

Bangor University

DOCTOR OF PHILOSOPHY

On-site Wastewater Treatment Systems as Sources of Phosphorus and other Pollutants in Rural Catchments: Characteristics and Tracing Approaches

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Award date:
2017

Awarding institution:
Bangor University

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On-site Wastewater Treatment Systems as
Sources of Phosphorus and other Pollutants in
Rural Catchments:
Characteristics and Tracing Approaches

This thesis is presented for the degree of Doctor of Philosophy in
Environmental Pollution, Bangor University

By
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College of Natural Sciences
School of Environment Natural Resources and Geography, 2016.

Abstract

This thesis investigated the influence of septic tanks (ST) on stream water quality. Characterisation of septic tank effluent (STE) revealed that STE were enriched in phosphorus (P), nitrogen (N), organic matter (OM) and metals relative to stream waters and large proportions of these parameters were present in the soluble reactive forms. Human factors such as tank design, number of users, dishwasher use and infrequent desludging significantly ($P < 0.05$) influenced effluent quality. ST that received roof runoff had reduced effluent retention time, while infrequent desludging was linked to increased OM, bacteria and P concentration in the effluent. Tanks that served larger numbers of people had elevated microbial abundance, P and N concentrations. Effluent composition was not consistent throughout the year, but exhibited similarity in warmer drier months that was different from effluent in colder wetter months for biological oxygen demand and heavy metals. Effluent attenuation in a test soil revealed that 14%-35% of P was attenuated by sorption processes, while saccharin was strongly attenuated by soil microbial degradation. The complex composition of STE reduced the ability of the test soil to adsorb P, as other substances in the effluent were competing for soil binding sites. Calculated P annual loadings from STE were 0.797 and 0.956 kgP/person/year for water usage of 150 and 180 l/person/day, respectively, while, effluents P load from detergents was 0.154 kg P/person/year. Newly developed tracing studies showed that ratios of chloride to other effluent indicators (e.g. EC, $\text{NH}_4\text{-N}$, TSS, turbidity, total coliforms, sucralose, saccharin and Zn) and the detection of effluent tryptophan-like peak by fluorescence spectroscopy may be useful in tracking effluent discharge to streams with low levels of dilution. However, effluent caffeine and saccharin were more effective tracers in streams with low and high levels of dilutions. A single individual tracer alone was not sufficient to evaluate STE contamination sources, but combined chemical and physical tracing approaches show promise as tools to identify STE inputs that continue to pose risks to watercourses and where mitigation measures could be effectively targeted.

Acknowledgments

A debt of gratitude goes to my supervisor Dr Marc Stutter in The James Hutton Institute, for the patience, help and continuous support he has provided me throughout the PhD processes that made this work possible. I am privileged to work with him and to have him as a supervisor and mentor for this research. I am also grateful to Professor Paul Withers of Bangor University for the advice and immense guidance he provided me every step of the way. Also I would like to express my sincere gratitude to Dr Eric Paterson in The James Hutton Institute for his valuable advice, support and encouragement, and for stepping in when I needed help. Without these three Musketeers, this project would not have been possible; to them I am truly grateful. I would like to thank The James Hutton Institute for financing this project and giving me the opportunity to pursue this PhD, and thanks to Bangor University for the help and support I received during this study.

This project would not have been possible without the support of many other people. I would like to thank Dr Colin McRoberts for the wonderful collaboration with AFBI and for over the phone advice and insightful comments. Also, my sincere thanks go to Dr Barry Thornton for his valuable advice and guidance throughout this research. Special thanks to David Richards, Luke Beesley and Mads Troldborg for assisting and helping me with field work throughout this project. And finally, I wish to thank my husband David Richards and my sons Kelvin Richards and Jonathan Richards for their immense support, patience, encouragement and love they provided me during this long process.

List of Publications

The following papers are derived from work in this thesis:

Richards, S., Paterson, E., Withers, P.J.A. Stutter, M., 2015. The contribution of household chemicals to environmental discharges via effluents: combining chemical and behavioural data. *Journal of Environmental Management* 150, 427-434.

Richards, S., Paterson, E., Withers, P.J.A., Stutter, M., 2016. Septic tank discharges as multi-pollutant hotspots in catchment. *Science of the Total Environment* 542, 854-863.

