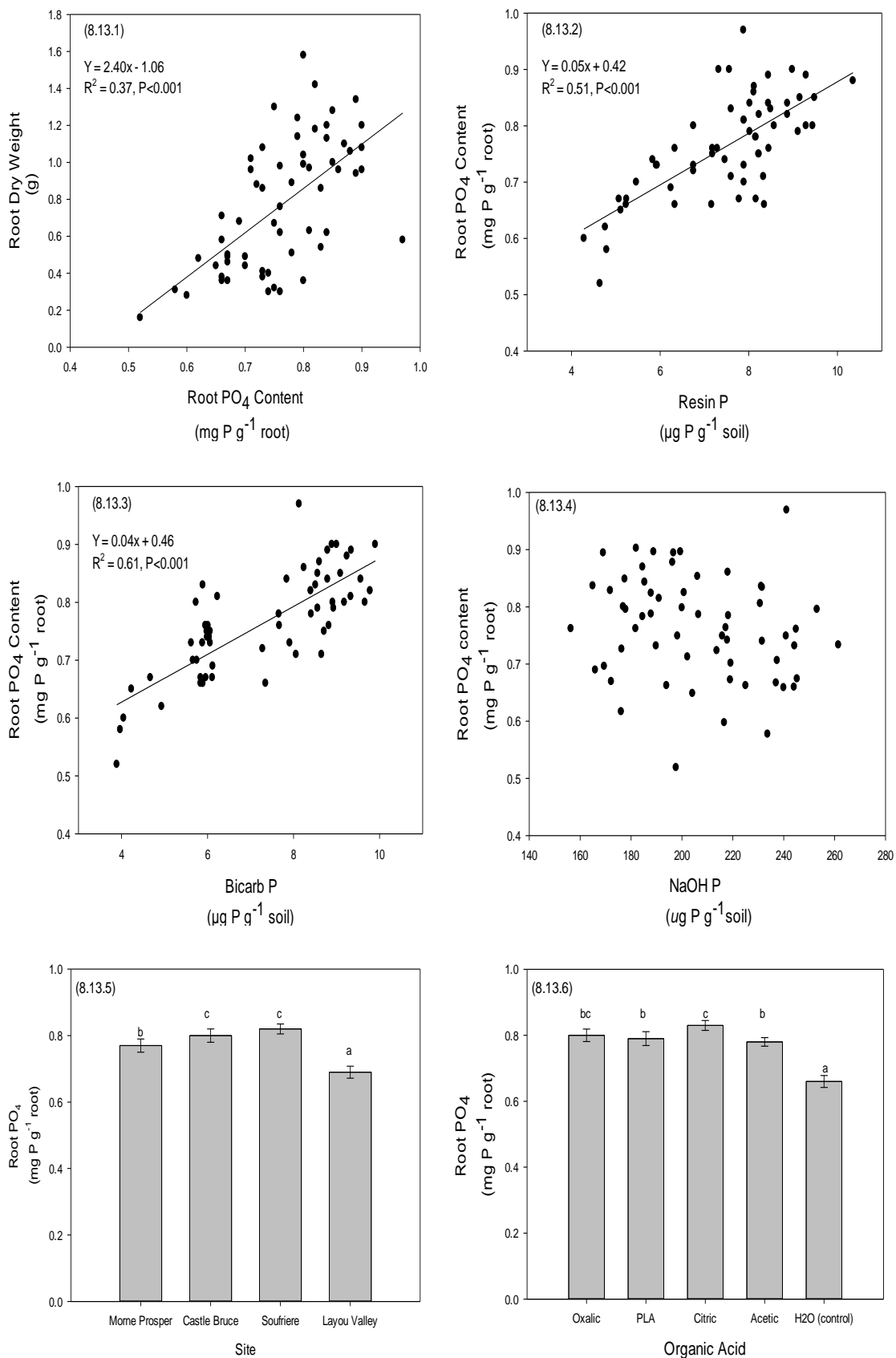


Fig. 8.13. Relationship between root PO₄ content (mg g⁻¹) and root dry weight (g); root PO₄ content in function of selected fractions of the Hedley sequential P extraction; and effect of organic acids on P uptake by maize. Correlation significant at $P < 0.001$. $n = 60$.

The relationship between shoot dry weight (g) and shoot PO₄ content (mg g⁻¹) showed a significant positive correlation (P<0.001). The fit of the curve (Fig. 8.12.1) tend to suggest that dry matter production, although showing tendencies to be linearly related to shoot PO₄ content was somewhat initially hindered (as can be seen from the distribution of the points) most probably at the expense of other metabolic processes, and hence an indication of P starvation. It can be observed that with subsequent increase in shoot PO₄ content (4.5 – 5.5 mg P g⁻¹ shoot), dry matter accumulation increases but reaches a peak where increasing shoot PO₄ content marginally translate to increases in shoot dry matter, with a number of points not following the trajectory. This underscores the importance of a balanced nutrient supply for adequate plant growth especially for heavy feeders like maize, tomato, and peppers.

However, the relationship with regards to shoot PO₄ content and the various fractions of the Hedley sequential P extraction has strongly underscored the general consensus that plant available P is primarily bound to the resin and bicarbonate fractions (Tiessen et al., 1984; Tiessen and Moir, 1993; Hedley et al., 1994; Cross and Schlesinger, 1995; Johnson et al., 2003; Shen et al., 2011). In the short term, biological processes influence P distribution because most of the plant-available P is derived from SOM as can be appreciated from the stronger correlation coefficient value for bicarbonate P. Shoot PO₄ content was positively correlated to resin P (P<0.001, R²= 0.66), and bicarbonate P (P<0.001, R² = 0.72) but failed to establish any significant relationship with NaOH P, Sonic NaOH P, HCl P and Residue P (Fig. 8.12.4).

Similar trends were observed for the relationship between root dry matter content and root PO₄ content (Fig. 8.13). The relationship yielded a significant (P<0.001) correlation coefficient. However, equally important was the relationship between root PO₄ content and the Hedley resin P (P<0.001); and root PO₄ content and the Hedley bicarbonate P (P<0.001). Analogous to the above mentioned, there was no significant relationship with between root PO₄ content and NaOH P, and the lower refractory fractions (Fig. 8.13.4).

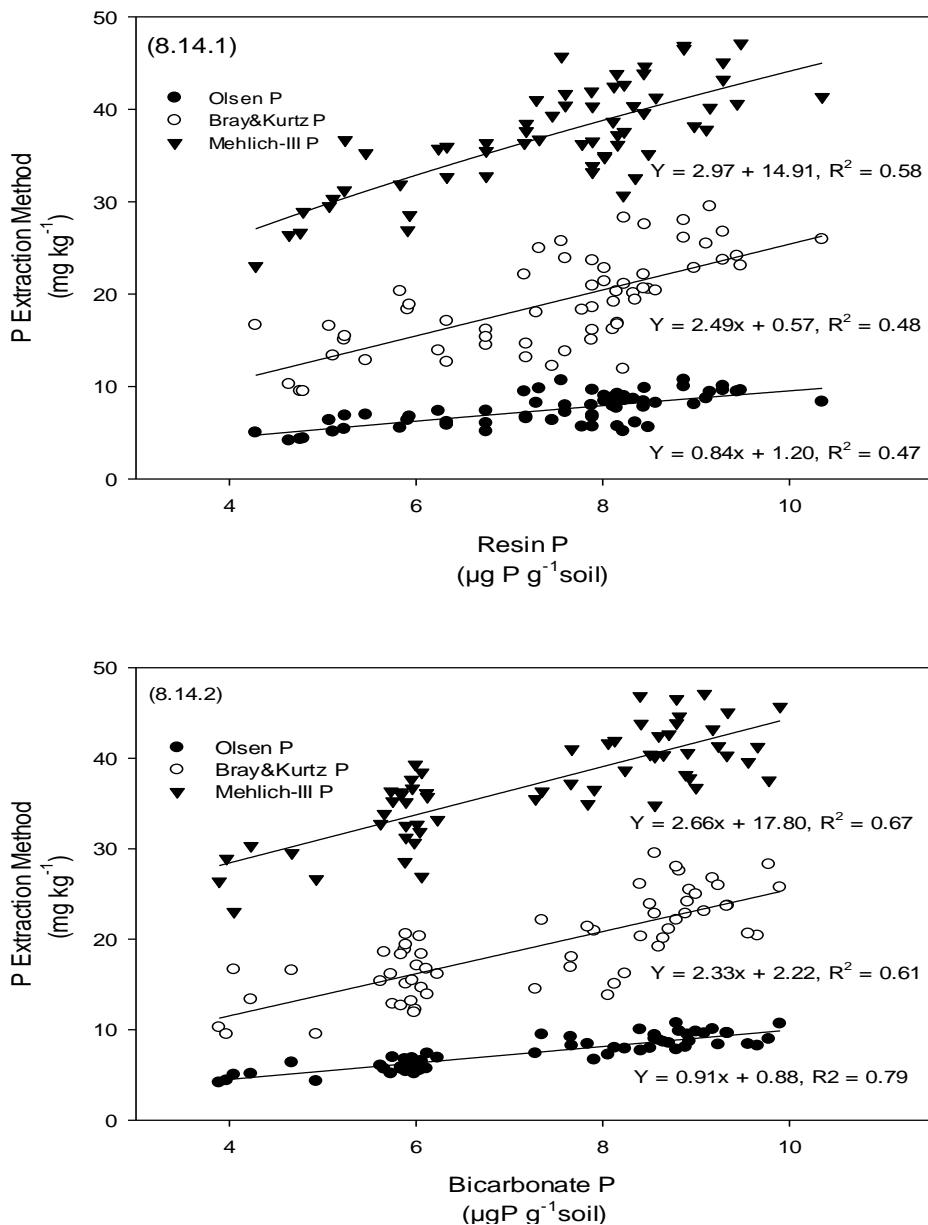


Fig. 8.14. Relationship between Resin P and Olsen, Bray & Kurtz, and Mehlich-III P (8.14.1) and Bicarbonate P and Olsen, Bray & Kurtz, and Mehlich-III P (8.14.2). Correlation significant at $P < 0.001$, $n = 60$.

The relationship between resin P and the various P extraction methods (Fig. 8.14.1) showed significant correlation ($P < 0.001$). The Mehlich-III P extraction method showed the strongest relationship amongst the three methods with the Olsen P extraction method and Bray & Kurtz P extraction method behaving similar. The bicarbonate fraction (Fig. 8.14.2) showed a stronger correlation with the various P extraction methods as compared to the resin fraction as can be appreciated from the R^2 values. With regards to the resin fraction, it can be noticed

that the Bray & Kurtz P extraction method behaved very similar to the Olsen P extraction method. However the Mehlich-III P extraction procedure yielded the strongest correlation coefficient. On the contrary, the Olsen P extraction method yielded the strongest relationship with regards to the bicarbonate fraction. This is most likely due to the equivalence of the procedure whereby 0.5 M NaHCO₃ (pH 8.5) is used as the extractant in both procedures.

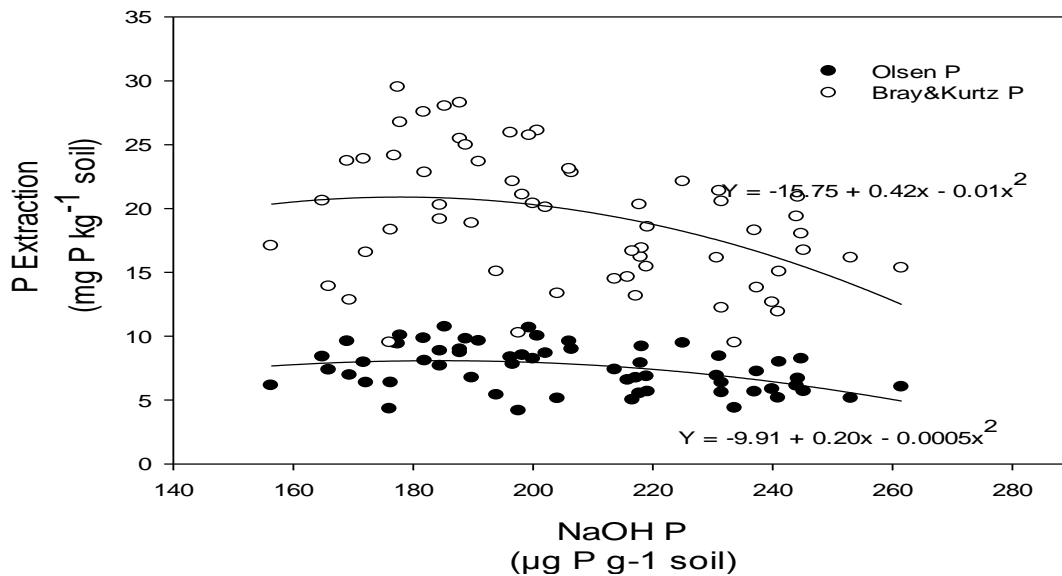


Fig. 8.15. Relationship between NaOH P fraction and Olsen and Bray & Kurtz extractable P. Correlation significant at $P < 0.01$, $n = 60$. No significant relationship encountered between NaOH P and Mehlich-III P.

There was no observed significant relationship of the various lower P fractions with the Olsen, Bray & Kurtz, and Mehlich-III P extraction procedures as was suspected given the results of shoot PO₄ content with these lower P fractions. In particular the Mehlich-III P method showed no relationship. However quite interestingly, the exception was a very weak negative yet significant relationship ($P < 0.01$, $R^2 = 0.187$) between the NaOH P fraction and the Olsen P extraction procedure as well as a very weak negative yet significant relationship ($P < 0.01$, $R^2 = 0.151$) between the NaOH P fraction and the Bray & Kurtz P extraction procedure. These results inconclusively tend to suggest that as plant available P pools are gradually exhausted, the refractory pools of P will become increasingly more dominant and hence more important in P availability (i.e. NaOH, Sonic NaOH P and HCl pools).

3.4 ^{33}P mobilization studies and LMWOAs

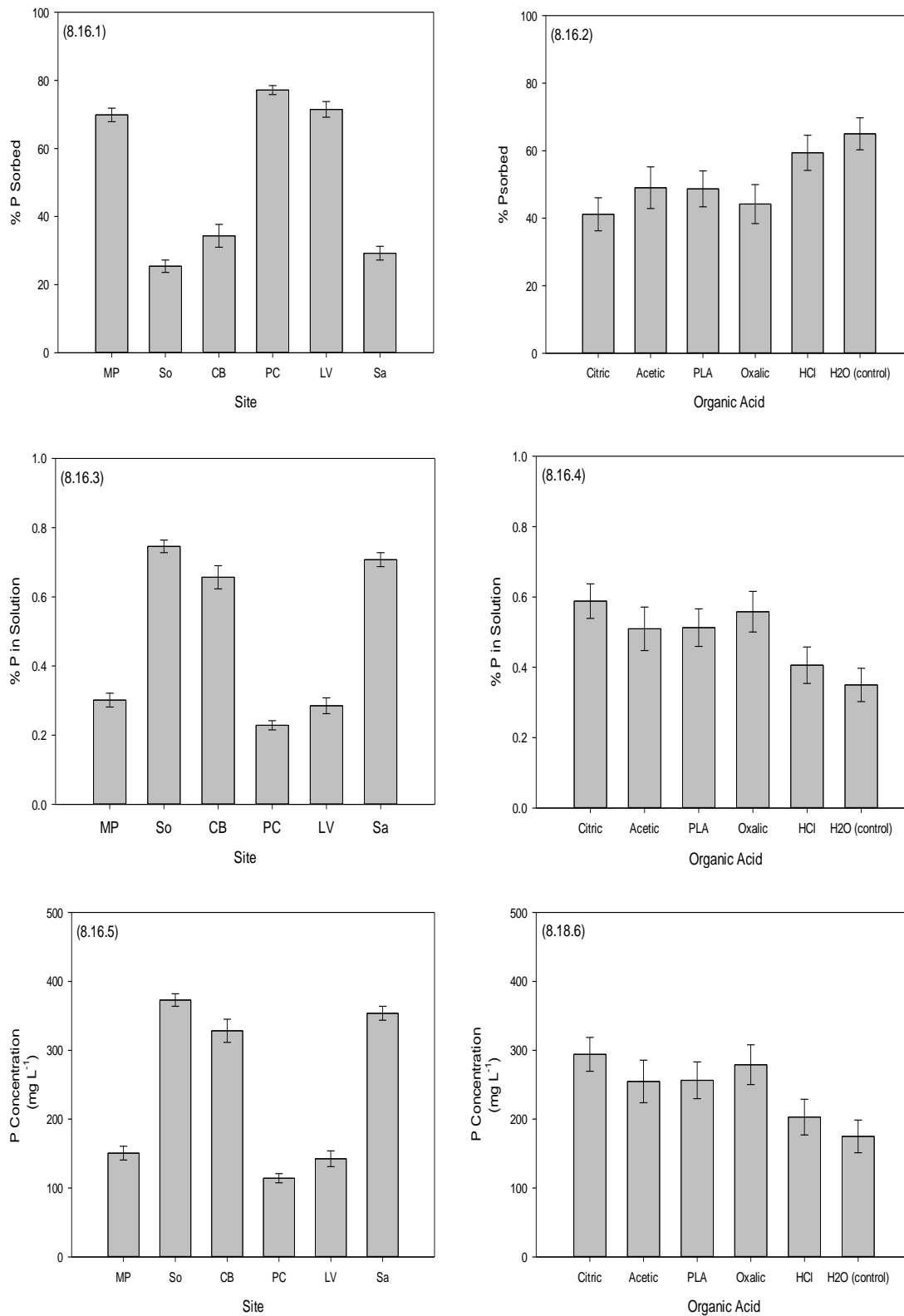


Fig. 8.16. Percentage P sorbed, percentage P in solution, and P concentration (8.14.2) in six agricultural soils from the Commonwealth of Dominica treated with 10 mM oxalic, citric, PLA, acetic, hydrochloric acid and a water control. ^{33}P labelled as $\text{KH}_2^{33}\text{PO}_4$ (0.17 kBq). Values represent means and error bars represent SEM. $n = 108$.

The analysis of variance (ANOVA) for percentage P sorbed revealed significant differences ($P < 0.001$, $R^2 = 0.996$) between sites ($F(5, 107) = 2761$, $PESq = 0.995$), organic acids ($F(5, 107) = 403.859$, $PESq = 0.966$), as well as the interaction between site and organic acid ($F(25, 107) = 13.490$, $PESq = 0.828$). The mean % P sorbed was 51.25% (2.29). Tukey HSD established five homogeneous subsets. Soils from Soufriere recorded the least percentage of P sorbed, 25.41% (1.82), followed by Salisbury, 29.24% (2.02), Castle Bruce, 34.34% (3.36), Morne Prosper, 69.86% (2.00) and Layou Valley, 71.49% (2.29) being equal at a value of ($P = 0.129$) and finally Pond Cassé, 77.15% (1.33) with the highest percentage P sorbed.

With regards to organic acids, Tukey HSD established five homogeneous subsets. Citric acid sorbed the least percentage P, 41.16% (4.91), followed by oxalic acid, 44.18% (5.78). PLA and acetic acid were not significantly different ($P = 0.995$) sorbing 48.70% (5.33) and 49.04% (6.19) respectively. The HCl positive control sorbed a mean percentage of 59.39% (5.20), highlighting the ineffectiveness of mineral acids when compared to organic acids, with the negative water control sorbing 65.02% (4.74).

The data tends to suggest that the LMWOAs were much more effective at sites with low P sorbing capacity (Fig. 8.16). In this regard the percentage P in solution as well as the P concentration (mg L^{-1}) is higher in soils from Soufriere, Salisbury, and to a lesser extent Castle Bruce reflected by the lower values for the mass of P sorbed (mg g^{-1}), hence the tendency to tentatively separate these volcanic soils into two distinct groups. In addition, soils properties tend to differ much more between these two groups of soils rather than within them. The inverse of this relationship is underscored by a lower percentage of P in solution as well as a lower P concentration in soils from Pond Cassé and Layou Valley reflected by the higher values for the mass of P sorbed. The results also tend to suggest that the degree of P availability is also dependent on type of acid. However, it should be noted that concentration, pH, and contact time with soil may well be important drivers in these soils (Johnson et al., 2003).