Richards, S., Withers, P.J.A., Paterson, E., McRoberts, C.W, Stutter, M., 2016. Temporal variability in domestic point source discharges and their associated impact on receiving waters. *Science of the Total Environment* 571, 1275-1283.

Richards, S., Withers, P.J.A., Paterson, E., McRoberts, C.W, Stutter, M., 2017. Removal and attenuation of sewage effluent combined tracer signals of phosphorus, caffeine and saccharin in soil. *Environmental Pollution* 223, 277-285.

Richards, S., Withers, P.J.A., Paterson, E., McRoberts, C.W, Stutter, M., 2017. Potential tracers for tracking septic tank effluent discharges in watercourses. *Environmental Pollution*.

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Abbreviations

ANOVA:	Analysis of variance
BAP:	Bioavailable phosphorus
BOD:	Biochemical oxygen demand
CI:	Confidence intervals
COD:	Chemical oxygen demand
CEC:	Cation exchange capacity
CFU:	Colony formed unites
CVA:	Canonical variates analysis
DEFRA:	Department for Environment, Food and Rural Affairs
DWD:	Dishwasher detergents
<i>E. coli:</i>	<i>Escherichia coli</i>
EDWD:	Eco dishwasher detergents
EF:	Enrichment factors
EEM:	Excitation emission matrix
ELD:	Eco laundry detergents
Em:	Emission
Ex:	Excitation
FIO:	Faecal indicator organisms
FIU:	Fluorescence intensity units
FS:	Fabric softeners
GCP:	General cleaning products
HS:	Hand soaps
INCA-P:	Integrated catchment model for phosphorus
K_d :	Distribution coefficient
K_{oc} :	Organic carbon normalised adsorption coefficient
LC-MS/MS:	Liquid chromatography tandem mass spectrometry

LD:	Laundry detergents
MANOVA:	Multivariate analysis of variance
MPN:	Most probable number
NTU:	Nephelometric turbidity units
OM:	Organic matter
OSWTS:	Onsite wastewater treatment system
Pe:	Péclet number
PSYCHIC:	Phosphorus and sediment yield characterisation in catchments
PV:	Pore volume
RDWD:	Regular dishwasher detergents
RLD:	Regular laundry detergents
SEPA:	Scottish Environment Protection Agency
SPE:	Solid phase extraction
SRP:	Soluble reactive phosphorus
SS:	Suspended solids
ST:	Septic tank
STE:	Septic tank effluent
STI:	Septic tank influent
STS:	Septic tank systems
STW:	Sewage treatment works
SUVA:	Specific ultra violet absorbance
TN:	Total nitrogen
TDP:	Total dissolved phosphorus
TP:	Total phosphorus
TVC:	Total viable counts
UV:	Ultraviolet
WUL:	Washing up liquids

WWTP: Waste water treatment plants

WWTW: Waste water treatment works

Chapter 1

Introduction and Thesis Structure

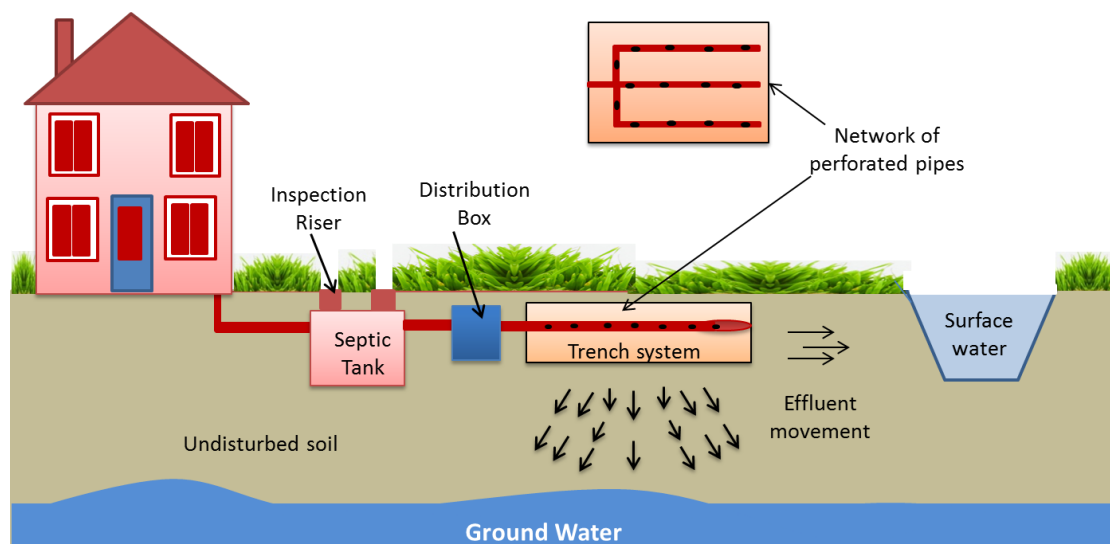


Figure 1.1: Septic tank system.

Phosphorus (P) plays an important role in water quality as it is considered a major pollutant when it enters fresh water systems from agricultural runoff or as a point source discharge from urban wastewater treatment plants (WWTP) or from onsite wastewater treatment systems (OSWTS) in rural areas such as septic tanks (ST). Septic tank systems (STS) are the most widely used systems for treatment and disposal of domestic wastewater around the world (Figure 1.1). Their use is particularly common in rural and semi-urban areas where connection to the mains sewerage network system is inaccessible or impractical and costly (Goonetilleke et al., 1999; Dudley and May, 2007). Four percent of the UK population rely on STS for domestic waste disposal (Defra, 2002), and more than 161000 properties in Scotland use ST as private sewage discharges, of which, only 38% are registered with the Scottish Environment Protection Agency (SEPA), (O’Keeffe et al., 2014). Over one third of Irish dwellings, 13% of Australian population and 25% of households in the United States are served by OSWTS (Dawes and Goonetilleke, 2003; Gill et al., 2004; D’Amato et al., 2008). The preferred use of STS is partly because of their relative simplicity, low costs and treatment capabilities (Beal et al., 2005), however, the performances of STS is highly variable and, hence, they

often produce effluent with varied quality. Septic tank systems often fail due to aging, user neglect, poor management and lack of maintenance (Goonetilleke et al., 1999; Dudley and May, 2007). Although most modern STS discharge their effluent to soil systems for contaminants removal in the soakaway/drainage field, soil treatment is highly variable and in the case of failing systems, contaminants often reach surface and groundwaters (Yates et al., 1985; Anderson 2010). Moreover, historically some tanks were designed to discharge directly to watercourses without secondary soil treatment (Dudley and May, 2007; Withers et al., 2011), posing ecological impacts on water quality.

Domestic wastewaters contain a wide variety of additional pollutants including pathogens, faecal bacteria, organic matter (OM), biochemical oxygen demand (BOD) and suspended solids (SS) as well as pharmaceutical organic compounds and household detergents and chemicals (Wilhelm et al., 1994; Gill et al., 2004; Katz et al., 2009; Kusk et al., 2011; Siegrist et al., 2012) that pose risks to fresh water resources. Bacterial contamination of watercourses from untreated septic tank effluent (STE) poses a risk of disease outbreaks in humans if it reaches and contaminates drinking water in nearby water wells (Harris et al., 2013). Yates (1985) reported that STE is the most frequent cause of groundwaters being contaminated with water borne diseases and that STS density was a crucial factor influencing water contamination. Anderson (2010) also highlighted the role of STS density in deteriorating surface water quality as reflected by many biological and chemical indicators. Septic tanks in the UK are neither regulated nor monitored for performance and often fail, with the consequence that they discharge their effluents to the environment without treatment (Gill et al., 2004, May et al., 2010; Withers et al., 2012). Unlike WWTP, ST as primary treatment are not designed to remove pollutants such as P and N from the effluent before discharging to surface and groundwaters.

Septic tank pollution is often evaluated in terms of the annual load of an environmentally targeted element such as P for its contribution to eutrophication of surface waters (White and Hammond 2009). Despite some views that STs' impacts on water quality are proportionally negligible relative to total pollutant loads (Sharpley et al., 1993; Haygarth et al., 2005), other studies have argued that wastewater discharges including ST pose greater risks to water quality than agricultural diffuse sources (Muscutt and Withers, 1996; Jarvie et al., 2006; Efroymson et al., 2007). Muscutt and Withers (1996) stated that point source pollution was the major source of P for most rivers in England as rural catchments were subjected to persistent P inputs from domestic sewage systems. Jarvie et al. (2006) considered point source effluents (e.g. sewage treatment works and ST) rather

than diffuse agricultural pollution sources of P to pose the most significant risk of eutrophication. With these contradictory views, it is important to evaluate STS discharges and to understand their loading impacts to place them in perspective with other rural diffuse pollution sources in order to prioritise and target effective mitigation measures.