3.4 Maize Rhizotube Trial.

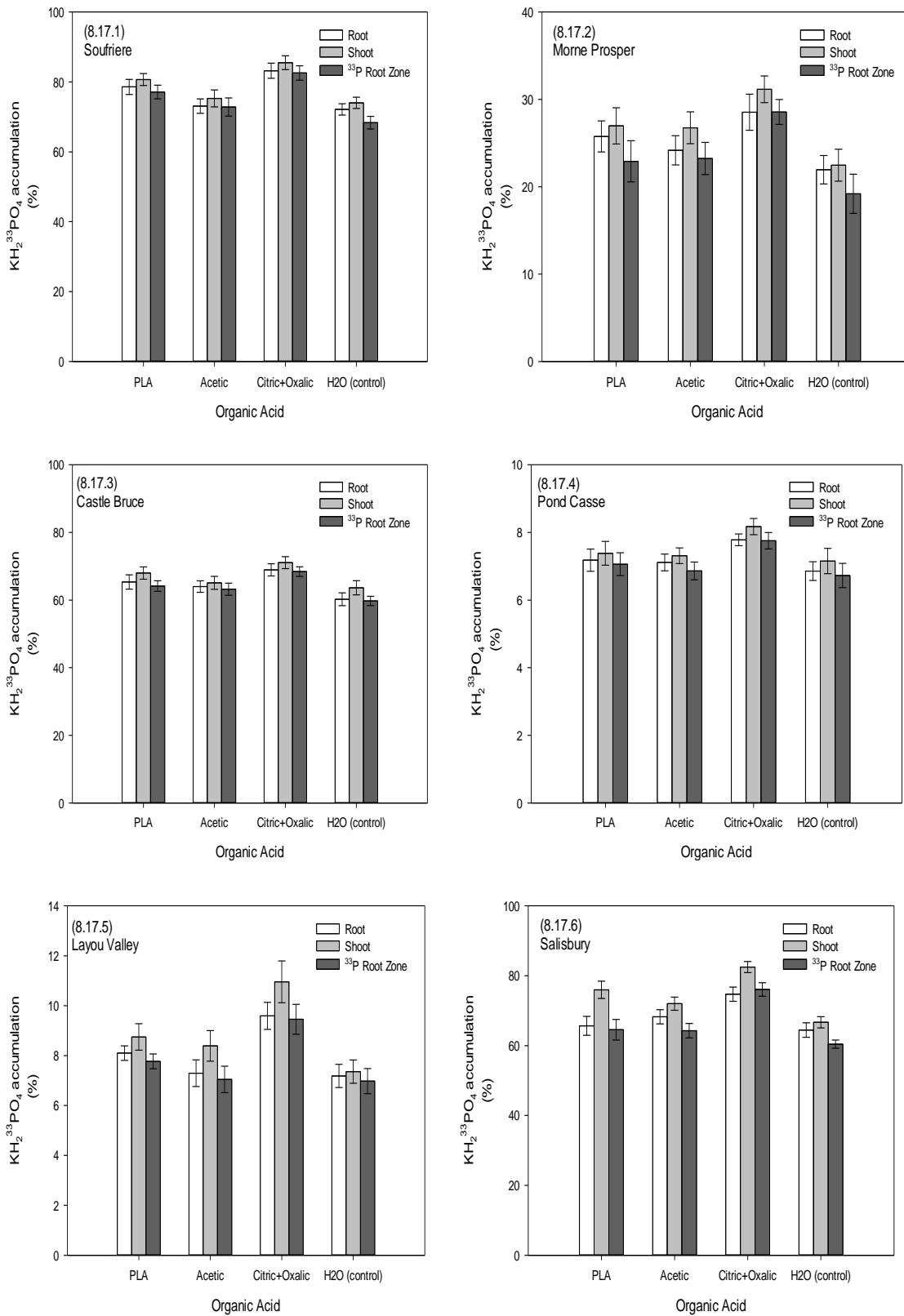


Fig. 8.17. Accumulation of $\text{KH}_2^{33}\text{PO}_4$ in maize roots, shoots, and ^{33}P labelled root zone, following growth of plants in six agricultural soils from the Commonwealth of Dominica to which either deionized water (control) or organic acids were added. Values represent means and error bars represent SEM. $n = 16$.

The analysis for $\text{KH}_2^{33}\text{PO}_4$ accumulation was approached in two ways. The first was to analyse the data where the sources of variation ($n = 96$) included site, organic acid and the interactions. With this approach it was expected and assumed that the influence of site would be a significant driver in terms of $\text{KH}_2^{33}\text{PO}_4$ accumulation based on the P-sorption capacity of these different soils, and as such the relative effect of the various organic acids within each individual site would not be fully understood.

However, with the experimental evidence that there exist significant differences between these various sites with regards to pH NaF, Fe- and Al-oxyhydroxide content, P adsorption capacity, base saturation, and CEC among other soil parameters studied, as a second approach, it was decided to single out site as a source of variation and analyse each site individually in relation the effect of the application of organic acids ($n = 16$). By so doing the effectiveness of the LMWOAs could be better understood in comparison to the control.

In the first approach, the results show significant differences ($P < 0.001$, $R^2 = 0.991$) with regards to root $\text{KH}_2^{33}\text{PO}_4$ accumulation between sites ($F(5, 95) = 1466.18$, $\text{PESq} = 0.991$) and organic acid ($F(3, 95) = 17.11$, $\text{PESq} = 0.427$). There was no significant interaction between site and organic acid. The mean was 41.68% (3.01). Post Hoc analysis established five homogeneous subsets. Plants grown on soils from Pond Cassé, 7.23% (0.15) and Layou Valley, 8.04% (0.32) did not differ from each other ($P = 0.983$) and recorded the lowest $\text{KH}_2^{33}\text{PO}_4$ root accumulation percentage. Plants grown on soils from Soufriere, 76.76% (1.46) recorded the highest $\text{KH}_2^{33}\text{PO}_4$ root accumulation percentage. Tukey HSD multiple comparison revealed that there were significant differences between all sites ($P < 0.001$) with the exception of the Salisbury compared to the Castle Bruce site ($P = 0.032$). The water control, 38.81% (5.76) and acetic acid, 40.66% (5.97) which did not significantly differ ($P = 0.225$) recorded the lowest root $\text{KH}_2^{33}\text{PO}_4$ accumulation. PLA, 41.77% (6.10) and acetic acid did not differ from each other ($P = 0.652$) and constituted a separate homogeneous group. The

citric+oxalic combination, 45.46% (6.52) recorded the highest root $\text{KH}_2^{33}\text{PO}_4$ accumulation. Tukey HSD multiple comparison showed that the H_2O control was significantly different from PLA ($P = 0.015$) and the citric+oxalic acid combination ($P < 0.001$).

Similar results were obtained for shoot $\text{KH}_2^{33}\text{PO}_4$ accumulation. There were significant differences ($P < 0.001$; $R^2 = 0.992$) between sites ($F(5, 95) = 1771.33$, $\text{PESq} = 0.992$), organic acid ($F(3, 95) = 17.11$, $\text{PESq} = 0.427$), and the interaction of site with organic acid ($P = 0.01$). The mean shoot $\text{KH}_2^{33}\text{PO}_4$ accumulation was 43.89% (3.15). There were five homogeneous subsets with plants grown on soils from Pond Cassé, 7.51% (0.17) and Layou Valley, 8.86% (0.44) recording the lowest values and being equal ($P = 0.828$). Plants grown on soils from Soufriere, 78.87% (1.47) recorded the highest shoot $\text{KH}_2^{33}\text{PO}_4$ values. Tukey HSD multiple comparison also showed significant differences between all sites ($P < 0.001$) with the exception of the Salisbury compared to the Soufriere site ($P < 0.01$). The water control, 40.22% (5.97) and acetic acid, 42.47% (6.11) equally recorded the lowest shoot $\text{KH}_2^{33}\text{PO}_4$ accumulation values ($P = 0.073$). Additionally, PLA, 44.63% (6.52) and acetic acid were equal ($P = 0.094$). However the combination of citric+oxalic acid, 48.23% (6.81) recorded the highest shoot $\text{KH}_2^{33}\text{PO}_4$ accumulation percentage. Tukey HSD multiple comparison showed that both PLA and the citric+oxalic acid combination were significantly different from the water control ($P < 0.001$).

With regards to the labelled ^{33}P root zone, there were significant differences ($P < 0.01$; $R^2 = 0.991$) between sites ($F(5, 95) = 1447.49$, $\text{PESq} = 0.991$), organic acid ($F(3, 95) = 28.42$, $\text{PESq} = 0.553$), and the interaction of site with organic acid ($P < 0.05$). The mean labelled ^{33}P root $\text{KH}_2^{33}\text{PO}_4$ accumulation was 40.64% (2.97). Plants grown on soils from Pond Cassé, 7.10% (0.17) and Layou Valley, 7.81% (0.34) recorded the lowest values, being equal at ($P = 0.990$). Plants grown on soils from Morne Prosper, 23.48% (1.24) formed an independent group. Plants grown on soils from Castle Bruce, 63.89% (1.06) and Salisbury, 66.33% (1.79)

also formed an independent group. However plants grown on soils from Soufriere, 75.22% (1.66) recorded the highest PO₄ accumulation in the labelled roots. Tukey HSD multiple comparison established significant differences between sites (P<0.01) with the exception of the Salisbury and Castle Bruce sites (P = 0.30). The water control, 36.91% (5.53) recorded the lowest PO₄ accumulation values in the labelled roots. Plants grown in soils amended with acetic acid, 39.58% (5.85) and PLA, 40.60% (6.04) formed an independent group. However plants grown on soils amended with the combination of citric+oxalic acid, 45.47% (6.53) recorded the highest PO₄ accumulation values in the labelled roots. Tukey HSD showed significant differences between the H₂O control and acetic acid (P = 0.031), PLA (P = 0.01), and the combination citric+oxalic acid (P<0.001).

The results for KH₂³³PO₄ accumulation using the second approach where n = 16, showed a matrix of mixed results (Fig. 8.17). Plants grown on soils from Soufriere showed significant differences between organic acids with regards to KH₂³³PO₄ accumulation in the roots, shoots and the ³³P labelled root zone. In terms of root behaviour, there were significant differences (P < 0.01, R² = 0.72, PESq = 0.687) between organic acids. The mean was 76.76% (1.46). Plants grown in the water control, 72.15% (1.62), and plants grown in soils amended with acetic acid, 73.10% (2.06), and PLA, 78.58% (2.16) were equal at (P = 0.177). Plants grown on soils amended with PLA, acetic acid and the combination of citric+oxalic acid, 83.21% (2.15) were also equal at (P = 0.410). However with respect to the control, the Tukey HSD multiple comparison showed that the citric+oxalic combination had a significant difference at P = 0.02.

There were also significant differences (P<0.01, R² = 0.69, PESq = 0.687) between organic acids in the ³³P labelled root zone. The water control, 68.35% (1.81), acetic acid, 72.83% (2.59), and PLA, 77.13% (1.95) were equal at (P = 0.105). The citric+oxalic combination, 82.57% (2.07), acetic acid and PLA were also equal at (P = 0.07). The mean was

75.22% (1.66). With respect to the control, the Tukey HSD multiple comparison showed that the citric+oxalic combination had a significant difference at $P < 0.01$.

Additionally, the ANOVA analysis detected significant differences ($P < 0.01$, $R^2 = 0.73$, $PESq = 0.704$) in $KH_2^{33}PO_4$ accumulation in the shoots. With a mean of 78.87% (1.47), plants grown on soils amended with the combination of citric+oxalic acid, 85.51% (1.98), PLA, 80.69% (1.71), and acetic acid, 75.28% (2.43) were equal at ($P = 0.367$). The water control, 74.01% (1.60), acetic acid and PLA were also equal at ($P = 0.149$). However the citric+oxalic acid combination showed a significant difference ($P = 0.01$) in comparison to the control.

Plants grown on soils from Salisbury generally behaved quite differently and showed no significant difference between organic acids with regards to $KH_2^{33}PO_4$ accumulation in the roots ($P = 0.06$, $R^2 = 0.58$, $PESq = 0.551$). The mean was 68.28% (1.43). Plants grown in the water control, 64.46% (2.07), and plants grown in soils amended with PLA, 65.67% (2.71), acetic acid, 68.26% (2.03), and the combination citric+oxalic acid, 74.72% (2.03) were equal at ($P = 0.06$), with the Tukey HSD multiple comparison showing the citric oxalic acid combination having the strongest inclination towards difference in contrast to the control.

However, there were significant differences ($P < 0.01$, $R^2 = 0.82$, $PESq = 0.798$) between organic acids in the ^{33}P labelled root zone. The water control, 60.43% (1.17), acetic acid, 64.28% (2.07), and PLA, 64.56% (2.95) were equal at ($P = 0.480$). The citric+oxalic combination, 76.07% (1.93) recorded the highest accumulation of $KH_2^{33}PO_4$ in the labelled root zone. The mean was 66.33% (1.79). With respect to the control, the Tukey HSD multiple comparison showed that the citric+oxalic combination had a significant difference at $P < 0.01$.

Additionally, there were significant differences ($P < 0.01$, $R^2 = 0.78$, $PESq = 0.774$) in $KH_2^{33}PO_4$ accumulation in the shoots. With a mean of 74.29% (1.72), plants grown on soils amended with the combination of citric+oxalic acid, 82.49% (1.57) and PLA, 75.98% (2.48)

recorded the highest $\text{KH}_2^{33}\text{PO}_4$ values in shoots being equal at ($P = 0.191$). However the citric+oxalic acid combination showed a significant difference ($P < 0.01$) in comparison to the control and the PLA showed a significant difference ($P < 0.05$) in comparison to the control. Furthermore, acetic acid, 72.01% (1.88) and PLA were equal at ($P = 0.557$) and the water control, 66.68% (1.61) and acetic acid were also equal at ($P = 0.327$).

Plants grown on soils from Castle Bruce (Fig. 8.17.3) behaved quite differently with regards to $\text{KH}_2^{33}\text{PO}_4$ accumulation in the roots, shoots and the ^{33}P labelled root zone. In terms of root behaviour, there were no significant differences ($P = 0.06$, $R^2 = 0.59$, $\text{PESq} = 0.537$) between organic acids. The mean was 64.64% (1.16). Plants grown in the water control, 60.25% (1.89), and plants grown in soils amended with acetic acid, 64.01% (1.69), and PLA, 65.35% (2.13) were equal at ($P = 0.303$). Plants grown on soils amended with PLA, acetic acid and the combination of citric+oxalic acid, 68.94% (1.81) were also equal at ($P = 0.329$). However with respect to the control, the Tukey HSD multiple comparison showed that the citric+oxalic combination had a significant difference at $P = 0.045$.

There were significant differences ($P < 0.05$, $R^2 = 0.57$, $\text{PESq} = 0.57$) between organic acids in the ^{33}P labelled root zone. The water control, 59.75% (1.38), acetic acid, 63.23% (1.79), and PLA, 64.15% (1.57) were equal at ($P = 0.357$). The citric+oxalic combination, 68.43% (1.42), acetic acid and PLA were also equal at ($P = 0.236$). The mean was 63.89% (1.06). With respect to the control, the Tukey HSD multiple comparison showed that the citric+oxalic combination had a significant difference at $P = 0.031$.

Conversely, there were no significant differences ($P = 0.09$, $R^2 = 0.57$, $\text{PESq} = 0.50$) in $\text{KH}_2^{33}\text{PO}_4$ accumulation in the shoots. With a mean of 66.95% (1.12), plants grown on soils amended with the combination of citric+oxalic acid, 71.07% (1.76), PLA, 68.0% (1.82), acetic acid, 65.10% (1.91), and the water control, 63.64% (2.10) were equal at ($P = 0.09$) with the

citric+oxalic acid combination showing strongest inclination towards difference in comparison to the control.

The results for plants grown in soils from Morne Prosper (Fig. 8.17.2) were quite different from the previous trends observed. There were no significant differences between organic acids with regards to $\text{KH}_2^{33}\text{PO}_4$ accumulation in the roots, shoots and ^{33}P labelled root zone. ANOVA failed to detect any significant difference between organic acids with regards to $\text{KH}_2^{33}\text{PO}_4$ accumulation in the roots ($P = 0.176$, $R^2 = 0.46$, $\text{PESq} = 0.407$). The mean was 25.11% (1.01). Plants grown in the water control, 21.95% (1.63), and plants grown in soils amended with acetic acid, 24.18% (1.67), PLA, 25.76% (1.78), and the combination citric+oxalic acid, 28.54% (2.06) were equal at ($P = 0.144$).

There were no significant differences ($P = 0.07$, $R^2 = 0.57$, $\text{PESq} = 0.525$) between organic acids with respect to the accumulation of $\text{KH}_2^{33}\text{PO}_4$ in the ^{33}P labelled root zone. The water control, 19.20% (2.25), PLA, 22.92% (2.36), acetic acid, 23.24% (1.84) were equal at ($P = 0.557$). The citric+oxalic combination, 28.56% (1.42), PLA and acetic acid were also equal at ($P = 0.298$). However, with respect to the control, the Tukey HSD multiple comparison showed that the citric+oxalic combination had a significant difference at $P = 0.05$.

Additionally, there were no significant differences ($P = 0.08$, $R^2 = 0.54$, $\text{PESq} = 0.514$) in $\text{KH}_2^{33}\text{PO}_4$ accumulation in the shoots. With a mean of 26.84% (1.13), plants grown on soils amended with the combination of citric+oxalic acid, 31.16% (1.53) and PLA, 26.98% (2.07), acetic acid, 26.75% (1.82), and the water control, 22.47% (1.83) were all equal ($P = 0.05$) but nonetheless, the citric+oxalic acid combination showing strongest inclination towards difference in comparison to the control ($P = 0.05$).

For plants grown on soils from Pond Cassé (Fig. 8.17.5), there were no significant differences between organic acids with regards to $\text{KH}_2^{33}\text{PO}_4$ accumulation in the roots, shoots and the ^{33}P labelled root zone. In terms of root $\text{KH}_2^{33}\text{PO}_4$ accumulation, the mean was 7.51%

(0.17) and ANOVA failed to detect any significant difference between organic acid ($P = 0.145$, $R^2 = 0.536$, $PESq = 0.435$). Plants grown on soils with the water control, 6.86% (0.28) were equal to plants grown on soils amended with acetic acid, 7.11% (0.25), PLA, 7.18% (0.33), and the combination of citric+oxalic acid, 7.78% (0.17) at a P value ($P = 0.120$).

Similarly there were no significant differences between organic acids in terms of $KH_2^{33}PO_4$ accumulation in the ^{33}P labelled root zone ($P = 0.211$, $R^2 = 0.410$, $PESq = 0.380$). Plants grown on soils with the water control, 6.73% (0.36) were equal to plants grown on soils amended with acetic acid, 6.87% (0.26), PLA, 7.06% (0.34), and the combination of citric+oxalic acid, 7.76% (0.24) at a P value ($P = 0.207$). The mean $KH_2^{33}PO_4$ accumulation in the ^{33}P labelled root zone was 7.10% (0.17).

With no surprise, the ANOVA also failed to detect any significant difference between organic acids with respect to $KH_2^{33}PO_4$ accumulation in shoots ($P = 0.176$, $R^2 = 0.481$, $PESq = 0.407$). The mean $KH_2^{33}PO_4$ accumulation in shoots was 7.51% (0.17). Plants grown on soils with the water control, 7.15% (0.37) were equal to plants grown on soils amended with acetic acid, 7.31% (0.23), PLA, 7.39% (0.35), and the combination of citric+oxalic acid, 8.18% (0.24) at a P value ($P = 0.176$).

A bit surprising, plants grown in soils from Layou Valley behaved differently. There were significant differences between organic acids in $KH_2^{33}PO_4$ accumulation in the roots and ^{33}P labelled root zone and significant differences with regards to $KH_2^{33}PO_4$ accumulation in shoots. With a mean of 8.04% (0.32) ANOVA detected significant differences ($P < 0.05$, $R^2 = 0.65$, $PESq = 0.622$) between organic acids in the roots. The water control, 7.19% (0.46), acetic acid, 7.30% (0.53), and PLA, 8.10% (0.30) were equal at ($P = 0.589$). PLA and the citric+oxalic acid combination, 9.59% (0.54) were also equal at ($P = 0.221$) however the Tukey HSD multiple comparison showed that the citric+oxalic combination had a significant difference with regards to the control at $P = 0.03$.

The labelled ^{33}P root zone also showed significant differences between organic acids ($P < 0.05$, $R^2 = 0.66$, $\text{PESq} = 0.63$). The water control, 6.98% (0.50), acetic acid, 7.05% (0.53), and PLA, 7.77% (0.30) were equal at ($P = 0.705$). Additionally, PLA and the combination of citric+oxalic acid, 9.46% (0.60) were equal at ($P = 0.167$). The mean was 7.81% (0.34). The Tukey HSD multiple comparison revealed that the combination citric+oxalic acid was significantly different from the water control ($P = 0.03$).

The ANOVA for the $\text{KH}_2^{33}\text{PO}_4$ accumulation in the shoots showed significant differences ($P < 0.01$, $R^2 = 0.75$, $\text{PESq} = 0.703$) between organic acids. The mean was 8.86% (0.44). Plants grown in the water control, 7.36% (0.47), and plants grown in soils amended with acetic acid, 8.39% (0.61), and PLA, 8.75% (0.53) were equal ($P = 0.364$). Plants grown in soils amended with the combination of citric+oxalic acid, 10.96% (0.84) were equal to plants grown in soils amended with PLA ($P = 0.087$). However the Tukey HSD multiple comparison revealed that the combination citric+oxalic acid was significantly different from the water control ($P < 0.01$). This suggest that site specific P_{ret} capacity influenced the ability of the LMWOAs to desorb Al- and Fe-P complexes. This is highlighted by the response of $\text{KH}_2^{33}\text{PO}_4$ accumulation in shoots of plants grown in soils from Morne Prosper as well when compared to plants grown in soils from Pond Cassé, with the highest percentage of P retention. The concentration and type of metals found in soils from Pond Cassé definitely influenced the degree of complexation and the displacement of PO_4 anions from the soil matrix (Jones, 1998).

From these varied results, the behaviour of the different organic acids in comparison to the control tends to suggest that their efficacy is highly dependent on their individual complexing ability and would likely be more apparent most probably in response to pH change (van Hees et al., 2001; Qin et al., 2004; Chatterjee et al., 2015), their ionic strength and molecular size (Antelo et al., 2007; Tsado et al., 2014a,b), as well as soil type in function of P sorption capacity (Mikutta et al., 2006; Pavinato et al., 2008; Wang et al., 2012a).

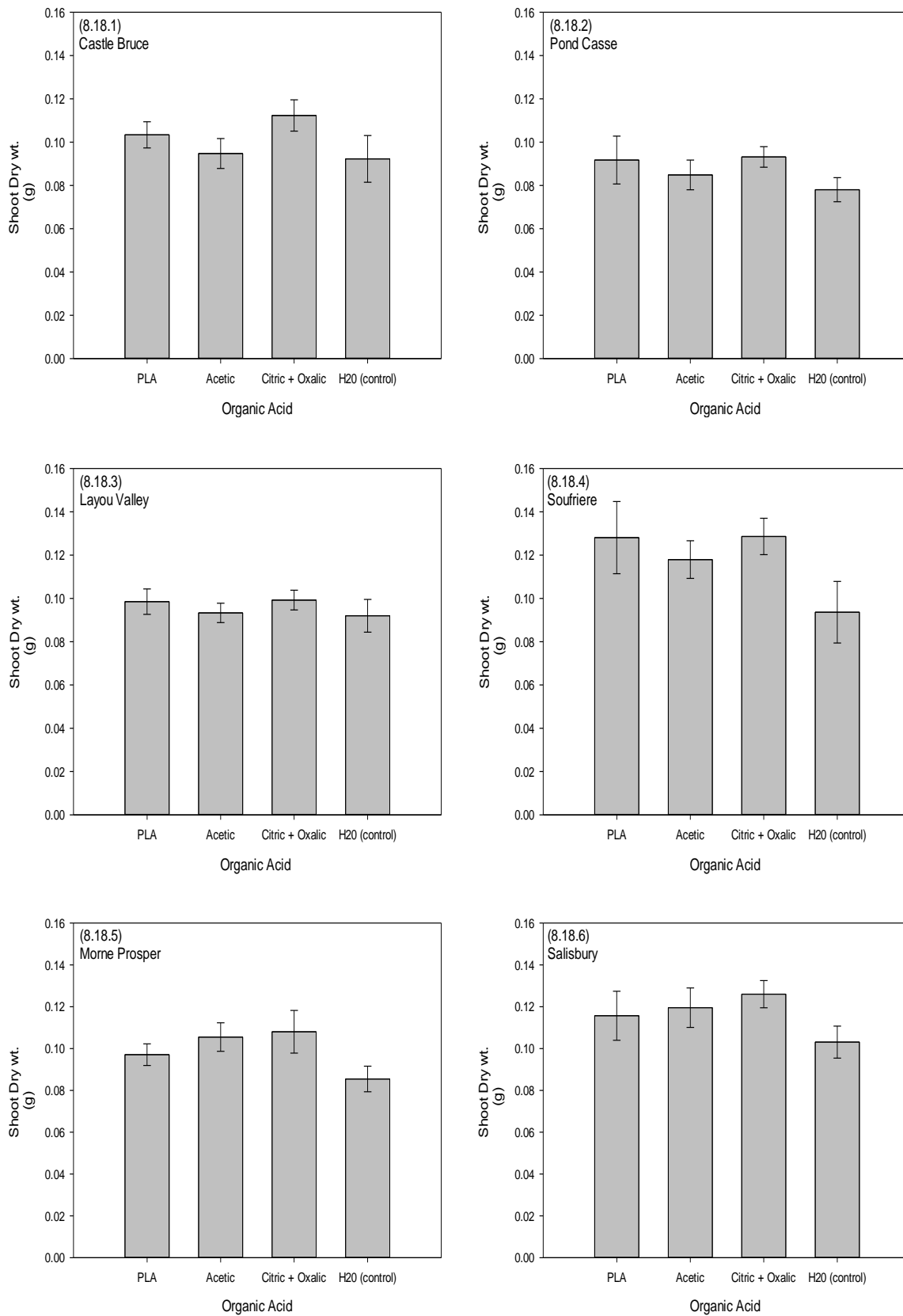


Fig. 8.18. Shoot dry matter (g) of maize plants grown in rhizotube with $\text{KH}_2^{33}\text{PO}_4$ injected with 50 mM organic acid on six agricultural soils of the Commonwealth of Dominica. Values represent means and error bars represent SEM. n = 16.

The results for the production of dry matter where $n = 16$ (Fig. 8.18) revealed no significant difference ($P = 0.36$, $R^2 = 0.393$, $PESq = 0.289$) for plants grown on soils from Castle Bruce (Fig. 8.18.1). The mean was 0.101 g ($4.10e^{-3}$). Plants grown in soils with the water control, 0.923 g (0.01) were equal to plants grown in soils amended with acetic acid, 0.948 g ($6.91e^{-3}$), PLA, 0.1034 g ($6.05e^{-3}$), and the combination citric+oxalic acid, 0.1123 g ($7.23e^{-3}$) at a P value ($P = 0.369$). Plants grown on soils from Pond Cassé (Fig. 8.18.2) also showed no significant difference ($P = 0.34$, $R^2 = 0.585$, $PESq = 0.301$). The mean was 0.087 g ($3.68e^{-3}$). Plants grown in soils with the water control, 0.078 g ($5.56e^{-3}$) were equal to plants grown in soils amended with acetic acid, 0.085 g ($6.88e^{-3}$), PLA, 0.092 g (0.01), and the combination citric+oxalic acid, 0.093 g ($4.74e^{-3}$) at a P value ($P = 0.356$).

Plants grown on soils from Layou Valley (Fig. 8.18.3) also showed no significant difference ($P = 0.81$, $R^2 = 0.158$, $PESq = 0.098$). The mean was 0.096 g ($2.70e^{-3}$). Plants grown in soils with the water control, 0.092 g (0.02) were equal to plants grown in soils amended with acetic acid, 0.093 g ($8.96e^{-3}$), PLA, 0.098 g ($5.88e^{-3}$), and the combination citric+oxalic acid, 0.099 g ($9.11e^{-3}$) at a P value ($P = 0.852$). Plants grown on soils from Salisbury (Fig. 8.18.4) also showed no significant difference ($P = 0.42$, $R^2 = 0.360$, $PESq = 0.257$). The mean was 0.12 g ($4.59e^{-3}$). Plants grown in soils with the water control, 0.103 g ($7.64e^{-3}$) were equal to plants grown in soils amended with PLA, 0.1157 g (0.01), acetic acid 0.1196 g ($9.44e^{-3}$), and the combination citric+oxalic acid, 0.1260 g ($6.51e^{-3}$) at a P value ($P = 0.373$).

Plants grown on soils from Morne Prosper (Fig. 8.18.5) also showed no significant difference ($P = 0.23$, $R^2 = 0.433$, $PESq = 0.365$). The mean was 0.099 g ($3.98e^{-3}$). Plants grown in soils with the water control, 0.086 g ($6.12e^{-3}$) were equal to plants grown in soils amended with PLA, 0.097 g ($5.16e^{-3}$), acetic acid, 0.1055 g ($6.82e^{-3}$) and the combination citric+oxalic acid, 0.1081 g (0.01) at a P value ($P = 0.237$). Plants grown on soils from

Soufriere (Fig. 8.16.6) also showed no significant difference ($P = 0.42$, $R^2 = 0.360$, $PESq = 0.257$). The mean was 0.12 g ($6.68e^{-3}$). Plants grown in soils with the water control, 0.094 g (0.01) were equal to plants grown in soils amended with acetic acid, 0.1180 g ($8.70e^{-3}$), PLA, 0.1281 g (0.02) and the combination citric+oxalic acid, 0.1286 g ($8.40e^{-3}$) at a P value ($P = 0.342$).

The results for the production of dry matter (Fig. 8.19) where $n = 96$ revealed significant differences ($P < 0.01$, $R^2 = 0.465$) between the various organic acids ($F(3, 95) = 5.83$, $PESq = 0.202$). The mean was 0.103 g ($2.09e^{-3}$). Plants grown in soils with the water control, 0.091 g ($3.67e^{-3}$), and plants grown in soils amended with acetic acid, 0.103 g ($3.78e^{-3}$), and PLA, 0.106 g ($4.53e^{-3}$) were equal in terms of shoot dry weight at ($P = 0.097$). Plants grown on soils amended with acetic acid, PLA and the combination citric+oxalic acid, 0.111 g ($3.75e^{-3}$) were equal at ($P = 0.34$). However, the Tukey HSD multiple comparison revealed that shoot dry weight of plants grown in soils amended with the combination citric+oxalic acid were significantly different from the water control ($P < 0.01$) and plants grown in soils amended with PLA were also significantly different from the water control ($P = 0.02$).

There were significant differences ($P < 0.001$) with regards to shoot dry weight between sites ($F(5, 95) = 7.25$, $PESq = 0.344$, $R^2 = 0.465$). Plants grown in soils from Pond Cassé, 0.087 g ($3.68e^{-3}$), Layou Valley, 0.096 g ($2.70e^{-3}$), Morne Prosper, 0.099 g ($4.00e^{-3}$), and Castle Bruce, 0.101 g ($4.10e^{-3}$) were equal ($P = 0.246$). Plants grown on soils from Morne Prosper, Castle Bruce, Salisbury, 0.116 g ($4.59e^{-3}$), and Soufriere, 0.117 g ($6.69e^{-3}$) were equal at ($P = 0.053$). The Tukey HSD multiple comparison revealed that shoot dry weight of plants grown in soils from Pond Cassé were significantly different from shoot dry weight of plants grown in soils from Soufriere ($P < 0.01$). Layou Valley was significantly different from Soufriere ($P = 0.013$) and Morne Prosper was different from soils from Soufriere ($P = 0.053$).

These results tend to strongly suggest that the production of dry matter was mostly influenced by site specific soil properties rather than being influenced by the various organic acid treatments, as can be seen from the partial eta squared values. Thus when the influence of site is removed from the analysis (n = 96) and the various sites are individually analysed in function of organic acid (n = 16), the ANOVA reveals no significant difference between the organic acids in relation to the water control suggesting severe P starvation, notwithstanding the general tendencies as can be appreciated by the numerical variation (Fig. 8.18).

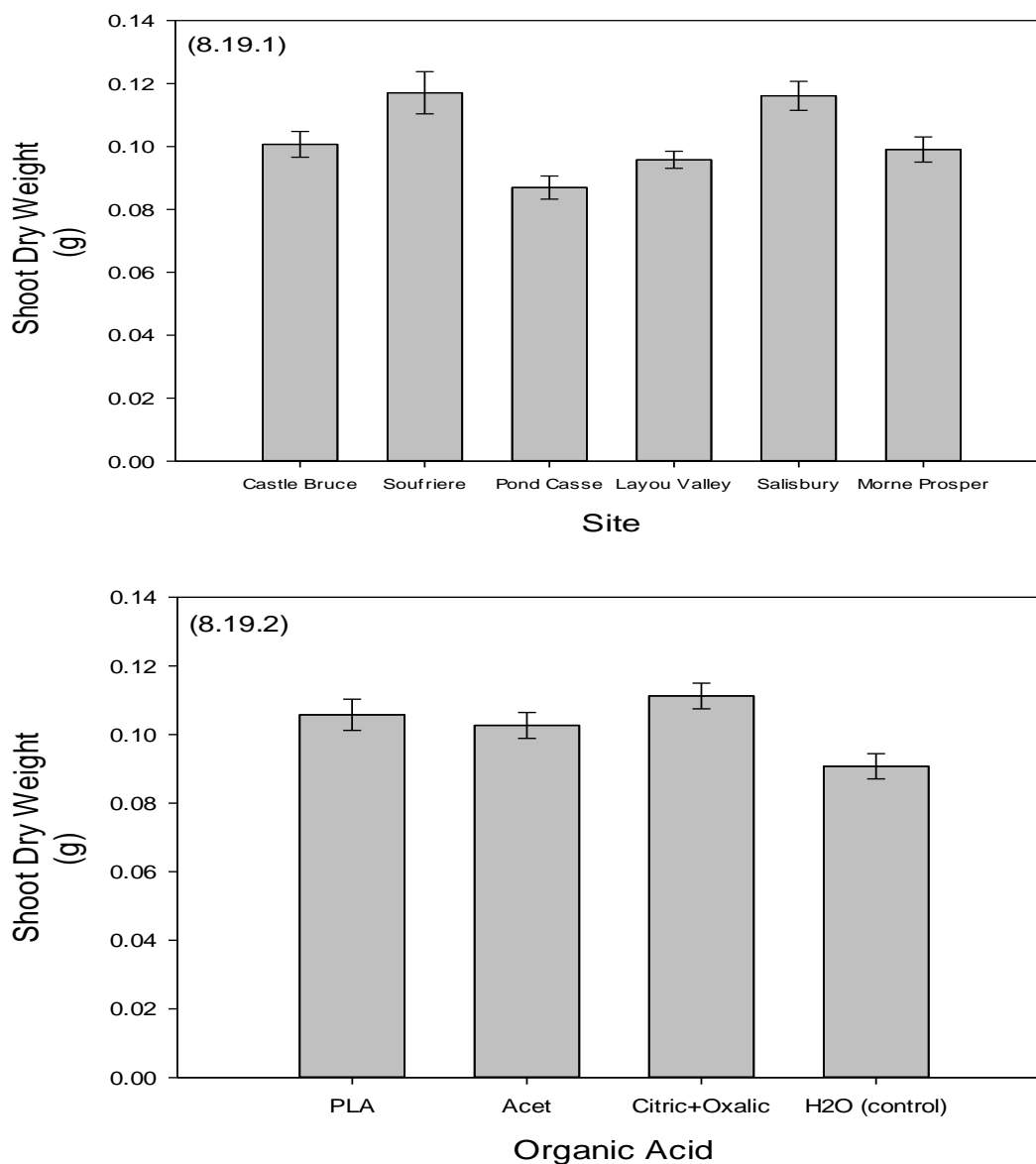


Fig. 8.19. Shoot dry matter (g) of maize plants grown in rhizotube with $\text{KH}_2^{33}\text{PO}_4$ injected with 50 mM organic acid on six agricultural soils of the Commonwealth of Dominica. Values represent means and error bars represent SEM. n = 96.

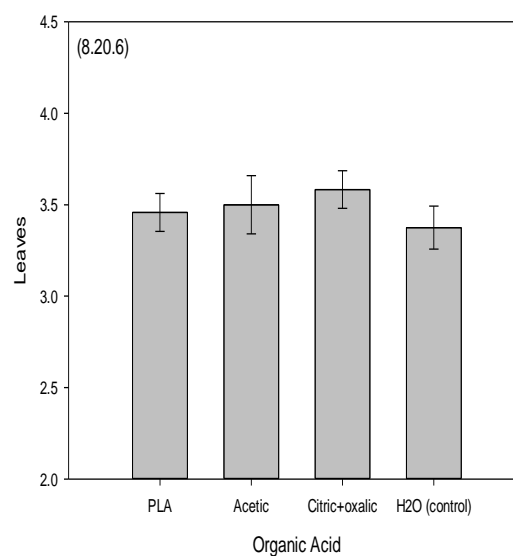
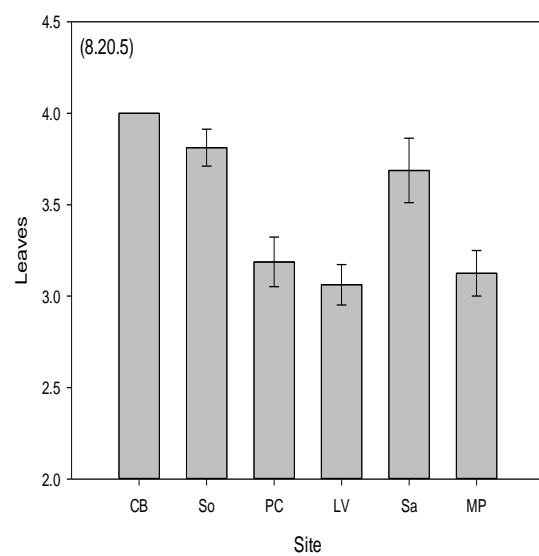
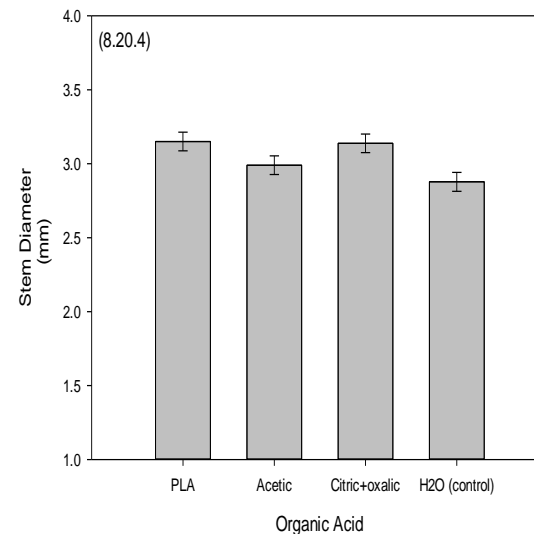
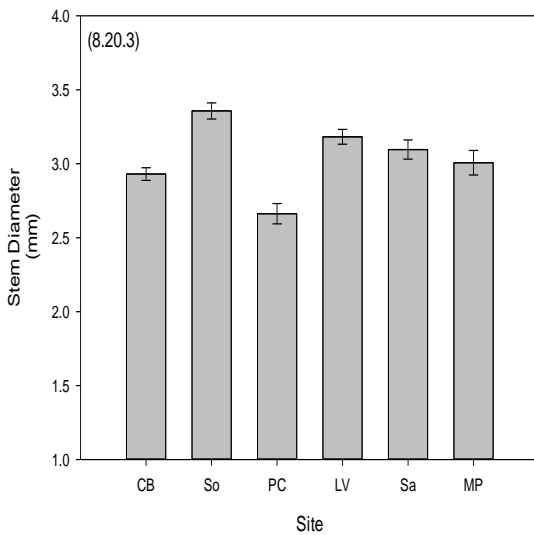
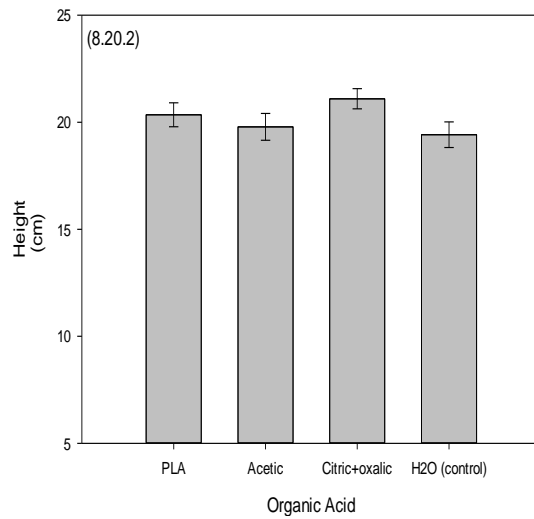
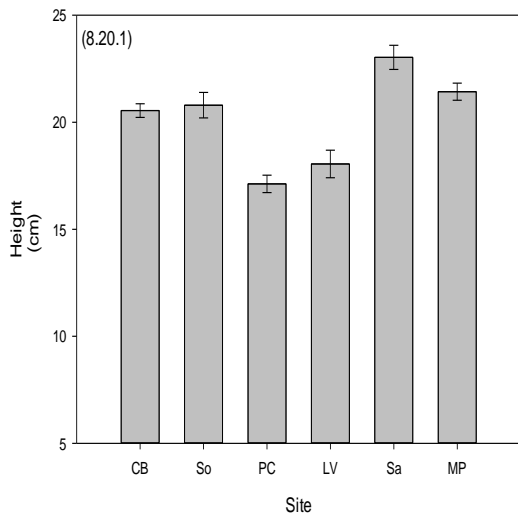


Fig. 8.20. Plant height (cm), stem diameter (mm), and number of leaves of maize plants grown in rhizotube with $\text{KH}_2^{33}\text{PO}_4$ and injected with 50 mM organic acid. Soils represent on six major agricultural soils of the Commonwealth of Dominica. Values represent means and error bars represent SEM. n = 96.