1.1 Thesis structure

The overall aim and focus of this thesis was to better characterise STS discharges, assess the risk they pose to water quality in headwater streams and develop methods to trace pollution (hotspots). Therefore, it was essential to carry out several investigations to address certain research questions:

- Determine phosphorus concentrations and loadings from detergents as additional human input to STE and evaluate detergents contribution to wastewater discharges.
- Comprehensively characterise STE to gain data on their impact with respect to factors such as tank type, management, users' number and water use behaviours.
- Examine the temporal variation in effluent quality and the impact on receiving waters.
- Investigate the attenuation of certain STE pollutants such as phosphorus and trace organic compounds on contact with the soil in the soakaway part of the STS.
- Estimate scenarios of annual P loadings from STE.
- Identify potential in-situ tracers that can aid in future source identification and mitigation of STE impacts.

1.1.1 Literature review, research gaps and key questions – Chapter 2

Reliance on STS for wastewater treatment and disposal is common practice in rural and semi-urban areas. Septic tank systems are often capable of treating domestic wastes if they are designed, sited, managed and maintained appropriately. However, due to their limited capability to remove nutrients and pathogens and for their low technology, STS often fail. Discharges from failing tanks pose environmental and human health risks. A literature review was undertaken (Chapter 2), firstly to assess the current status of knowledge, and to critically review relevant research outcomes, on STS, discharges and their impacts on water quality. Secondly, the review identified aspects of the subject area for which currently there is a lack of data leading to inadequate knowledge (research gaps). The literature review was focused on septic tanks, effluent attenuation in soil, effluent quality, tank failure, the impact on water quality, evaluation approaches of ST pollution and the potential role of effluent tracers in tracking pollutants from STS in headwater catchment.

1.1.2 Detergents P contributions to ST discharges – Chapter 3

The focus of this chapter was to evaluate household detergent and other chemical product inputs to STE. Detergents use was based on a survey sent to septic tank users to acquire information about households: tank usage and design, management, water and detergent use (Appendix 1). This novel work examined sources of P from detergents (Publication 1, Richards et al., 2015) and the potential use of detergent compositions of trace and major elements as a tracer for STE discharges to watercourses.

1.1.3 Effluent characterisation – Chapter 4

Chapter 4 investigated STS discharges to surface waters in terms of effluent fingerprinting including the first comprehensive full elemental characterisation, the fluorescence spectroscopy of STE and the potential enrichment of ST discharges to watercourses. It also examined tank factors such as age, design, type of tank, tank management, dishwasher use and number of users that may influence the quality of septic tank effluent (Publication 2, Richards et al., 2016a).

1.1.4 Effluent seasonal variation – Chapter 5

Chapter 5 focused on monitoring the consistency of STE quality in terms of physicochemical and microbial composition during different seasons (e.g. warmer drier months and colder wetter months) and the potential consequential effects on adjacent receiving stream waters (Publication 3, Richards et al., 2016b). Data on temporal variation of STE is lacking in literature.

1.1.5 The attenuation of P, caffeine and saccharin – Chapter 6

This chapter evaluated the biotic and abiotic attenuation of both environmentally regulated elements such as P and of potential STE tracers for identifying the P contributions from ST discharges. The attenuation of P and two trace organic compounds (caffeine and saccharin at concentrations found in STE) by a test soil was investigated by batch equilibrium and column sorption experiments using aqueous and real STE matrices (Publication 4, Richards et al., 2017).

1.1.6 Phosphorus annual loading from STE – Chapter 7

It is important to understand annual loading of nutrient from ST to headwaters to prioritise and target mitigation measures to control nutrient enrichment and reduce the risk of eutrophication. In this chapter, scenarios of P annual loading from STE were calculated based on mean P concentration, spatial and temporal P data. The effect of effluent release to soakaway soil pH and bioavailable P were also investigated, for the first time on actual soakaway soils.