Quite contrasting trends were observed for shoot height (cm), stem diameter (mm) and number of leaves (Fig. 8.20). When the sources of variation of organic acid and site are analysed as an interaction effect ($n = 96$) the ANOVA revealed significant differences ($P < 0.05$, $R^2 = 0.621$) between organic acid ($F(3, 96) = 3.119$, $PESq = 0.119$) and significant differences ($P < 0.001$, $R^2 = 0.621$) between sites ($F(5, 96) = 18.770$, $PESq = 0.576$) with respect to height of plant, which had a mean of 20.16 cm (0.29). Plants grown in soils from Pond Cassé, 17.12 cm (0.41) and Layou Valley, 18.05 cm (0.65) were equal ($P = 0.784$). Plants grown on soils from Castle Bruce, 20.55 cm (0.32), Soufriere, 20.80 cm (0.59) and Morne Prosper, 21.43 cm (0.40) were also equal ($P = 0.818$). However plants grown on soils from Morne Prosper and Salisbury, 23.03 cm (0.56) were equal ($P = 0.236$) and recorded the highest plant height. Plants grown in soils with the H₂O control, 19.42 cm (0.60), and plants grown in soils amended with acetic acid, 19.79 cm (0.63), and PLA, 20.35 cm (0.56) were equal ($P = 0.392$). However plants grown in soils amended with acetic acid, PLA, and the combination citric+oxalic acid, 21.10 cm (0.50) were equal ($P = 0.123$). Nonetheless, Tukey HSD multiple comparison showed that plants grown in soils with the water control were significantly different from plants grown in soils amended with the combination citric+oxalic acid ($P = 0.03$).

With a mean of 3.04 mm (0.03), similar trends were observed for stem diameter with significant differences ($P < 0.001$, $R^2 = 0.672$) between organic acids ($F(3, 96) = 8.576$, $PESq = 0.269$) and site ($F(5, 96) = 18.770$, $PESq = 0.576$). Plants grown in soils from Pond Cassé, 2.66 mm (0.07) recorded the lowest stem diameter values. Plants grown in soils from Castle Bruce, 2.93 mm (0.04), Morne Prosper, 3.01 mm (0.08) and Salisbury, 3.10 mm (0.06) were equal ($P = 0.277$). Furthermore, plants grown in soils from Castle Bruce, Morne Prosper, Salisbury, and Layou Valley, 3.18 mm (0.05) were equal ($P = 0.222$). However, plants grown on soils from Layou Valley and Soufriere, 3.36 mm (0.05) recorded the highest stem diameter values being equal ($P = 0.222$). Tukey HSD multiple comparison showed a matrix of

differences between sites. However, plants grown in soils with the H₂O control, 2.87 mm (0.06), and plants grown in soils amended with acetic acid, 2.99 cm (0.06) were equal ($P = 0.293$). On the other hand, plants grown on soils amended with acetic acid, the combination citric+oxalic acid, 3.14 mm (0.06) and PLA, 3.15 mm (0.06) were also equal ($P = 0.06$). Nonetheless, Tukey HSD multiple comparison showed that plants grown in soils with the water control were significantly different from plants grown in soils amended with the combination citric+oxalic acid and PLA ($P < 0.001$).

The ANOVA for number of leaves showed no significant difference between organic acids, and a significant difference ($P < 0.001$, $R^2 = 0.756$) between site ($F(5, 96) = 21.567$, $PESq = 0.610$) and the interaction of site with organic acid ($F(5, 96) = 6.079$, $PESq = 0.569$). The overall mean was 3.48 (0.06), however plants grown in soils from Layou Valley, 3.06 (0.11), Morne Prosper, 3.13 (0.13), and Pond Cassé, 3.19 (0.14) were equal ($P = 0.910$). Plants grown on soils from Salisbury, 3.69 (0.18), Soufriere, 3.81 (0.10), and Castle Bruce, 4.00 (0.00) were also equal ($P = 0.124$). The Tukey HSD multiple comparison showed a matrix of results highlighting significant differences between plants grown on soils from Castle Bruce and Morne Prosper, Layou Valley, and Pond Cassé ($P < 0.001$). The ANOVA failed to detect any significant difference between organic acids, with the H₂O control, 3.38 (0.12), PLA, 3.46 (0.11), acetic acid, 3.50 (0.16), and the combination citric+oxalic acid, 3.58 (0.10) all being equal at ($P = 0.169$).

Moreover, when the effect of site is removed from the analysis ($n = 96$) and the source of variation attributed to organic acid ($n = 16$), contrasting trends are observed across individual sites (Fig. 8.21). Firstly, across all sites there was no significant difference in comparison to the H₂O control with regards to plant height. Plants grown on soils from Salisbury had a mean of 23.03 cm (0.56), Morne Prosper, 21.43 cm (0.40), Soufriere, 20.80 cm (0.59), Castle Bruce, 20.55 cm (0.32), Layou Valley, 18.05 cm (0.65), and Pond Cassé, 17.12 cm (0.41). Secondly,

mean stem diameter showed significant differences for plants grown in soils amended with organic acids in comparison to the water control on soils from Castle Bruce ($P = 0.014$, $R^2 = 0.703$, $PESq = 0.673$). With a mean of 2.93 mm (0.04) plants grown in soils with the H₂O control, 2.80 mm (0.02), acetic acid, 2.87 mm (0.06), and PLA, 2.91 mm (0.09) were equal ($P = 0.591$). Furthermore plants grown on soils amended with PLA and the combination citric+oxalic acid, 3.15 mm (0.05) were also equal ($P = 0.087$). However Tukey HSD multiple comparison showed that the combination citric+oxalic acid was significantly different from the H₂O control ($P < 0.05$).

Plants grown on soils from Soufriere with a mean of 3.36 (0.05) also showed significant difference with regards to the H₂O control ($P = 0.03$, $R^2 = 0.64$, $PESq = 0.615$). Plants grown in soils amended with PLA, 3.39 mm (0.10) were equal to the plants grown in soils with the H₂O control ($P = 0.120$). However, plants grown in soils amended with PLA, acetic acid, 3.48 mm (0.06), and the combination citric+oxalic acid, 3.48 mm (0.07) were also equal ($P = 0.884$). Additionally, Tukey HSD multiple comparison showed that acetic acid and the combination of citric+oxalic acid were significantly different from the H₂O control both at a P value ($P < 0.05$).

Plants grown in soils from Pond Cassé with a mean of 2.66 mm (0.07) showed significant differences ($P = 0.014$, $R^2 = 0.69$, $PESq = 0.674$). Plants grown in soils with the H₂O control, 2.37 mm (0.05), acetic acid, 2.62 mm (0.09), and the combination citric+oxalic acid, 2.69 mm (0.28) were equal ($P = 0.166$). Additionally, plants grown on soils amended with PLA, 2.97 mm (0.05) were also equal to plants grown on soils amended with acetic acid and the combination citric+oxalic acid ($P = 0.128$). However Tukey HSD multiple comparison showed that PLA was significantly different from the H₂O control ($P < 0.01$). Plants grown on soils from Layou Valley, 3.18 mm (0.05), Salisbury, 3.10 mm (0.06), and Morne Prosper, 3.01 mm (0.08) showed no significant difference between organic acid to stem diameter.

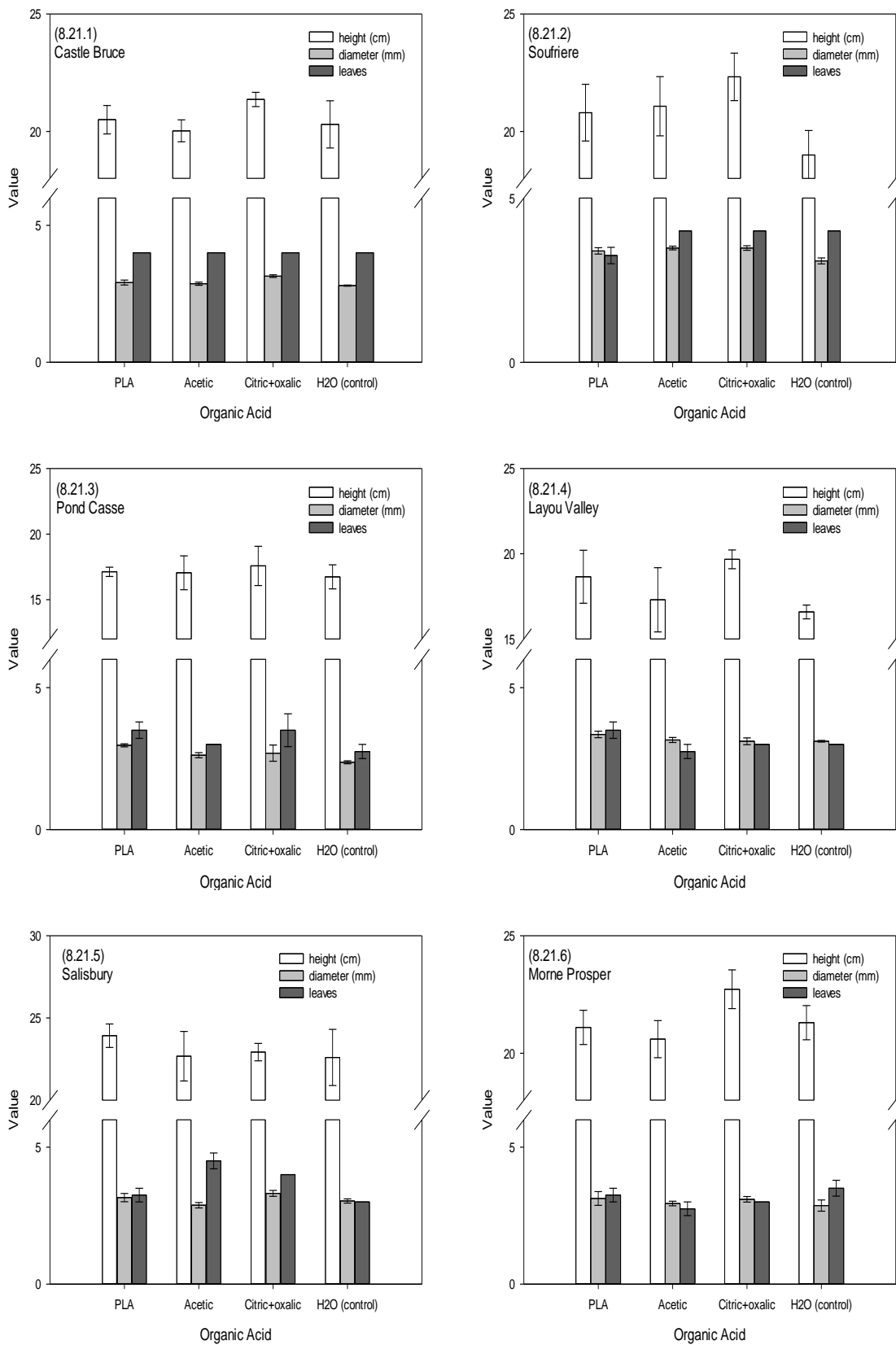


Fig. 8.21. Plant height (cm), stem diameter (mm), and number of leaves of maize plants grown in rhizotube with $\text{KH}_2^{33}\text{PO}_4$ injected with 50 mM organic acid on six agricultural soils of the Commonwealth of Dominica. Values represent means and error bars represent SEM. $n = 16$.

Thirdly, the ANOVA for number of leaves only showed significant differences for plants grown on soils from Soufriere with a mean of 3.81 (0.10) ($P < 0.01$, $R^2 = 0.769$, $PESq = 0.75$). Tukey HSD multiple comparison showed that plants grown on soils amended with PLA was significantly different from plants grown on soils with the H₂O control ($P < 0.01$). ANOVA also showed significant differences for plants grown on soils from Salisbury ($P < 0.01$, $R^2 = 0.857$, $PESq = 0.843$). HSD multiple comparison revealed significant differences between acetic acid and the H₂O control ($P < 0.001$) and the combination citric+oxalic acid and H₂O control ($P < 0.05$). However, the mean number of leaves for sites at Castle Bruce, 4.00 (0.00), Pond Cassé, 3.19 (0.14), Layou Valley, 3.06 (0.11), and Morne Prosper (3.13 (0.13) clearly shows that with the exception of the Castle Bruce site, the total number of emerged leaves, as determined by the leaf-tip method, at these different sites were numerically lower when compared to the Soufriere and Salisbury sites. Furthermore, Tukey HSD multiple comparison showed that leaf emergence for plants grown on soils from Pond Cassé with the H₂O control showed a subtle tendency of difference from that of plants grown in soils amended with PLA and the combination citric+oxalic acid ($P = 0.053$).

These results tend to suggest that dry matter accumulation was primarily attributable to site specific soils properties and associated traits (hence the tendency to separate the studied volcanic soils into two distinct groups of soils with soil properties differing much more between these two groups of soils rather than within them) but was also responsive to organic acid treatment across all sites as was reflected by plant leaf emergence, stem diameter engorgement, as well as plant height elongation. However, the phenologic data evaluated (i.e. plant height, stem diameter, and number of leaves) does not give a clear and comprehensive explanation of the response (i.e. accumulation of dry matter). Hence, it is being postulated that besides the beneficial P acquisition effect, these LMWOAs might be affecting overall plant development in other ways besides Fe and Al dissolution.

As an example, it has been reported in the literature that the application of LMWOAs will modify the rhizosphere pH to a slightly acidic environment where soil microbes are most active and plant nutrients are readily available (Huang et al., 2003; van Hees et al., 2005). It is also reported that the application of LMWOAs might similarly increase mycorrhizal occurrences and establishment, decreasing decomposition and nutrient transformation for root growth, both essential for nutrient uptake (van Hees et al., 2005; Steiner et al., 2008). More specifically, it has been reported in the literature that PLA stimulates the hormone like substances with a possible synergistic effects on plant growth (Mu et al., 2003; Zulkarami et al., 2014) or even induces the hormones of the plant itself (Mu et al., 2006) at trace amounts or increases the photosynthesis of the leaves, further regulating the growth of the plant. These mechanisms are not clear but needs to be explored by further studies on plants. This element of research and development will be critical, as PLA has preliminarily shown its usefulness and is destined to play an important role in allophanic soil management.

4. Discussion

4.1 ³³P mobilization and rhizotube trials

LMWOAs generally contribute between 0.5-15% of total soil acidity due to their high content of carboxyl groups (van Hees et al., 2000) and the soil concentration of organic acids is normally between 0.5 - 0.10 μ M (Jones, 1998). The mechanism of LMWOAs' effects on P adsorption, and the sorption to both external and internal surfaces of the mineral colloid (Tsado et al., 2014a,b) can be divided into two main aspects: (1) inhibition caused by competition for adsorption sites at the mineral surface reducing the number or activity of reactive sites (Welch and Ullman, 1999) and (2) promotion due to the activation of crystalline Fe/Al and the prevention of the crystallization of Fe/Al (Varadachari et al., 1994; Wang et al., 2012a). The dominant action ultimately depends on the properties of the specific LMWOAs and soil properties. Thus it has been suggested that the ratio between anions and cations released by

protons added from organic acids (i.e. citric, oxalic) are greater than those from mineral acids (i.e. HCl). This may be related to the number and proximity of carboxylic groups and varying affinities for oxide surfaces. Chatterjee et al., (2015) noted that inorganic or mineral acids, having lower dissociation constants, are considered as strong noncomplex-forming acids and thus the capacity of LMWOAs to complex metals is more important in soils.

In this study, the combination of citric+oxalic acid may have inhibited P adsorption through a stronger ability to compete for adsorption sites. However, acetic acid and pyroligneous acid also improved P desorption (Fig. 8.16) specifically on low P fixing soils most probably because of their inherent ability to produce protons which are attached to oxygen sites at the mineral surface. Similar but comparable results were obtained by Tsado et al., (2012) working with LMWOAs in Alfisols of the Nigerian Guinea Savannah. It is known that when protons which are produced by LMWOAs are attached to oxygen sites, they weaken the metal-oxygen bond, and catalyse dissolution reaction (Terry, 1983; Barman et al., 1992; Welch and Ullman, 1993, Drever, 1994; Goyne et al., 2006; Shao et al., 2011). However this effect was not visibly noticed on high P fixing soils most likely due to a higher content of aluminosilicates which ultimately determines the Fe- and Al-P complexes and their relative susceptibility to dissolution.

The persistence of organic acids in the soil (Johnson et al., 2003; Qin et al., 2004), likewise the concentration and number of carboxylate groups (Hue et al., 1986; Pavinato et al., 2008) are also important variables affecting the efficacy of these LMWOAs, with the monocarboxylic acids (acetic and pyroligneous) performing less effectively than the combination of the dicarboxylic and tricarboxylic acids. However, it has been reported that many of these LMWOAs are degraded within hours or days after being applied (Jones and Brassington, 1998) and may have a limited effect in competing with ions for adsorption sites in soil. Thus it is likely that a substantial percentage of these LMWOAs were sorbed and potentially diminished

their effectiveness to mobilize P. Furthermore, it is possible that these LMWOAs were short-lived in the soil environment due to rapid mineralization via thermal degradation or biodegradation reactions (Lundström and Øhman, 1990; Jones, 1998; van Hees et al., 2005). This might potentially explain the non-significant differences observed between the various organic acids in the maize pot trial, particularly PO₄ content in plants roots and PO₄ content in plant shoots (Fig. 8.6) when compared to the results of the rhizotube experiment. However, the results tends to suggest conditions of severe P starvation as can be deduced from the root-to-shoot ratio (Fig. 8.7) which might have led to the overall poor performance. Nonetheless, PLA performed markedly better than acetic acid most probably on account of its greater carbon constituent and thus stimulating microbial activity leading to P mineralization and eventual P acquisition (Merritt et al., 2007; Mungkunkamchao et al., 2013; Nair et al., 2014).

The citric + oxalic acid combination must have increased the availability of P in soils most likely through both decreased adsorption of P and increased solubilization of P compounds (Bolan et al., 1994; Drever and Stilings, 1997; Jones, 1998; Hinsinger, 2001; Dakora and Phillips, 2002; Hinsinger et al., 2011). The presence of LMWOAs might have disturbed the equilibrium between the labile metals on the solid phase and in soil solution, and thus enhanced the release of metals from solid phase to soil solution (van Hees et al., 2001). Notwithstanding these LMWOAs are reported to have little direct effect on the removal of the more stable cations such as Na⁺ and Ca²⁺ from the mineral surface (Goyne et al., 2006), but they do indirectly increase the release rate of these ions by increasing the dissolution rate of the framework elements, Si and Al (Welch and Ullman, 1993).

It can also be noted that the degree of P dissolution was also highly dependent on site. The monocarboxylic acids, in comparison with the water control, were relatively effective on the soils with a lower P sorption capacity. However, as the degree of P sorption progressively increased in soils from Morne Prosper→Layou Valley→Pond Cassé, the relative effectiveness

of these weak acids was not as evident and on the contrary only the citric acid + oxalic acid combination was able to undertake dissolution of phosphate held by the secondary P minerals (Fe- and Al-phosphates). Presumably low dissolution constants of acetic and PLA provided fewer protons to attach to oxygen sites at the mineral surface and fewer anions for complexing with metals (Terry, 1983; Barman et al., 1992; Welch and Ullman, 1993).

The suggestion for the poor performance of these LMWOAs is that they did not lead to any significant change in the solubility and dissolution of aluminosilicate minerals and probably did not lead to any significant change in soil solution pH affecting P availability. It has been reported that when soil solution pH is lower than the isoelectric point of hydrous Fe and Al oxides, the availability of P to plants is strongly reduced because of its sorption to positively charged hydrous Fe and Al oxide surfaces (Agbenin, 2004; Mikutta et al, 2006), to the point that LMWOAs can promote P adsorption through activating crystalline Fe/Al and preventing crystallization of amorphous Fe/Al to increase P adsorption sites (Varadachari et al., 1994; Wang et al., 2012a).

The difference in the outcome of P availability by these LMWOAs suggests effects related to their chemical structures. Acetic acid and most probably PLA are only able to form monodentate complexes with metals, while ions of citric and oxalic acids carrying two or three $-COO$ groups (β -hydroxyl functional groups) can form chelates with 5- or 6- membered ring structure, which are much more stable than monodentate complexes and cause a more rapid rate of metal dissolution in soil (Hue et al., 1986; Jones et al., 2003; Wang et al., 2012a; Chatterjee et al., 2015). This implies that there is some sort of competition between LMWOAs and PO_4 for surface soil. The overall consensus is that LMWOAs may have greater affinity for Fe- and Al-oxides than PO_4 and will strongly compete with P for adsorption sites on Fe- and Al-oxide systems (Chatterjee et al., 2015), suggesting that P would be more available in soil solution via the action of LMWOAs.

Furthermore, Drever and Stilings (1997) noted that LMWOAs may affect the speciation in solution of ions such as Al^{3+} affecting mineral dissolution rate. In the presence of an organic ligand, such as oxalate, Al will most likely be present in solution as an organic complex, and the activity and concentration of the free ion and hydrolysis products will be greatly reduced (Drever and Stilings, 1997). Of importance, Alva et al., (1986) and Hue et al., (1986) reported that total solution Al can be partitioned into monomeric Al (Al^{3+} + hydroxy-Al species) and complexed Al (Al-organic acid complexes). The second authors reported that Al-organic acid complexes can account for 76-93% of the total solution Al concentration. Hence, the determination of inorganic monomeric Al is essential in characterizing soil solutions for their likely degree of Al toxicity to plants (Kinraide and Parker, 1987; Anderson, 1988; Fageria et al., 1988; Close and Powell, 1989; Delhaize and Ryan, 1995). The inorganic monomeric forms of Al have been shown to be the toxic forms limiting plant growth (Blamey et al., 1983, 1990) as Al bound to organic ligands has been shown to be much less toxic (Bartlett and Riego, 1972; Hue et al., 1986; Kerven et al., 1989a,b; Carr et al., 1991; Ryan and Kochian, 1993).

Organic acid-induced P release depends on many factors, including pH and soil mineralogy (Bolan et al., 1994; Fox and Comerford, 1990; Jones and Darrah, 1994; van Hees et al., 2001; Jones et al., 2003). In addition, organic acids may play a dominant role in silicate mineral weathering at conditions of near-neutral pH, where proton-promoted dissolution effects are minimal (Blake and Walter, 1999). Similarly, Jones and Darrah (1994) showed that organic acids can be expected to be of little consequence in nutrient mobilization from high pH soils, whilst in acid soils they may be involved both in a more general mechanism for micronutrient uptake or as a potential Al detoxification mechanism (Jones, 1998).

It should be noted that citrate and oxalate have a high affinity for trivalent metals such as Al^{3+} and Fe^{3+} and it is indeed these metals which are immobilised most readily by organic acids in most soils, forming strong complexes and releasing P held tightly by soil constituents

in the solid phase and bring P into solution (Hue et al., 1986; Pohlman and McColl, 1986; Jones and Kochian, 1996). Dissolution also appears to depend on the amount of P associated with the ferric (Fe^{3+}) hydroxide surface and on the composition of the other ions in solution (Jones, 1998). Hence the difference in the effectiveness of LMWOAs for desorbing Fe- and Al-oxides is closely related to their molecular structure and stability constant of the metal-LMWOA complexes (Wang et al., 2012a). However, the effects of LMWOAs can change from inhibition to promotion with increase of adsorption time (Wang et al., 2012a) whereby promoting the combination of P with Fe and Al (Fox and Comerford, 1990; Welch and Ullman, 1999). This variation in behaviour is strongly associated with a rise in pH with the inhibitory action of LMWOAs on P adsorption weakening and gradually changing to promotion. The ability of LMWOAs on the sorption capacity of P tends to increase with acidity and short-range-ordered aluminosilicate content (Strahm and Harrison, 2008) which is inherently associated to the magnitude of the difference between the positive charge on the mineral surface and the negative charge of the LMWOA (Strahm and Harrison, 2008).

The impact of organic acids on silicate mineral weathering, on mass transfer, and on secondary products depends on several factors including the concentrations of organic ligands, cation concentrations, and other solution properties (temperature, pH, ionic strength), and on the subsequent fate of Al and Si following release from dissolving minerals (Blake and Walter, 1999; Jones et al., 2003). The ultimate fate of dissolved Al depends on the stability of the organic acid and Al-organic complexes. According to Terry (1983), the action of acids on silicate produces one of the following: (1) complete breakdown of the silicate structure with the dissolution of metal cations and silica whereby silica gel may then be formed due to ready polymerisation of silica in aqueous solutions, (2) partial decomposition of the silicate structure leading to dissolution of cations and leaving a siliceous residue, and (3) essentially no reaction

at all. The greater the affinity of a LMWOA for a particular metal cation, the stronger the tendency for that acid to form a stable complex with cations, influencing P desorption.

4.2 Maize pot trial and Hedley Sequential Fractionation

The resin and bicarbonate fraction of the Hedley sequential fractionation showed significant relationship with the Olsen, Bray & Kurtz, and Mehlich-III P extraction methods, results which again highlight the significance of these aforementioned fractions in terms of P plant availability (Fernandes et al., 1999). This is most likely due to the strong acidic nature of both the Bray & Kurtz (pH 2.6) and Mehlich-III (pH 2.5) extracting solutions when compared to the Olsen (pH 8.5). In addition, it has been noted that for acid soils, the fluoride in the Bray & Kurtz as well as in the Mehlich-III extractant enhances P release from Al phosphates by decreasing Al activity in solution through the formation of various Al-F complexes (Sims, 2000a,b) and suppressing the re-adsorption of solubilized P by soil colloids (Holford, 1980).

The results for the relationship between the resin fraction and the Olsen (bicarbonate) extraction (Fig. 8.14) tend to suggest that although the 0.5 M NaHCO₃ (pH 8.5) Olsen solution is known to contribute in decreasing the solution concentrations of soluble Ca²⁺, Al³⁺ and Fe³⁺, the increased surface negative charges and/or decreased number of sorption sites on Fe and Al oxides surfaces was not sufficient enough to significantly enhance desorption of available P into solution and thus increasing P solubility.

The relationship between the bicarbonate P and the various P extraction methods showed significant correlation (P<0.001). However the relationship was strongest with regards to the Olsen P extraction method (Fig. 8.12.2). Indeed, the bicarbonate P and Olsen P extraction utilize the same extracting reagents and it should be expected that a strong relationship would exist. It is plausible that the Bray & Kurtz method might have underestimated available P by not fully decreasing Al activity in solution through the formation

of various Al-F complexes (Sims, 2000a,b) as well as by not fully suppressing the re-adsorption of solubilized P by soil colloids (Holford, 1980).

With regards to the Mehlich-III P extraction, it is more than likely that the acetic and nitric acid in the extractant contributed to an increased solubility of Fe and Al phosphates. Furthermore it is known that the acidic nature of the extractant (pH 2.6) should also contribute to dissolution of available P from Al, Ca, and Fe-bound forms, with fluoride serving to complex Al cations that potentially bind with phosphates, thereby increasing the quantity of orthophosphate in solution. To this end it is more than likely that the results for the Bray & Kurtz method might have probably underestimated available P and hence a similar relationship when compared to Olsen with regards to resin P content.

The Mehlich-III method had the strongest relationship with the resin fraction while the Olsen method had the strongest relationship with the bicarbonate fraction. However, it has been suggested (Menon et al., 1989, 1990) that the Olsen, Bray & Kurtz and the Mehlich-III extractable P procedures, developed to measure plant available P in soils treated with soluble fertilizers, may not be suitable when water insoluble fertilizers, such as phosphate rocks, are applied. In particular Menon et al., (1989) noted that the Olsen P method may underestimate P by not dissolving P from phosphate rocks. Hence, the approach is to develop separate calibrations for rock phosphate based on fertilizer use history (Sims, 1989). However this may be problematic for small island economies with limited use of P fertilizers.

According to Menon et al., (1997) when rock phosphate fertilizers are used, residues may be present in the soil and the reaction products of rock phosphate in the soil may be different from those with soluble P fertilizers. Hence, calibrations based on soluble P fertilizers may not be suitable when rock phosphate fertilizers are used. The soil tests which are routinely used in soil testing laboratories have certain limitations (Alva, 1993; Habib et al., 1998) and their ability to predict bioavailability of P in soils with widely differing properties is somewhat

limited. Nevertheless the Olsen, Bray & Kurtz and Mehlich-III all highlight low plant available P based on established values (Sims, 2000a,b). Furthermore, rock phosphate is a slow release fertilizer and its effectiveness depends on its reactivity, soil properties (i.e. P sorption characteristics becomes extremely important hence site specific uses), climatic conditions, and crop species (Menon et al., 1997).

The results for leaf emergence, plant height and stem diameter engrossment tend to suggest that throughout the growing period the effect of the different organic acids significantly varied notwithstanding that it was noticeable that the water control performed the poorest. With regards to PLA it is plausible that other chemical constituents contributed to the overall performance of the maize plants as has been reported by a number of workers (Focht, 1999; Balat, 2011; Dou et al., 2012; Lashari et al., 2013). Furthermore it is known that PLA enhances different growing characteristics (Kadota and Niimi, 2004; Wanderley et al., 2012); as well as reported effects of PLA on enhancing the composition of chlorophyll (Ping et al., 2010; Abdelgadir et al., 2013) and enhancing the production of growth hormones (Lashari et al., 2013) with phyto-hormonal properties (Zulkarami et al., 2014). A number of researchers (Merritt et al., 2007; Mungkunkamchao et al., 2013; Nair et al., 2014) have reported on the role that bicyclic, heteroatomic organic compounds such as karrikinolide and karrikins found in PLA plays in regulating plant growth. According to Mungkunkamchao et al., (2013), PLA may therefore have an effect on cell division and subsequently result in appreciable increases in above ground biomass.

PLA has been reported to act in a similar way to cytokinins and auxins (Aremu et al., 2012), enhancing gibberellin activity (Abdelgadir et al., 2013; Kumari et al., 2015) thus stimulating rooting, seedling growth and flowering (Papenfus et al., 2015). This implies that liquid smoke extract may play a vital role on overall plant growth, photosynthetic pigments and phenolic content (Aremu et al., 2012). Within contemporary literature, a numbers of

researchers have highlighted the possible mode of action (Aremu et al., 2012; Papenfus et al., 2015; Kumari et al., 2015). Accordingly, these authors point to the likelihood of pyroligenous acid influencing the biosynthesis or metabolism of plant hormones, changing membrane permeability and enhancing the transport of phytohormones to active sites.

Aremu et al., (2012) further pointed out that liquid smoke extracts could be used in conjunction with auxin to increase the number of roots based on the photosynthetic pigment levels. The evidence that smoke solutions are active at extremely low concentrations and have no toxic effects on crops (Nair et al., 2014; Zulkarami et al., 2014) potentially makes them attractive options as alternative, cheaper and faster approaches in plant propagation and nutrient management. Furthermore, it is reported that the phytohormones (**brassinosteroids**) have important functions in different physiological processes including induction of stem elongation, and photosynthesis (Abdelgadir et al., 2013) and adaptive responses to environmental stresses (Zulkarami et al., 2014) to possibly include P starvation. Hence, the advantage of PLA is that it is a readily available and captured resource on an island where charcoal is an important cooking fuel.

4.3 Root-to-shoot ratio

The results for the root-to-shoot ratio shows that plants grown in soils from low P fixing soils responded better most probably due to more favourable growing conditions (Harris, 1992). The decrease in the root-to-shoot ratio, on the other hand, tend to suggest that plants were probably growing under less favourable conditions (i.e. plants grown in soils from Layou Valley). Furthermore, the root-to-shoot ratio of maize plants grown on these volcanic soils tend to suggest that shoot growth was more severely reduced than root growth. However within the contemporary literature, unclear results are still found with regards to the effects of P on root growth. The associated hypothesis, which underlies existing models, highlights that P deficiency affects root growth through its effect on carbon partitioning between shoots and

roots (Mollier and Pellerin, 1999). Nacry et al., (2005) indicated that low P induces a biphasic response with, first, an increase in lateral root growth with no effect on primary root elongation, and, later on, a general negative effect on growth of all roots. Some authors have indicated that when the supply of Pi is limited, plants could either singly or in combination grow more roots, increase the rate of uptake by roots from the soil, re-translocate Pi from older leaves, or deplete the vacuolar stores of Pi (Föhse et al., 1988; Koide, 1991; Gahoonia and Nielsen, 2004).

Although by no means conclusive, the high root-to-shoot ratio observed for the water control in comparison to the organic acids in soils from the Layou Valley (Fig.8.7.1) tends to suggest that dry matter accumulation was severely hindered most probably owed to the low availability of plant nutrients and starvation to P. However, Mollier and Pellerin (1999) indicated that root response to P deficiency (i.e. increase or decrease) depends on the time scale of the experiment. Given the duration of the experiment (8 weeks) it appears P deficiency progressively and severely reduced leaf growth. When leaf demand for carbohydrates is reduced more carbohydrates tend to be available for root growth, hence a slight stimulation of root growth a few days after P starvation would be expected (Mollier and Pellerin, 1999; Corrales et al., 2007; Postma et al., 2014). Symptoms of P deficiency were readily observable in the production of anthocyanin (reddish-purplish coloration) in the leaf sheaths (Fig. 8.1b,d).

With the passage of time however, it would be anticipated that because of reduce leaf area of P-deprived plants, their capacity to intercept light is severely reduced. Hence it is more than plausible that the lower shoot demand for carbohydrates might not have compensated for their lower source capacity in that not only shoot but root growth was eventually reduced, as a longer term consequence of P deficiency. Therefore nutrient uptake by plants growing in soils depends on the configuration and growth rate of the roots system (Sulpice et al., 2014), the nutrient uptake characteristics per unit of root, and the nutrient supply characteristics of the soil (Itoh and Barber, 1983; Burkitt et al., 2001; Hinsinger et al., 2011).

5. Conclusion

Due to the removal of P from the soil solution, plant-available P content is often very low when compared to the total amount of P bound to the soil minerals and charged sites, in addition to being fixed into organic forms which is not available to plants. The availability of P to plants is limited, to a large extent, by the rate of reactions that replenish soluble P pools. Furthermore, P availability depends not only on pool sizes of the labile chemical forms of P, but also on P concentration in the soil solution, net rates of desorption/release from a variety of inorganic and organic soil constituents, the duration of growth (hence the duration of P demand), and a variety of microbial influences (Johnson et al., 2003).

From these preliminary studies the results tend to suggest that phosphate availability and efficiency could be improved by a combination of inorganic PO_4 fertilizer and organic manure, probably due to the effects of organic-ligand in reducing PO_4 adsorption and increasing PO_4 desorption in these tropical volcanic soils. More importantly, the amount of PO_4 sorbed when treated with organic acids is known to be dependent on the sequences of their addition (Violante and Gianfreda, 1995; He et al., 1999; Tsado et al., 2014b), influencing P adsorption as a result of competition for sorption sites between the organic acid and PO_4 .

In the addition of organic acids before P, the organic acids tend to occupy the surface site first, and P will only be adsorbed through desorption of some weakly held organic acid so that a maximum reduction of P adsorption occurs (He et al., 1999). These LMWOAs could also be interposed between PO_4 and reactive sites, protecting PO_4 from direct interaction or bonding with soil surface-reactive sites and reducing PO_4 adsorption (Agbenin, 2004; Antelo et al., 2007; Tsado et al., 2014a). The addition of P before the organic acids will result to P occupying the surface sites more easily (Tsado et al., 2014b). In this case, the addition of organic acids will only result in desorption or displacement of P which are adsorbed weakly to the surface, so that maximum adsorption of P occurs (Violante and Gianfreda, 1995; He et al.,

1999). Conversely, when P and organic acids are added to the soil simultaneously, either of them could arrive at the adsorption sites at different speed and as such the binding sites could also trap these ligand ions at a different or similar way (Antelo et al., 2007; Tsado et al., 2014b).

The results with the use of PLA are extremely encouraging, as can be observed for soils from Morne Prosper and Castle Bruce, but warrants further attention given the growing concerns and new insights with regards to soil pollution and acidity which can be induced at high concentrations of PLA (Debela et al., 2013; Togoro et al., 2014). Additionally, it can also be observed that PLA was quite effective on the low P sorbing soils, and given the relative ease of producing this resource, a by-product of charcoal production, warrants further research with regards to its use and application, as well as the economic analysis associated with the cost of PLA application to include gross and net benefits from cumulative release of P worked out on the basis of prevailing market prices.

For the high P sorbing soils, the effectiveness of PLA utilization, as a low cost on-farm derived soil amendment, most probably lies in refining and manipulating the observations of He et al., (1999), Johnson et al., (2003), and Tsado et al., (2014b) whereby concentration, contact time, sequence, method and frequency of application becomes important considerations to be addressed. Indeed, the influence of pH cannot be overlooked (Struthers and Sieling, 1950; Hajós and Nagy, 1998), as it has been shown that in tropical acidic soils, pH change in the rhizosphere and the presence of LMWOAs may increase organic P solubility by complexing Fe- and Al-oxides (Jones, 1998; Debela et al., 2013), besides the competition for adsorption sites promoted by the carboxylate groups (Guppy et al., 2005; Pavinato et al., 2008; Wang et al., 2012a; Chatterjee et al., 2015), attributed to direct site blocking, electrostatic repulsion or diffusion of LMWOA anions into small nm pores of the adsorbent (Mikutta et al., 2006).