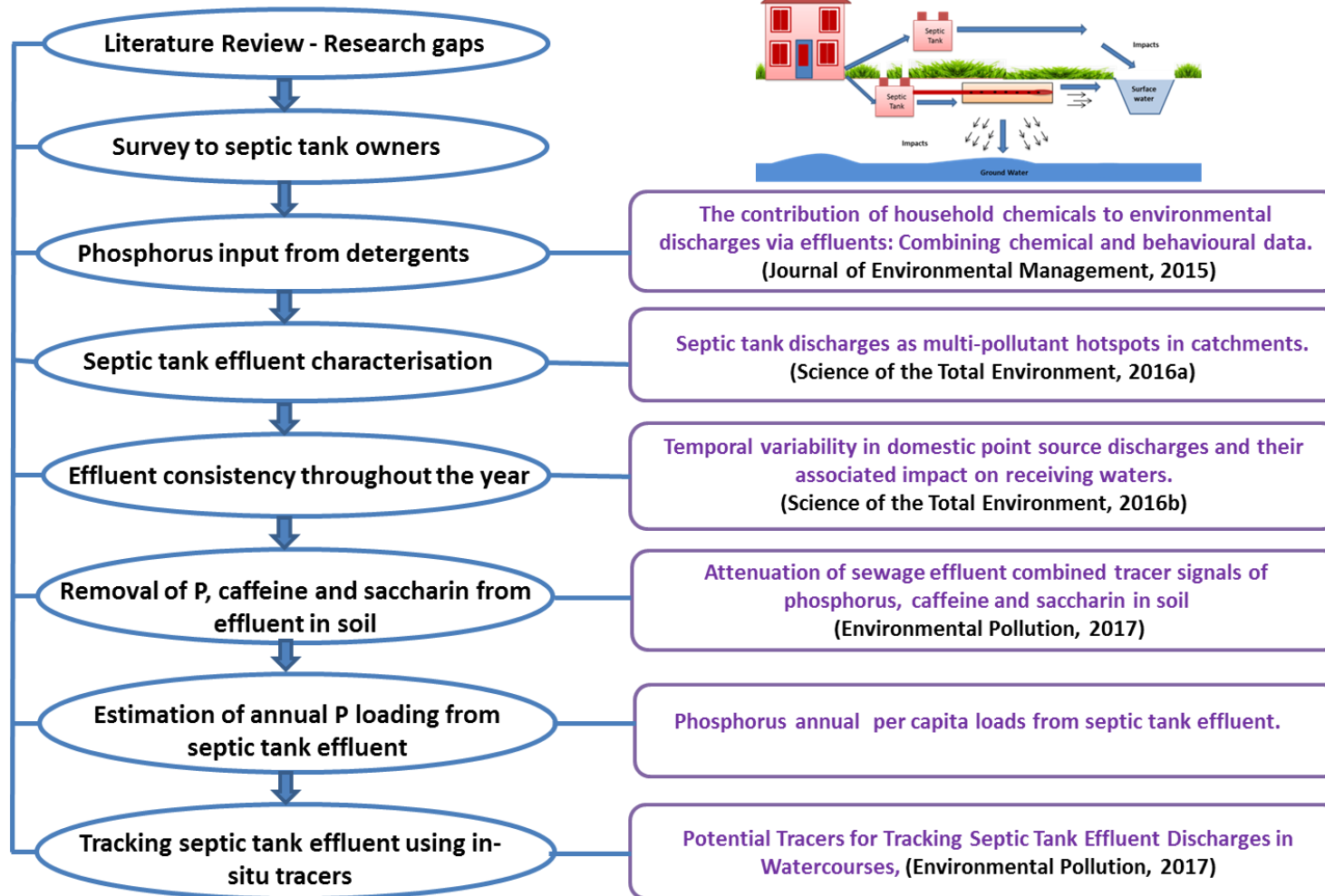
1.1.7 Tracking effluent discharge using in-situ tracers – Chapter 8

Tracing techniques can provide a powerful tool for investigating the relative inputs of STE pollutants to streams, their movement and impacts on water quality. Therefore, chapter 8 assessed the potential for compounds normally present in STE, such as caffeine and artificial sweeteners (acesulfame K, saccharin, sodium cyclamate and sucralose) as well as effluent fluorescence spectroscopy of organic matter, to be used for tracking STE contamination (Publication 5, in review).