The acidic nature of PLA may have an effect on displacement of Al- and Fe-oxides from the soil exchange complex which potentially could lead to an improved P nutrient

availability. However, increased displacement could possibly result to leaching of substances through the soil profile (Jones, 1998). For this reason studies on the impact of the use of this kind of product are of great agricultural and environmental importance, and absolutely necessary to support the correct and safe application of this alternative agricultural amendment on the soil (Benzon et al., 2015).

Furthermore, increased concentrations of PLA could possibly induce severe increases in the potential acidity, and a decrease in pH, base saturation, total cation exchange capacity, and Ca concentration (Togoro et al., 2014). At higher concentration (>4% v:v), PLA may induce a displacement of exchangeable bases and consequently lead to losses of these bases during water percolation as a result of the acidity (H^+) coming from the PLA (Togoro et al., 2014), inducing a downward movement of cations through the soil. Thus, the application of high concentrations of PLA, and subsequent irrigation and/or intense or prolonged rainfall may potentially lead to nutrient loss from top to deeper layers within the soil profile (Togoro et al., 2014).

In order to utilize rock phosphate in combination with PLA as a low cost option to increase the P status in these tropical volcanic soils, data on the interactive effect of pH and the ionic environment on the dissolution reactions of rock phosphate and the kinetics of the process are required via field trials. This research data is also needed to develop practical guidelines for direct application in the field in order to synchronize the rate and timing of application properly to meet crop requirements. To utilize PLA most effectively more research is needed in order to fully evaluate changes to the surface characteristics of soil. Detailed studies looking at the competitive distribution of metal ions between soil surface and PLA in the solution, its complexing ability, and the order of release of cations are just a few areas which needs to be addressed as priority. Therefore the development of application recommendations for use by farmers is imperative which has to be preceded by further laboratory and field studies.

CHAPTER 9

GENERAL DISCUSSION AND THE WAY FORWARD

From the inception and throughout the realization of this research, a number of relevant questions kept on surfacing which underscored the complexity of this thematic area. Such pertinent queries as to why do volcanic soils have rather unique morphological, physical and chemical properties? Why are certain secondary minerals so prevalent? Why does organic matter tend to persist? Why is their formation relatively rapid? Why are young volcanic soils among the most productive soils in the world notwithstanding being among the most infertile agricultural soils on a global scale? The discussion which pursues is not meant to repeat or synthesize results findings but rather to develop exchange of ideas emanating from the results as it relates to the overall management of volcanic soils in the Commonwealth of Dominica.

The response to these relevant questions which kept on surfacing generally highlighted the influence of parent material on which these soils have been formed (Lang, 1967; Ugolini and Dahlgren, 2002; Nanyzo, 2005) and the influence of various soil constituents which dictates their behaviour (Shoji et al., 1993; García-Rodeja et al., 2004; Vacca et al., 2009; Kubotera et al., 2009). This was captured in (Chapter 5) where Al and Fe forms were estimated and (Chapter 7) where P retention and desorption capacities were explored. Hence the unique chemical properties of these volcanic soils are basically due to their Al-rich composition, the highly reactive nature of their colloidal fractions, and their high surface area (Parfitt, 1979; Allbrook, 1985; Van Ranst et al., 2004, 2008; Pizzeghello, 2011).

9.1 Physical properties: Aggregate stability and SOM

Volcanic soils generally have high physical fertility (tilth) and mature soils are relatively resilient to erosion and compaction (Dahlgren et al., 2004a; Bronick and Lal, 2005) and to this extent, these soils are among the most productive soils globally (Shoji and

Takahashi, 2002; Nugroho, 2010). To maximize their productivity, proper management based on multi-disciplinary research of their unique physical, chemical, and mineralogical properties must be seen as a continuous exercise. Initiatives such as the use of crop rotations and diverse cropping systems combined with minimal to zero tillage practices with sound fertilization and irrigation should enhance SOC sequestration and soil particle aggregation (Nyamadzawo et al., 2009) hence the importance of setting new benchmarks as was captured in (Chapter 4).

Soil aggregation can be improved by land management practices that decrease agro-ecosystem disturbances, thereby improving soil fertility, increasing organic inputs, plant cover, and decreasing SOM decomposition rates (Schroth and Sinclair, 2003; Wei et al., 2006; Jose, 2009; Schroth and McNeely, 2011). These strategies can be gradually incorporated into the farming landscape through the development and use of high nature value farming indicators (Andersen et al., 2007; Paracchini et al., 2008; Lomba et al., 2014) as a monitoring tool of production activities and as a branding and promotional strategy targeting niche markets.

The presence of large amount of SOM, as was determined from exploratory baseline studies (Chapter 4) and the presence of allophane (Chapter 5) are responsible in part for the formation of large pore space because soils with high OM content tend to be well aggregated and consequently have better porosity (Yatno and Zauyah, 2008). These properties provide a conducive soil environment for deeper rooting activity and therefore supply more nutrients and water for vigorous plant growth (Shoji et al., 1993). In addition, low bulk density and friable consistency contribute to favourable soil tilth leading to easy tillage, seedling emergence, and root development.

Aggregates of volcanic soils are highly stable, being cemented by non-crystalline materials and SOM. Stable aggregates and high porosity of these soils minimizes water erosion (Rouse, 1990; Reading, 1991; Rao, 1996; Armas-Herrera et al., 2004). According to Rad et al., (2006, 2007) their pyroclastic formations are dominant, creating a very porous surface,

which allows water to percolate through infiltration; and thus important subsurface weathering mechanisms are affected by the intensity, frequency, seasonality and duration of rainfall (Rad et al., 2013) which affects the leaching effectiveness. These properties significantly contribute towards sustaining their high productivity, therefore linkages between SOM and soil conservation must be clearly established within land management initiatives and measurable indicators demonstrating land stewardship needs to be established along with systematic and realistic monitoring programmes that are time-bound.

Volcanic ash by its nature provides little resistance to weathering (Dahlgren et al., 2004a; Georgoulis and Moustaka, 2010). The fragile nature of volcanic glass which forms the basic component of volcanic material contributes to its rapid weathering (Shoji et al., 1975; Le Bas, 1986). Of interest, a few studies highlight that chemical weathering of andesitic–dacitic material on high-standing islands (HSIs) show these terrains to have some of the highest observed rates of chemical weathering and associated CO₂ consumption (Rad et al., 2006; Goldsmith et al., 2010; Kao et al., 2014), and as such the degree of crystallinity of tephra in andesitic terrains play an important role in determining weathering fluxes (Goldsmith et al., 2010). These HSIs are characterized by having stream headwaters which lie at elevations in excess of 1000 metres and given their geographic proximity to oceans they experience rainfall events at high frequency and intensity (Goldsmith et al., 2010). With an abundance of short rivers and steep gradient they also tend to have a rapid transport of sediment to oceans. Given the hydrology of Dominica the use of various environmentally oriented P soil test methods (Chapter 6) were explored whereby P saturation and potential P losses were investigated.

Volcanic soils tend to be rich in disordered non-crystalline allophane which does not orient on shearing thus producing high residual strength (Rouse, 1990; Rao, 1996) and the shear strength of slopes found in allophanic soil deposits have been observed to fail only during rainfall of exceptionally high intensities (Rouse et al., 1986, Reading, 1991) as was experienced

on 27th August 2015 by the passage of tropical storm Erika which resulted in massive island-wide landslides and severe soil erosion on the island of Dominica which led to the enormous transport of sediment to oceans with some coastal villages being partially buried under silt!

High resistance against biodegradation of SOM has been attributed to the strong interactions existing between allophanic particles and organic colloids (Borie and Zunino, 1983) and high structural and aggregate stability is mainly controlled by the association of SOM with Al and Fe (Warkentin and Maeda, 1980; Aran et al., 2001). This implies that preservation of organic matter is critical for long-term soil productivity as well as for sustained soil conservation. The practical significance of the management of soil organic matter thus lies in the conservation measures necessary to prevent the depletion of organic carbon which can result from intensive cropping (Sibanda and Young, 1986). Hence the concept of zero to minimal tillage and improved fallow systems (Nyamadzawo et al., 2009) has to be given due consideration. Given the erosion potential of SOC and the depletion of soil nutrients leading to losses via sediment transport, land base activities need to be designed so as to encourage mitigation practices such as strip cropping and planting along the contour which would minimize against soil loss and the negative effects on the marine coastal environment.

Soil structure is a key factor in the functioning of soil, its ability to support plant life, and its ability to moderate environmental quality with particular emphasis on soil carbon sequestration and water quality (Bronick and Lal, 2005; Woignier et al., 2007). Volcanic soils combine a number of seemingly incompatible properties in maintaining the overall integrity and functionality of these soil systems. These properties include: (i) severe degradation of primary plant-derived SOM, including the most recalcitrant compounds, (ii) relative abundance of microbial SOM, and (iii) considerable accumulation of SOM in general (Buurman et al., 2007). The presence of > 5% of allophane appears to favour, rather than hamper, decomposition of primary plant litter (Chapter 4) and the decomposition of plant-derived SOM

and the relative contribution of microbial SOM tends to be greater in allophanic soils than in non-allophanic ones (Buurman et al., 2007), classification differences which need to be better understood for improved management of these volcanic soils.

9.2 Chemical properties and nutrient availability

The creation of surface negative charges on allophane through interaction with humic substances has implications for the management of allophanic soils (Senesi et al., 1977; Yuan et al., 2000; Ugolini and Dahlgren, 2002). Carrying only a small negative charge at pH <6, allophane by itself would be ineffective in retaining nutrient cations and heavy metals in the pH range of most soils (Yuan et al., 2000). By developing an excess of surface negative charge, the formation of complexes with organic matter (humus) would substantially increase the capacity of these soil to retain and immobilize positively charged species and organic contaminants (Yuan, et al., 2000; Krull et al., 2004; Bruce et al., 2009). By promoting the interaction between minerals and humic material, the addition of Ca²⁺ ions through the application of agricultural lime, gypsum or Ca salts would help considerably in the stabilization of organic matter in allophanic soils (Sollins et al., 1996) thus preventing surface crusting.

Nonetheless, it is often assumed that soil will continue to behave as it has in the past. However, the impact of drastic shifts in land use may alter soil properties, functions and processes leading to a rapid depletion of available nutrients and as a consequence a threat to food security (Taylor et al., 2012; Bahr et al., 2014). Typically, tropical regions largely comprise strongly weathered and nutrient-impooverished soils that are relatively unsuited for the development of intensive agriculture (Juo and Franzluebbers, 2003) and as such sustainable agricultural development in the tropics will need to focus on soil fertility maintenance for viable crop production in the present and for future generations. The background justification which gave rise to this discourse was captured in (Chapter 4) with the aim of establishing a new benchmark since the soils of Dominica were first studied in a relatively detailed way back

in 1967. For many tropical countries and for the Commonwealth of Dominica, the agro-environmental challenge and hidden economic opportunity is to limit deforestation, increase SOM storage in cultivated soils and reduce current erosion of terrestrial SOC and its delivery by rivers to oceans (Feller et al., 2001; Schroth and McNeely, 2011; Kao et al., 2014).

Some researchers have postulated that a combination of P-efficient crops or cultivars (Sahrawat et al., 2001; Gahoonia and Nielsen, 2004; Cornish, 2009; López-Arredondo et al., 2014) and P fertilization practices (Horst et al., 2001; Sahrawat et al., 2001) may provide a better strategy for sustainable crop production on soils where P availability is a major constraint. Plants that are efficient in the absorption and utilization of nutrients greatly enhance the efficiency of applied fertilizers (Shenoy and Kalagudi, 2005), reducing cost of inputs (Sahrawat et al., 2001; Johnston et al., 2001; Jat et al., 2012), and preventing losses of nutrients to ecosystems (Sharpley, 1993; Baligar et al., 2001; Sharpley et al., 2013) hence the importance of encouraging species diversity from both economic and agro-ecological perspectives.

9.3 Phosphorus transformation in volcanic soils

All native P in soil is originally derived from apatite from which P is released by weathering and then formed into inorganic pyrophosphates and polyphosphates, inorganic Ca, Fe, or Al phosphates, occluded P of Fe and Al oxides, or organic P compounds (Shen et al., 2011). In addition, phosphorus is the one major element in soil which must be supplied almost entirely by the parent material of unfertilised soils because of low atmospheric returns. Furthermore, because nearly all soil P is unavailable for immediate use by soil microbes and plant roots, relationships between labile and recalcitrant P must be fully understood. In warm, wet, acidic soils such as those of the Commonwealth of Dominica, Fe and Al phosphates predominate, and organic P forms would tend to be rapidly mineralized. Furthermore, since the various forms of phosphates differ in their solubility, their distribution might give an

indication about availability of P in the soil (Hedley et al., 1982; Cross and Schlesinger, 1995), although the latter is largely determined by the amount of surface of the various forms.

During soil development, P from weathered minerals is usually exhausted, leaving residual P to be cycled through organic matter or into occluded and strongly recalcitrant inorganic P. However, as was highlighted by Schmidt et al., (1996) over time scales longer than a growing season, slowly cycling fractions of P make significant contributions to P bioavailability, and can ultimately determine ecosystem productivity, organic matter storage and sustainability. Hence the concept of P bioavailability has critical temporal and spatial dimensions that are related to the sink strengths of plants and soil organisms in a given locale.

Assessing available P is fundamental to managing many of these soils. Fractionation of soil phosphorus (Chapter 6, 8) permits tracing the fate of applied phosphate fertilizer under different soil conditions due to the fact that, unlike other nutrients, chemical compounds associated with soil P lend themselves to sequential chemical extractions that can describe soil P in operationally discrete fractions (Chang and Jackson, 1957; Hedley et al., 1982). Current data on the properties of Dominican soils, however, are still incomplete and there is a paucity of information with regards to microbial activity and soil organic P dynamics. Thus, it is important to improve the study scope and research latitude of these soils to provide more all-encompassing information of their behaviour and performance to support their management.

9.3.1 Plant availability P in volcanic soils

The functional relationship between plant uptake of P, and the P status of soil is governed by an intensity factor (I) which describes the concentration or activity of the phosphate ion in solution; a quantity term (q), which measures the amount of P in reserve associated with the solid phase; and a buffering capacity term (b), which measures the resistance of the soil system to change in (I) (Olsen and Watanabe, 1963; Olsen and Khasawneh, 1980; Barber, 1995; Grant et al., 2005). There exist several possible ways to

increase P availability in soil. The traditional ones include the use of slow-release fertilizers (Shaviv and Mikkelsen, 1993; Shaviv, 2001; Pickering et al., 2002; Tylliszczak et al., 2009), foliar applications (Boynton, 1954; Koontz and Biddulph, 1957; Mosali et al., 2006; Girma et al., 2007), and special methods of fertilizer application in the field (Westerman and Edlund, 1985; Sharpley et al., 1994, 2000; Kimmell et al., 2001; Jing et al., 2010) which stimulate root proliferation and rhizosphere acidification through the use of LMWOAs (Chapter 8).

The very limited movement of phosphate ions also explains why it is necessary to have a sufficient supply of readily-available P throughout the volume of soil explored by roots if the demand for P by a crop is to be met during its most active period of growth (Chapter 7). As such good responses are often obtained by placing P fertilizer near where the roots of a crop are expected to grow. However, Randall (1995) highlighted that responsiveness should be distinguished from efficiency to the extent that responsive plants would be most desirable in fertilized, high-input systems, while P-efficient plants, which produce high yields at low levels of P, are likely to be most valuable in low-fertility situations. For annual crops, fertilisers with high P solubility are essential in meeting the crops early P requirements. On the other hand, a slow release P fertiliser will be more suitable for slow growth perennial species. Additionally, slow release P fertilisers may also improve P use efficiency in high-rainfall areas and/or on coarse-textured soils where dissolved P can possibly be lost via leaching (McLaughlin et al., 2011) and as such the importance of site specific P fertilizer programmes.

In order to solve the serious problems caused by unsuitable management and to sustain the functionality of volcanic soils, crop rotation, soil structure improvement, and precision agriculture along with programmed fertilization will need to be encouraged (Shoji and Takahashi, 2002; Syers et al., 2008) among other remedial and mitigation exercises. Hence trade-offs between ecosystem conservation and agricultural production will need to integrate

biodiversity friendly land use systems into developmental strategies at the landscape scale (Schroth and McNeely, 2011) in an attempt to sustainably intensify agriculture production.

Agricultural practices carried out in the Commonwealth of Dominica are based on medium input farming but with an ever increasing demand for P as is the case in many tropical developing countries where P deficiency is severe. Despite the limited analytical capacity, renewed attention is being paid to soil chemical, physical and biological conditions. National initiatives include technical and human capacity building within the ministry of agriculture as it relates to crop nutrient management. It is expected that farmers and extension agents will be better able to address the challenges associated with soil fertility, including the use and management of fertilizers for sustainable crop production. As a result, due attention must be particularly given to P dynamics in the soil/rhizosphere – plant continuum to include P acquisition, translocation and utilization, as well as the regulatory processes (C-P trade off, shoot-root regulation) in understanding P transformation and movement in the soil and plant (Shen et al., 2011). With the long-term trend of minimal P fertiliser use (Chapter 3) and the seemingly glut of applied P fertilisers when compared to P removal in harvested produce, it is of no surprise that there has been a gradual depletion of P in most Dominican agricultural soils.

In terms of soil management for both agricultural production and environmental protection, the addition of organic matter and lime provides a route. Their addition to these tropical volcanic soils would undoubtedly enhance the capacity of allophanic soils to retain nutrient cations and even reduce heavy metal contamination. The application of P fertilizers and liming coupled with efficient placement can be recommended to enhance P availability and reduce Al toxicity. In addition, organic matter can be used to reduce Al toxicity but nonetheless, soil conservation strategies needs to be considered, especially on steep slopes and in high rainfall areas. The application of phosphate fertilizers will undeniably enhance the productivity of these soils but attention has to be given to the accumulation of fluoride, which

is almost always present as a contaminant in superphosphate and other P fertilizers (Taylor et al., 2012; Marimon et al., 2013). Furthermore, attention has to be paid to the use of phosphate rocks since high concentrations of As, U, Zn and Cd might also limit the direct use (Syers et al., 1986; Rochayati et al., 2011).

The use of LMWOAs shows a promising route, especially the application of PLA on low P fixing soils, demonstrating that organic ligands generally enhance both the solubility and dissolution of aluminosilicate minerals (Jones, 1998; Jones and Brassington, 1998; Ström et al., 2002; Huang et al., 2003; van Hees et al., 2005, Ström et al., 2005; Li et al., 2008; Shao et al., 2011; Wang et al., 2012a). Results with the use of PLA are not conclusive but encouraging, which warrants further investigation amidst the growing concerns and new insights with regards to soil pollution and acidity possibly induced at high concentrations of PLA (Debela et al., 2013; Togoro et al., 2014). However, the unique properties of PLA create opportunities for the development of alternative agricultural inputs and given the challenges in combating pest and disease infestation and soil fertility issues, from an economic standpoint, the development of these low cost options might just prove to be a step in the right direction.

In these tropical volcanic soils, improvements in P-nutrition may however have to be eventually sought by shifting the P-equilibrium toward root absorption (Itoh and Barber, 1983; Gahoonia and Nielsen, 2004; Gaxiola et al., 2011), by taking into account the special environment and the composition of P-sinks. This is one reason why husbandry as well as agronomic aspects of the soil must be optimized before plants will perform at their best. To achieve this it is essential to understand the mechanisms by which native vegetation absorbs P to satisfy their requirements (Chapin III, 1980; Chapin III et al., 1986; Aerts and Chapin III, 2000). This ultimately will require additional research with regards to N and P cycling, Al toxicity, acidity amelioration, mycorrhizae interactions, C-P trade-offs among other thematic areas, and the role these play in soil quality and sustainable land management.

9.4 Volcanic soils and ecosystem functions

It has been suggested that volcanic soils are of interest in terms of controlling the greenhouse effect (Bronick and Lal, 2005; Woignier et al., 2007). Hence the non-visible direct monetary benefits of ecosystem services such as watershed protection and carbon sequestration by natural and complex agro-ecosystems has to be pivotal in defining agricultural developmental strategies which are oriented towards biodiversity friendly land use systems (Jose, 2009; Schroth and McNeely, 2011) and as such the importance of economic incentives and policies to promote integrated landscape solutions. Given the limited expanse of arable land for agricultural production, these landscapes will now have to contribute even more meaningfully towards the conservation of biotic species and ecosystems. Hence there is need for the consideration of best management practices initiated at the policy level whereby due attention is given to the role of combining agricultural productivity and profitability with critical habitat and ecosystem functions.

The soil microbial community plays an important role in nutrient cycling and availability (Acosta-Martinez et al., 2007; Steiner et al., 2008; Nyamadzawo et al., 2009) and the development of technologies which incorporate soil microbes such as VA mycorrhizae and P solubilizing bacteria in plant P acquisition would be critical in any integrated plan to increase P availability (Smith and Read, 1997; Feddermann et al., 2010; Heydari, 2013). Consideration also has to be given to other low cost mechanisms which has potential in enhancing P mineralization and cycling. Green manuring with crops like *Tithonia*, *Crotalaria* (George et al., 2001; 2002; Scrase, 2004), *Sesbania*, *Lantana*, *Leucaena*, *Gliricidia* and *Croton* (Kwabiah et al., 2003) can be aligned to the concept of participatory crop improvement (PCI) through the development of farmer field schools (FFS). Given the susceptibility of the Dominican agrarian base economy to external shocks and natural hazards, sustained agricultural development will need to occur to the benefit of natural ecosystems.

9.5 Phosphorus fertilizers in volcanic soils

The goal of P fertilizer management is to optimize crop production while minimizing the risks of environmental impacts, such as toxic metal accumulation in soils and eutrophication of water bodies (Vance, 2001; McDowell and Catto, 2005; Chien et al., 2011). Management practices, such as method of placement, timing of application, incubation time, sources of nitrogen application, irrigation and moisture content, and lime application can influence the effectiveness of PR or water-soluble P-fertilizer (Bolan and Hedley, 1989; Chien and Menon, 1995; Rajan et al., 1991; McDowell et al., 2005; Nelson and Janke, 2007; Roberts, 2007; Al-Ouds, 2011). Haynes (1992) reported that the acidification of the rhizosphere commonly occurs when plants are using NH_4^+ as their major N-source and as such the equivalent sum of cations absorbed by a plant exceeds that of anions resulting in a net efflux of H^+ . On the contrary, when NO_3^- is the major N-source the equivalent sum of anions exceeds that of cations resulting in a net efflux of OH^- ions (Kirkby and Knight, 1977; Haynes, 1992).

Following the addition of soluble P fertiliser to soil, a series of reactions occurs between P, soil constituents, and non-P components of the applied fertiliser that remove P from the solution phase, making P less bioavailable (Grant et al., 2005; Chien et al., 2011). These may include both adsorption reactions on the surface of soil particles, diffusion reactions where surface P becomes incorporated into soil particles, as well as precipitation reactions that form new solids in the soil (McLaughlin et al., 2011, Barrow and Debnath, 2014).

Granulation and band application of water-soluble P fertiliser may enhance nutrient-use efficiency by reducing the amount of P that becomes fixed to soil surfaces (Kumar et al., 1993; Maene, 2001, 2003). However, banding PR rather than broadcast and incorporating tends to reduce the rate of PR dissolution (Khasawneh and Doll 1978; Kanabo and Gilkes, 1988; Sale and Mokwunye 1993; Kumar et al., 1993; Chien and Menon, 1995; Chien et al., 2010) because dissolution is restricted by the build-up of components that are released resulting

from limited contact of PR particles with the soil (Chapter 8). In addition, Chien et al., (2010) noted that the solubility of PR generally increases with smaller particle size but the relative agronomic effectiveness of ground and unground highly reactive PR sources may vary considerably reflecting mineralogical and chemical characteristics of origin of the P mineral.

Timing the application of PRs is important for their effective use. Cabala-Rosand and Wild (1982) demonstrated that the effectiveness of low soluble PR was enhanced when applied directly on acid soils well in advance of crop planting. Complementary to the aforementioned, Rajan and Watkinson (1992) concluded that biennial application of PR may be more beneficial from the point of its agronomic effectiveness. However, Hammond et al., (1986b) reported that it is expected that early application of PR would allow some time for dissolution to begin, but when applied to high P-sorbing soils the effectiveness of rock phosphate could actually be reduced when the PR is applied too early. In addition, DeMoranville and Davenport (1997) reported on application timing, to the point these authors recommend that slow-release forms of PR may be applied in a single early season application with subsequent residual effects.

In underscoring the importance of management factors affecting PR effectiveness, McDowell and Catto (2005) concluded that the potential for incidental P loss via fertiliser application declines exponentially with time and is related to solubility in water, meaning slow release fertilisers such as reactive phosphate rock pose much less risk soon after application than highly soluble superphosphate. In addition, Nelson and Janke (2007) highlighted that among the best management practices for reducing source P losses is the timing of application to correspond to periods of low runoff risk based on climatic conditions. Nonetheless, the efficiency of fertilizer use is also often related to placement. Since phosphate is generally not very mobile in the soil, it must be placed in a moist zone of the soil in order for the plant to derive maximum benefit (Chien et al., 2011). Thus the practice of banding or broadcasting fertilizer places a large fraction of the nutrients away from the plant (Bationo et al., 1992).

It has also been reported that lime application can influence the effectiveness of PR or water-soluble P-fertilizer (Sánchez and Salinas 1981; Bangar et al., 1985; Hammond et al., 1986b; Mackay and Syers, 1986). Since rock phosphates essentially comprise of calcium phosphate compounds, removal of Ca from rock phosphate will release P into solution (Nying and Robinson, 2006; Kumari and Phogat, 2008). Liming as a management option will aid in increasing pH and reduce exchangeable Al^{3+} concentration, especially for crops that are sensitive to Al. However, when increasing the pH through liming, the PR dissolution is decreased due to increased Ca concentration (Bolan and Hedley, 1989; Chien and Menon, 1995; He et al., 2005; Kumari and Phogat, 2008) and reduced acidity. In essence, a decrease in plant available P from PRs after liming can be attributed to an increase in the adsorption of inorganic P with an increase in soil pH (Bolan and Hedley, 1990; Chien et al., 2010).

According to Sánchez and Salinas (1981), a practical approach to overcome the two contrasting effects is to apply the PR well in advance of the application of liming materials, as long as the P-sorption capacity of the soil is not high. However, under field conditions where Ca may be removed by plant uptake and/or due to leaching, this effect may be minimized (Kumari and Phogat, 2008). In addition, Mackay et al., (1986) obtained varying results for PR dissolution in soils of varying pH which was modelled on a modified Mitscherlich equation and suggested that soil pH, per se, is not the over-riding factor controlling the dissolution of a PR in soils and Ca in lime may play a role independent of pH in the dissolution.

9.6 Volcanic soils and their potential to sediment P loss

The concept of “feed the soil and not the plant” has been a central theme of many organic programmes globally (Papendick and Parr, 1992; Watson et al., 2002; Magdoff and Weil, 2004; Badgley and Perfecto, 2007; Simpson, 2010). Indeed, these sentiments were persuasively conveyed to a number of subsistence farmers in developing and underdeveloped countries, and by inclusion, the Dominican farming community in the embryonic days of

organic agriculture production systems (IFOAM, 2002). However, re-classifying the P fertility status of Dominican volcanic soils taking into consideration the degree of P saturation will not only enhance the management of recommended P but could also lead to possible consequential benefits to water quality which is of great concern within the Dominican eco-system given the country's abundance of free-flowing streams and rivers (Chapter 6). A concerted effort is needed towards rethinking P management strategies (Jones et al., 2013; Withers et al., 2014; 2015; Schoumans et al., 2015) in terms of the effects on plant P supply as well as PSB and VAM development (Grant et al., 2005; Heydari, 2013) in order to sustainably intensify agricultural production in meeting current food production requirements and into the future.

The results from this present study provides a base platform for future experimental exercises with regards to P fertiliser management strategies by taking into account both production and environmental imperatives. They also point to an urgent need for field crop experimentation particularly in high rainfall areas, such as Pond Cassé which are potentially very productive under suitable management systems, where allophanic clays are predominant (Lang, 1967). Therefore from a managerial and technical perspective, any P fertiliser recommendations for crops in the near distance future should ideally be based on the same soil tests that are used to make assessment of environmental risk (Sharpley, 1996; Sims, 1998).

The influence of soil type and the vulnerability of these Dominican soils to P losses has important implications from both productivity and environmental viewpoints. It is extremely critical to determine which agricultural producing catchments within a given watershed is P sorption highest and what is the spatial pattern of distribution given current land use. This would be valuable information that policy makers, agricultural technicians, farmers, and community-based organizations could use to implement nutrient management plans. The information generated would then need to be incorporated in GIS databases from which further relationships among watershed characteristics, and nutrient retention could be investigated.

9.7 Allophanic versus non-allophanic Andosols: The need for international classification

An important factor determining the extent of sorption reactions, particularly in acidic and slightly acidic pH soils, is the abundance and type of Al and Fe minerals present in the soil (Bolan et al., 1985; Gilkes and Hughes, 1994; Fontes and Weed, 1996; Quang et al., 1996; Bruland and Richardson, 2006). Hydrous oxides of Al and Fe are the most abundant form of Al and Fe in soil, and therefore they tend to sorb more P than layer silicates and other crystalline forms of Al and Fe. As a result the re-classification of these volcanic soils based on these differences is needed to better understand their behaviour for improved management.

Volcanic Andosols can be differentiated between allophanic and non-allophanic Andosols (Wada and Kakuto, 1985a,b). Indeed the transition between allophanic and non-allophanic Andosols are not fully understood, nor are transitions between non-crystalline versus crystalline mineralogical assemblages (Chapter 5). It has been shown that although there are similarities in behaviour, these soils have quite distinct features (Shoji, 1985; Shoji et al., 1993; Armas-Herrera et al., 2004; Nanyzo, 2005; Vacca et al., 2009; Kubotera et al., 2009) which unfortunately has far reaching consequences from their mismanagement.

Based on the current research, there is a tendency which strongly suggest that soils from Soufriere and Salisbury as well as Castle Bruce do not behave as classical allophanic Andosols. This observation is reflected by their low pH NaF, low P retention values in addition to other soil constituents, notably Al, Fe and Si content as extracted with dithionite (crystalline), oxalate (non-crystalline amorphous) and pyrophosphate (organic bound) reagents. Dissolution analysis and TB metachromasis highlighted that the accumulation of stable organo-mineral complexes or short-range-order minerals such as allophane, imogolite and ferrihydrite was negligible in these soils when compared to the higher P fixing soils. The results suggest that weathering of silicate material leading to the formation of stable organo-mineral complexes

was not intense and coupled with low Si content in the dissolution of primary and secondary minerals favoured a low expression of andic properties (Shoji, 1985; Shoji et al., 1996).

Different pedogenic trends of these soils, which is also time dependent, are affected by their hydraulic properties of the parent material (Vacca et al., 2003, 2009). Allophanic soils tend to develop in younger, porous, permeable ash deposits where rapid glass weathering is favoured and Al and Si are readily available for allophane formation, observations which were made by Lang (1967) who postulated the accumulation of allophane in the volcanic “young soils” of Dominica. By contrast, non-allophanic soils tend to develop in older, less porous, and less permeable scoria and consolidated tuffs where pedogenesis induces the neogenesis of crystalline clays and hydrated halloysite is probably formed by in situ weathering of volcanic glass.

According to the world reference base (FAO, 2006), soil classification consist of three fundamental steps namely: (1) The expression, thickness and depth of layers are checked against the requirements of WRB diagnostic horizons, properties and materials, which are defined in terms of morphology and/or analytical criteria, (2) The described combination of diagnostic horizons, properties and materials is compared with the WRB key in order to find the reference soil group, which is the first level of WRB classification, and (3) For the second level of WRB classification, qualifiers are used. The qualifiers are listed in the key with each RSG as prefix and suffix qualifiers. The use of a common language is of prime importance notwithstanding the availability of reliable information on soil morphology and other characteristics obtained through examination and description of the soil in the field (FAO, 1998, SSS, 2003; Jahn et al., 2006). With restricted sampling and absence of morphological analysis, conclusive evidence is currently unavailable and warrants further investigation.

According to Ugolini and Dahlgren (2002), very old and highly weathered volcanic soils may no longer be Andosols but could possibly be Ultisols or even Oxisols. In the case of

the Commonwealth of Dominica a major shift in the focus of volcanism was evident about 1.6 Ma ago with activity switching from the northern to southern half of the island (Lindsay et al., 2003, 2005a,b; Joseph et al., 2011) where most of the study sites were located. In addition, Lang (1967) developed a sequence for Dominican residual soils taking into account the degree of weathering and intensity of leaching (Chapter 3) and based on estimated present day limit of development, these volcanic soils show signs of being smectoid – montmorillinite rich clays in the seasonally dry areas to allophane – allophane rich clays in the perennially wet areas (Lang, 1967). Moreover there have been arguments which suggest that allophanic and non-allophanic soils can coexist in similar landscapes under similar climatic conditions (Vacca et al., 2003, 2009) which gives further support for the need to re-classify them accordingly.

As a consequence of these observations, management strategies would differ significantly across these soils (Rouse, 1990; Reading, 1991; Rao, 1996; Rad et al., 2007, 2013) and hence this study highlights the need to critically re-classify these tropical volcanic soils in accordance to international norms (e.g. FAO, 1988, 1998, SSS, 2003; FAO, 2006) as was highlighted by Deckers et al., (1998), Spaargaren and Deckers (1998), and Spaargaren (2004) whereby soil classification systems could be correlated and ongoing soil classification work harmonized. This would increase the understanding of their behaviour and hence their management, ultimately leading to increased functionality and well-organized use.

Nanzyo (2005) highlighted that when agricultural crops are planted in newly reclaimed Andosols, such as from forest clearing, they show inferior growth to that of younger soils. The reasons for this are often related to their low content of plant-available nutrient elements, especially P, and some micronutrients (Chapter 8). In addition, this inferior growth is sometimes related to a high toxic Al content, the highly sorptive properties of the nutrient ions and stabilization of soil organic N (Nanzyo, 2005). Amelioration of these shortcomings has to take into account site specific peculiarities to include use of P fertilizers related to P sorption

characteristics (Holford et al., 1974; Barrow and Debnath, 2014). A key to establishing threshold conditions is to understand processes regulating aqueous Al and Si activities and kinetic factors regulating aqueous-solid phase interactions (Dahlgren et al., 2004b). Moreover exploring the application of silicate fertilizers as an option, via field trials, may possibly enhance P availability by increasing the zero point charge (ZPC) thereby decreasing the P sorption potential in high P fixing soils (e.g. Pond Cassé and Layou Valley).

Crop uptake is generally only 10–20% of the P fertilizer applied in the first year, but a substantial part of applied P accumulates in the soil as residual P (Wolf et al., 1987; Syers et al., 2008). P uptake not only depends on the amount of available P in the soil but also on plant properties (Föhse et al., 1988; Wissuwa, 2003; Wasaki et al., 2003; Nacry et al., 2005). Differences in the agricultural productivity among Andosols are largely attributed to the colloidal composition in the rooting zone, namely allophanic versus non-allophanic properties related to subsoil acidity, active Al and variable charge (Shoji, 1985; Dahlgren and Saigusa, 1994; Matsuyama et al., 2012).

Allophanic and non-allophanic soils show contrasting effects on the behaviour of KCl-extractable and water soluble Al (Takahashi and Dahlgren, 1998). These forms of Al are toxic to many sensitive crops such as cereals and beans (Kochian et al., 2005; Silva, 2012) with the content higher in non-allophanic Andosols and lower in allophanic Andosols (Nanzyo, 2005) as well as organic C and Si content affecting water-extractable Al levels. Hence in non-allophanic soils, severe acidity tends to result in poor rooting towards the subsoil (Matsuyama, et al., 2012; Silva, 2012). In addition, the clay fraction of allophanic soils tends to be allophane/imogolite which has a weakly acidic character whilst non-allophanic clays tend to be dominated by 2:1-2:1:1 minerals showing strong acidic character (Matsuyama et al., 2012).

Understanding these mineralogical and chemico-physical differences opens up numerous opportunities in developing practical solutions for volcanic soils to important

agronomic and environmental issues. According to Dahlgren et al., (2004a,b), high anion exchange capacity provides an opportunity for attenuating nitrate leaching in agricultural systems. The abundance of non-crystalline materials and SOM provides a high capacity to retain heavy metals, trace elements and organic compounds making them a good candidate for disposing of bio-solids, and high P fixing soils will more than likely act as long-term P-sinks in sensitive watersheds.

The association of different physical and chemical properties, especially those related to short-range-order minerals and organic components, is responsible for the structural stability of the Andosols (Warkentin and Maeda, 1980). In addition, Armas-Herrera et al., (2004) demonstrated that structural stability to wetting and water-drop impact is generally very high, findings which were also reported by Rouse (1990), Reading (1991), Rao (1996), and Rad et al., (2007, 2013) with regards to the stability of Dominican allophanic soil slopes. However, non-allophanic Andosols generally have higher CND values although not significantly different from allophanic soils with regards to water stable aggregates. Furthermore, in allophanic Andosols, disaggregation by wetting and stability to water-drop impact is correlated with fractions of complexed/humified organic carbon and Fe and Al bound to organic compounds, while in the non-allophanic Andosols disaggregation by water-drop impact is the main separation mechanism determined by physical and chemical properties of the organo-mineral complexes, particularly Fe_p and Al_p (Armas-Herrera et al., 2004).

Non-allophanic soils tend to be muddy when wet and compacted when dry because of a relatively low plastic limit and a weak aggregation structure (Matsuyama et al., 2012), therefore cultural practices such as land preparation and tillage can severely and irreversibly affect soil structure and microbial activity (Nyamadzawo et al., 2009). The structural stability in relation to their erodibility varies and warrants different management strategies to the extent

that increasing soil organic matter content and decreasing SOM decomposition rates will need to be seriously considered to include “green” policy incentives in susceptible areas.

Of significant importance, it should be fully appreciated that soil water plays a significant role in P use efficiency through the interaction with soil chemical reactions, and the diffusion of P to the rhizosphere (Payne et al., 1992; Baligar et al., 2001; Tilman et al., 2002; Syers et al., 2008). Dry conditions may exacerbate P precipitation reactions with the solid phase in fertiliser bands by increasing the concentration of P around the point of application (McLaughlin et al., 2011). When water is inadequate, P diffusion is also reduced due to reduced water-filled porosity and increased curvature of water filled pores. Therefore, the efficiency of P use in soils with adequate water is much higher than in dry soils and the placement of P may be critical in determining P use efficiency (Schröder et al., 2011).

Notwithstanding all the aforementioned, there is still no clear consensus as to the ultimate fate of fertiliser P added to the soil due to the fact that this is inherently dependent on soil properties, environmental conditions and time (McLaughlin et al., 2011). However, it is clear that a large proportion of added P fertilisers in cropping systems will remain in the inorganic pool, sorbed or precipitated to Al, Ca and Fe compounds (Imai et al., 1981; Parfitt, 1989a,b; Pardo and Guadalix, 1990). This is more than likely to occur especially when one considers P fertilizer application and placement methods (i.e. broadcasting versus band application versus sub-soil application) which has significant impact on the microbial community in the immobilisation and incorporation into soil organic matter (Makoi et al., 2010; Shen et al., 2011; Giles et al., 2014; Zhang et al., 2014).