1.1.8 Summary, conclusions and future work– Chapter 9

Chapter 9 reflected on the research questions, discussed major finding of this thesis and suggested recommendations for further investigations.

1.2 Research flowchart



Chapter 2

Literature review, research gaps and key questions

2.1 Septic tank history, design, function and size

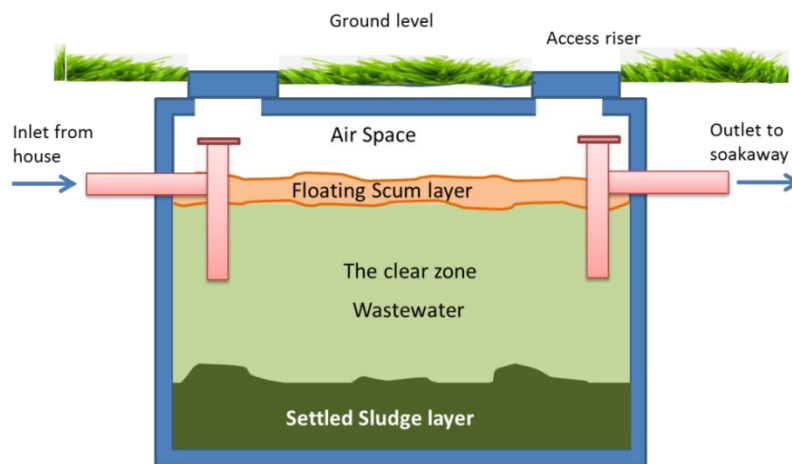


Figure 2.1: Typical box shaped one chamber septic tank showing the layers of sewage effluent.

Septic tank systems (STS) are widely used all over the world for onsite wastewater treatment system (OSWTS) from individual households, particularly in rural areas where connection to mains sewerage network systems is not available or impractical and costly (Dudley and May, 2007; Environment Alliance PPG4, 2006). Septic tanks originated in France in 1860 when John Louis Mouras designed and built a concrete septic tank (ST) in his yard and connected it with clay pipes from his home (Butler and Payne, 1995). When John Mouras dismantled the ST 10 years later, he found that the tank was virtually empty of any solid wastes and only contained the effluent scum layer. Mouras was granted a patent in 1881 and named it “Mouras Automatic Scavenger” (Seabloom et al., 2005). Septic tanks were first introduced to the United States and to the UK in 1884 and 1895, respectively (Butler and Payne, 1995) and later were introduced to many other countries by the British Military (Canter and Knox, 1985). Historically, ST were made from bricks or concrete (May et al., 1996) and comprised of one rectangular chamber connected with lowered T shaped pipes at the inlet and outlet of the tank (Figure 2.1) to prevent raw material (sludge and scum) from leaving the tank and entering the drainage field unprocessed (Canter and Knox, 1985).

Septic tanks are designed to store wastewater and maximise the removal of solids and pollutants by physical settlement and microbial hydrolysis of organic material into inorganic soluble simple molecules (primary treatment) (D'Amato et al., 2008). A typical STS comprises of a ST unit, a drainage field (soakaway) with a network of perforated pipes for effluent distribution (Figure 2.2) for further physical chemical and biological processing by soil particles (secondary treatment) (Beal et al., 2005). Although most STS discharge their effluent to soil systems for contaminant removal in the soakaway, some tanks discharge directly to watercourses without secondary treatment (Dudley and May, 2007; Withers et al., 2011), posing detrimental ecological impacts on water quality. Okeeffe et al. (2015) reported that 21% of private sewage registered by SEPA discharge to inland waters in Scotland.