From a trade and industry perspective, phosphorus is one of the most expensive and widely used major nutrients used in global crop production (Cordell et al., 2009; Smit et al., 2009; Cordell, 2010; Dawson and Hilton, 2011; Schoumans et al., 2015). Therefore, there is a major economic benefit in developing a soil test capable of accurately predicting the P status

of a soil (Mason et al., 2010), which in turn will facilitate efficient fertilisation strategies and reduce the risks of environmental pollution due to over fertilising (Withers et al., 2001; Potter et al., 2010; MacDonald et al., 2011; Lemaire et al., 2014) as well as managing the associated economic cost more efficiently. Hence, predicting the potential supply of accumulated P to crops by use of accurate soil testing is an important part of using P fertiliser effectively to maximize yield output economic returns.

With increasing costs of P fertiliser inputs, various technologies have been suggested to improve P efficiency, but few have provided solid field evidence for efficacy. Notwithstanding these constraints, the use of pyroligneous acid (PLA) has been proven to have additional physiological benefits for overall crop production (Merritt et al., 2007; Ping et al., 2010; Aremu et al., 2012; Abdelgadir et al., 2013; Nair et al., 2014; Papenfus et al., 2015) as opposed to the limited knowledge of its role in the dissolution of secondary P minerals. Consequently, products that target existing P sources rather than adding new P sources into the soil have considerable potential such as the use of PLA and other low cost strategies which can be developed in and around the farm unit of production.

In conclusion, the future of food security depends upon securing the long-term availability of and accessibility to phosphorus (Cordell et al., 2009; Scholz et al., 2014; Schoumans et al., 2015), especially for agrarian based economies of the tropics where the demand for P to sustainably improve crop productivity and overall crop production is warranted. Hence the concept of recycling P becomes even more important for cash-strapped economies. However, attention has to be paid to soil health and the conservation and efficient use of water (Swaminathan, 2005) coupled with better management of production factors. In this regard some researchers (Carter, 1993; Peverill et al., 1999) have strongly advocated that programmes and activities geared at improving soil fertility, especially plant nutrient availability by multi-faceted approaches is of utmost importance for sustainable production.

Key Recommendations in Charting the Way Forward

- Initiate the development regulatory mechanisms, aided with improved soil sampling and analysis, whereby the use of P fertilizers is in accordance to soil specific P sorption properties, incorporating the concept of degree of P saturation into the re-classification of P fertility status of Dominican volcanic soils.
- Explore the application of other forms of fertilizers (e.g. silicate), through applied on-farm research initiatives, to enhance P availability thereby reducing P adsorption in high P fixing soils. However, attention needs to be given to implications with regards to the soil biological physical characteristics. Research initiatives are also needed to explore the application of Al and Fe ions on low P fixing soils to avoid potential P losses in addition to lime application in enhancing the overall P status.
- Initiate the development of production instruments which encourages the use of crop rotations and diverse cropping systems combined with zero to minimal tillage practices with well-regulated fertilization and irrigation schemes. This will ultimately lead to increase soil functionality, productivity, and soil resilience to include impacts of climate change.
- Encourage land management practices, through “green incentives” and appropriate policy that decreases agro-ecosystem disturbance, improves soil fertility, increases organic inputs and plant cover, and decreases SOM decomposition rate.
- Explore the use of high nature value farming indicators as an overall management strategy and monitoring tool for agricultural production through participatory approaches. These will include management programmes which limit deforestation, increase organic matter (OM) storage in cultivated soils and reduce current erosion.
- Initiate the development of production programmes which will combine P-efficient crops and cultivars as well as efficient P fertilization practices. Moreover P fertiliser management strategies needs to take into account both production and environmental imperatives. This can be pursued through the development of on-farm trials through participatory approaches using the farmer field school (FFS) concept.
- Initiate the integration of biodiversity friendly land use systems into developmental strategies at the landscape scale which focuses on trade-offs between ecosystem conservation and agricultural production, e.g. REDD+ and PES national initiatives.
- Explore the possibilities of developing of technologies which incorporate soil microbes such as mycorrhizae in plant P nutrition through post-graduate and doctoral research.
- Explore the incorporation of participatory crop improvement programmes (PCI) with emphasis on nutrient enhancement through the development of farmer field schools (FFS). More importantly, pursue the development of field crop experimentation particularly in high rainfall areas, which will serve as models of nutrient management in these areas with crops better suited for cultivation on acid soils.

- Gradually strengthen existing GIS databases to concertedly include spatial nutrient distribution across major agricultural production zones from which further relationships among watershed characteristics, and nutrient retention could be investigated. In the short-term these initiatives could be pursued via bilateral agreements with public partners, private research institutions and academia, as well as leading industry figures. However the strategy will ultimately need to look at strengthening local capacity through post-graduate and doctoral research.
- Improve the study scope and depth of these soils to provide more all-encompassing information of their behaviour and performance to support their management by partnering with friendly governments, NGOs, academia and research institutions.

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Glossary of Selected Terms

Absorption: The process by which one substance, such as a solid or liquid, takes up another substance, such as a liquid or gas, through minute pores or spaces between its molecules.

Adsorption: The adhesion of atoms, ions, or molecules from a gas, liquid, or dissolved solid to a surface. This process creates a film of the adsorbate on the surface of the adsorbent.

Aliphatic Groups: Pertaining to non-aromatic hydrocarbon compounds in which the constituent carbon atoms can be straight-chain, branched chain, or cyclic, as in alicyclic compounds; saturated, as in the paraffins; or unsaturated, as in the olefins and alkynes.

Alluviation: The horizontal running water transfer. The process that results in deposits of clay, silt, sand, or gravel at places in rivers or estuaries, or along the shores of lakes or seas, where stream velocity is decreased.

Alteromorphs: Secondary structures derived from complete weathering of primary minerals in the weathering mantle in comparison to the original structure. The specific shape is replaced by a secondary mineral with preservation of the characteristic shape of the former whatever the mineralogical and chemical composition of the latter.

Andesitic Rocks: Rocks formed from the cooling of volcanic lava of moderate viscosity which forms thick lava flows and domes. They occur mainly as surface deposits and, to a lesser extent, as dikes and small plugs.

Anoxia: A condition which is characterized by the absence of oxygen supply.

Aromatic Groups: Organic compounds containing a planar unsaturated ring of atoms which is stabilized by an interaction of the bonds forming the ring, e.g. benzene and its derivatives.

Basaltic Rocks: A common dark coloured volcanic rock formed from the rapid cooling of lava exposed at or very near the surface of the earth.

Biphasic Response: Two individual and distinct responses that are separated in time.

Brassinosteroids: A group of some 40 different steroids that are synthesized by plants and are potent hormones affecting many aspects of plant growth. They are essentially a class of polyhydroxysteroids that have been recognized as a sixth class of plant hormone.

British Thermal Unit: Traditional work unit equal to about 1055 joules. It is the amount of work required to raise the temperature of one pound of water by one degree Fahrenheit.

Bulk Flow: Mass transport of water molecules down a positive or negative hydrostatic pressure gradient independent of solute concentration in soil solution.

Bulk Solution: That part of the solution where the solution's molecules are influenced only by other solution molecules, and not by any solid or gas molecules.

Chelates and Chelating Agents: Chemical compound composed of a metal ion and a chelating agent. A chelating agent is a substance whose molecules can form several bonds to a single metal ion. In other words, a chelating agent is a multidentate ligand.

Colloidal System: Solution that has particles ranging between 1-1000 nm in diameter yet are still able to remain evenly distributed throughout the soil solution. Essentially the soil particles are dispersed and remain suspended in solution.

Colluvial Movements: The movement of unconsolidated sediments that have been deposited at the base of hillslopes by either rainwash, sheetwash, slow continuous downslope creep, or a variable combination of these processes.

Complexation: A chemical reaction which consists of a central atom or ion, which is usually metallic and is called the coordination centre, and a surrounding array of bound molecules or ions, that are in turn known as ligands or complexing agents.

Compressibility (of soil): A measure of the relative volume change of a soil as a response to a pressure (or mean stress) change.

Congruent Dissolution: Transition from a solid substance to a liquid of the same composition.

Coulombic Interaction: The electrostatic interaction between electrically charged particles. The magnitude of the electric force is directly proportional to the amount of one electric charge multiplied by the other electric charge and inversely proportional to the square of the distance between their centres. Hence like charges repel and unlike charges attract.

Dacitic Rocks: This is a fine-grained, matrix supported pyroclastic rock of intermediate composition between andesite and rhyolite. It is often found associated with andesite, and forms lava flows, dikes, and, in some cases, massive intrusions in the centres of old volcanoes.

Denudation: The long-term sum of processes that causes the wearing away of the Earth's surface leading to a reduction in elevation and relief of landforms and landscapes.

Depolymerizing: The process of converting a polymer into a monomer or a mixture of monomers.

Desilication: It is the process by which silica, together with many bases, is removed from a soil profile by intense weathering and leaching. It is characteristic of humid, tropical areas and leads to development of ferralsol soils. Such soils often have low organic content because of rapid decomposition by micro-organisms.

Diffusion: the movement of ions along a concentration gradient, i.e. from a higher to a lower concentration.

Ectomycorrhiza: Symbiotic relationship between a fungal symbiont and the roots of various plant species. These fungi do not penetrate the host cell walls, forming an entirely intercellular interface, consisting of highly branched hyphae forming a latticework between epidermal and cortical root cells.

Electrostatic Potential: The amount of electric potential energy that a unitary point electric charge would have if located at any point in space, and is equal to the work done by an electric field in carrying a unit positive charge from infinity.

Eluviation: The transport of soil material from upper layers of soil to lower levels by downward precipitation of water across soil horizons, and accumulation of this material (illuvial deposit) in lower levels.

Eolian Sediments: Wind deposited materials that consist primarily of sand or silt-sized particles. These materials tend to be extremely well sorted and free of coarse fragments.

Epipedon: A diagnostic surface horizon that includes the upper part of the soil that is darkened by organic matter, or the upper eluvial horizons, or both.

Ericoid Mycorrhiza: Mutualistic symbiosis between members of the plant family Ericaceae and several lineages of fungi formed in the epidermal cells of the fine hair roots of ericaceous species. The symbiosis represents an important adaptation to acidic and nutrient poor soils that species in the Ericaceae typically inhabit. Ericoid mycorrhizal fungi establish loose hyphal networks around the outside of hair roots, from which they penetrate the walls of cortical cells to form intracellular coils that can densely pack individual plant cells. However, the fungi do not penetrate plasma membranes of plant cells.

Eutrophication: A process where water bodies receive excess nutrients that stimulate excessive plant growth.

First Order Kinetics: A reaction that proceeds at a rate that depends *linearly* on only one reactant concentration.

Flocculation: A chemical reaction causing colloids and other suspended particles in liquids to aggregate, forming a floc.

Gravimetric Water Content: The ratio of the mass of the liquid phase (water) in a given soil sample to the mass of the solid material.

Humification: A process involving the decay and conversion of organic matter into humic and fulvic acids and humin typically under oxygenated conditions in soils and peatlands.

Hydrophobic Character: The physical property of a molecule (known as a hydrophobe) that is seemingly repelled from a mass of water. (Strictly speaking, there is no repulsive force involved; it is an absence of attraction.

Hypoxia: A condition which is characterized by the diminished availability of oxygen.

Igneous Rocks: Formed from the cooling and solidification of magma or lava. They may form with or without crystallization, either below the surface as intrusive (plutonic) rocks or on the surface as extrusive (volcanic) rocks.

Illuviation: The introduction of salts or colloids into one soil horizon from another by percolating water. A water-assisted transport in a basically vertical direction.

I_{max}: The maximum rate of nutrient uptake per unit surface area of root. Absorption rate per unit of root regarded as the influx.

Immobilization: The conversion of inorganic compounds to organic compounds by micro-organisms or plants, by which it is prevented from being accessible to plants.

Incongruent Dissolution: Dissolution of a mineral with decomposition or reaction in the presence of a liquid, converting one solid phase into another. A mass dissolution between two phases which involves a change in composition.

Ionic Bridging: The connection of two or more atoms, usually metal ions. The ligand may be atomic or polyatomic. Virtually all complex organic compounds can serve as bridging ligands, so the term is usually restricted to ligands that are specifically designed to link two metals.

Ionization: The process by which an atom or a molecule acquires a negative or positive charge by gaining or losing electrons to form ions, often in conjunction with other chemical changes.

Iso-electric Points: The pH at which a particular molecule carries no net electrical charge. The net charge on the molecule is affected by pH of its surrounding environment and can become more positively or negatively charged due to the gain or loss, respectively, of protons (H⁺).

Isomorphic Substitution: The substitution of one element for another in a mineral without a significant change in the crystal structure. Elements that can substitute for each other usually have similar ionic radii and valence state.

Isovolumetric Weathering: The weathering of minerals whereby the original shapes and volumes of the dissolved minerals are maintained.

Karrikins: A chemically defined family of plant growth regulators discovered in smoke from burning plant material. They are formed by the heating or combustion of carbohydrates including sugars and cellulose when plant material burns.

Karrikinolides: Active chemical in smoke previously referred to as 'butenolide' or 3-methyl-2*H*-furo[2,3-*c*]pyran-2-one.

Kinetics: The study of chemical reaction rates and how different experimental conditions can influence the speed of a chemical reaction. It yields information about the reaction's mechanism and transition states, as well as the construction of mathematical models that can describe the characteristics of a chemical reaction.

Laterisation: This is a weathering process by which iron and aluminium oxides become concentrated in the upper layer of the soil. It is common in tropical and subtropical areas where wet and dry seasons alternate

Ligand Exchange Reaction: The substitution of one or more ligands in a complex ion with one or more different ligands.

Ligand: An ion or molecule (functional group) that binds to a central metal atom to form a coordination complex. The bonding between metal and *ligand* generally involves formal donation of one or more of the *ligand's* electron pairs.

Low Molecular Weight Organic Acid: Substances with molecules containing carbon with acidic properties. Usually the most common are the carboxylic acids whose acidity is associated with their carboxyl group (-COOH). They are generally weak acids which do not dissociate completely in water but very soluble in organic solvents.

Metamorphic Rocks: A result of a transformation of a pre-existing rock. The original rock is subjected to very high heat and pressure, which cause obvious physical and/or chemical changes.

Mineralization: Decomposition or oxidation of the chemical compounds in organic matter into plant-accessible forms.

Mobilization: The process of releasing or making available chemical substances (plant nutrients).

Monomeric: A molecule of low molecular weight capable of reacting with identical or different molecules of low molecular weight to form a polymer.

Non-specific Adsorption: Adsorption of ions principally bound by electrostatic attraction.

Nucleation: The time dependent process that determines how long before the new phase or self-organized structure appears.

Partial Oxidation: A type of chemical reaction that occurs when a sub stoichiometric fuel-air mixture is partially combusted in a reformer, creating a hydrogen-rich syngas which can then be put to further use, for example in a fuel cell.

Peptization: The process responsible for the formation of stable dispersion of colloidal particles in dispersion medium. A process of converting a precipitate into colloidal sol by shaking it with dispersion medium in the presence of small amount of electrolyte.

Permittivity: The measure of the resistance that is encountered when forming an electric field in a medium. It is the ability of a substance to store electrical energy in an electric field.

Phosphatase: Enzyme that removes a PO_4^{3-} group from its substrate by hydrolysing phosphoric acid monoesters into a PO_4^{3-} ion and a molecule with a free hydroxyl group.

Phosphate Buffer Capacity: Ability of a soil to maintain a constant solution P concentration in response to plant uptake.

Podsolization: A process of soil formation especially in humid regions involving principally leaching of the upper layers with accumulation of material in lower layers and development of characteristic horizons; specifically: the development of a podzol.

Point Zero Charge: A concept relating to the phenomenon of adsorption, and it describes the condition when the electrical charge density on a surface is zero.

Polymers: Very large molecules made when many smaller molecules join together, end to end. The smaller molecules are called monomers.

Precipitation: The creation of a solid. Without sufficient force of gravity (settling) to bring the solid particles together, the precipitate remains in suspension.

Proteoid Roots: Also known as *cluster roots*, are plant *roots* that form clusters of closely spaced short lateral rootlets. They may form a two- to five-centimetre-thick mat just beneath the leaf litter.

Protonation: The chemical process of transferring a proton (a hydrogen atom) to another atom, molecule or ion, i.e. the reception of H^+ ions by a base.

Prototrophic Bacteria: Bacteria requiring only inorganic substances for growth.

Pyroligneous Acid: A dark liquid produced through the natural act of carbonization, which occurs when wood is heated in an airless container during charcoal production.

Pyrolysis: The chemical changes occurring when heat is applied to a material (biomass) in the absence of oxygen.

Re-crystallisation: The dissolution of a substance in an appropriate solvent and then having it come out of the solution in a crystalline form. The nucleation and growth of strain free grains in certain areas of the material, which grow to consume the deformed or recovered microstructure.

Respiratory Metabolism: Reactions and processes that take place in the cells of organisms to convert biochemical energy from nutrients into adenosine triphosphate (ATP), and then release waste products.

Respiratory Quotient: The ratio of the volume of CO_2 evolved to that of O_2 consumed by an organism, tissue or cell in a given time when organic matter is being metabolized.

Rhizosphere: The narrow region of soil that is directly influenced by root secretions and associated soil microorganisms.

Rhyolitic Rocks: Volcanic rock with a very high silica content. It is usually pink or grey in colour with small grains. They are formed from magma that has partially cooled in the subsurface.

Saprolite: Soft thoroughly decomposed and porous rocks often rich in clay. They are formed in-situ by chemical weathering of igneous, metamorphic and sedimentary rocks.

Second Order Kinetics: The sum of the exponents in the rate law is equal to two. The rate of a second-order reaction may be proportional to one concentration squared or (more commonly) to the product of two concentrations. Doubling the concentration of reactant A will quadruple the rate of the reaction.

Secondary Plant Metabolites: Organic compounds that are not directly involved in the normal growth, development, or reproduction of an organism (flavonoids, terpenoids and alkaloids).

Sedimentary Rocks: Formed by the deposition of material at the Earth's surface and within bodies of H₂O.

Short-range-order Minerals: Minerals with local clusters of atoms that occur either more or less frequently than predicted by a random distribution.

Specific Adsorption: Adsorption of ions principally bound by chemical attraction (covalent or coordinate bond). Specific adsorption of ions on a solid surface will be essentially regarded as a growth of the solid phase or forming of a new solid phase in aqueous solution.

Stoichiometry: The calculation of relative quantities of reactants and products in chemical reactions. The relationships between reactants and/or products in a chemical reaction to determine desired quantitative data.

Symbiont: An organism that is very closely associated with another, usually larger, organism. This larger organism is usually called the host.

Thixotropic Qualities: A time-dependent shear thinning property. Certain gels or fluids that are thick (viscous) under static conditions will flow (become thin, less viscous) over time when shaken, agitated, or otherwise stressed (time dependent viscosity).

Translocation: The movement of soil materials in solution or suspension from one horizon to another.

Udic Moisture: Humid climates which have well-distributed rainfall, or which have enough rain in summer so that the amount of stored moisture plus rainfall is approximately equal to, or exceeds, the amount of evapotranspiration.

Variable Charge: Soil particles carry a net electrical charge, positive (+), negative (-) or zero. Depending on the activity of one or more species of a potential determining ion in the solution phase contacting the surface: H⁺ or OH⁻.

Vesicular Arbuscular Mycorrhiza: A fungus that penetrates the roots of a vascular plant in order to help them to capture nutrients from the soil. They are well known for their ability to uptake and transport mineral nutrients from the soil directly into host plant roots. Formed by the symbiotic association between certain phycomycetous fungi and angiosperm roots.

Volumetric Water Content: The fraction of the total volume of soil that is occupied by the water contained in the soil.

Water Electrolysis: The decomposition of water (H₂O) into oxygen (O₂) and hydrogen gas (H₂) due to an electric current being passed through the water.

Xeric Moisture: Containing little moisture; very dry. Conditions whereby soil displays little moisture retention, excessively drained. Water is removed very rapidly in relation to supply; soil is moist for brief periods following precipitation.