2.1.1 Septic tank system design and function

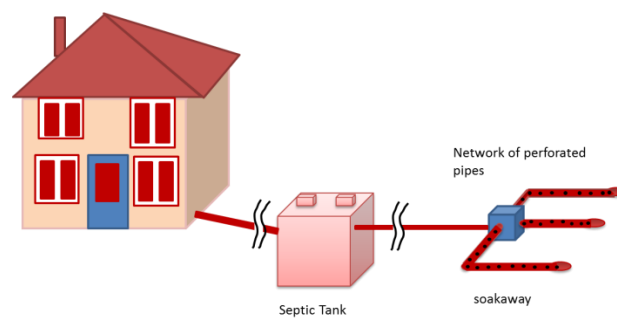


Figure 2.2: A simple septic tank system comprise of a typical box shaped unit connected to a network of perforated pipes for discharging effluent to a soakaway area for soil treatment.

A ST unit can be a single, double or multi-chambered, watertight, corrosion-resistant vessel that provides storage and the initial treatment of household wastewater (Laak, 1980). It is usually buried with access raisers at ground level for inspection and emptying. Effluent exit the tank via a distribution box, which distributes the partially treated effluent material to the soakaway (Figure 2.2) through a number of perforated pipes laid in trenches under the ground or to soil beds that allow the effluent to be dispersed into the soil for secondary treatment (Canter and Knox, 1985; Environmental Alliance PPG4, 2006).

A ST unit must be designed to safely accommodate the vertical soil pressure and to provide minimum effluent retention time of at least 24 hours (Seabloom et al., 2005; The Environment Agency, UK, 2012). Its primary functions are storage of waste material, solids removal by settling and accumulation, breakdown of organic solid material into soluble inorganic simple molecules in an anaerobic digestion process and finally discharge partially treated effluent to soakaway soil for secondary treatment (Canter and Knox, 1985; Dudley and May, 2007; D’Amato et al., 2008). Gravity and displacement play an important part in septic tank operation: if 10 litres wastewater were run from the kitchen sink and dropped into the tank, 10 litres of partially treated sewage effluent will exit the tank to the soakaway soil system. Septic tanks should be pumped out (desludged) to remove the accumulated sludge and scum layers regularly (2-5 years), (EA, UK, 2012).

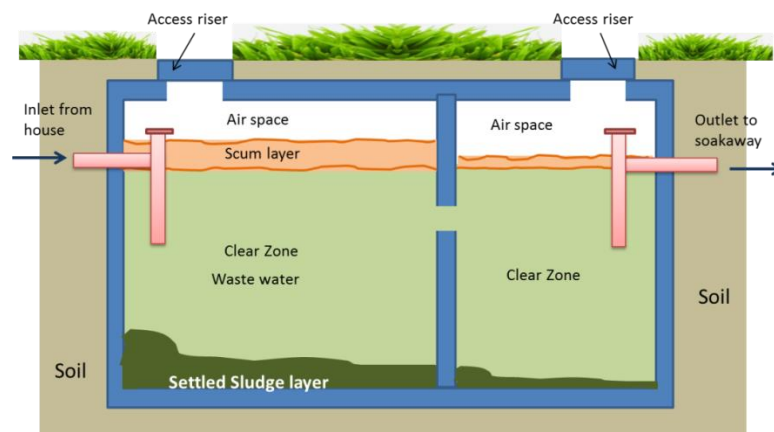


Figure 2.3: A typical two chambers septic tank where solids material accumulate at the bottom (sludge layer) and fats float on the top (scum layer) creating a clear zone of wastewater liquids in between.

A modern ST is made from prefabricated watertight and corrosion resistant materials such as glass reinforced polyester; fiberglass, polyethylene or reinforced concrete, with variable shapes depending on the material used (Seabloom et al., 2005). Plastic and fiberglass tanks are often criticized for susceptibility to structural failure and damage during installation, despite being light and resistant to corrosion (D’Amato et al., 2008). Seabloom et al. (2005) declared that a well-designed and maintained concrete or fiberglass tank should last for 50 years. A typical ST is design to hold wastewater for sufficient time (minimum of 24 hours), (US Environmental Protection Agency, 1980; The Environment Agency, UK, 2012) to allow solid material to settle out to form a sludge layer at the bottom of the tank, and for oils, greases and fats to float to the surface forming a scum layer above the sewage liquid (Willhelm et al., 1994; Seabloom et al., 2005; D’Amato et al., 2008). This initial segregation creates a clear wastewater zone between the sludge and the scum layer (Figure 2.3).

2.1.2 The Size of Septic Tank

Septic tank size is crucial to the success and the effectiveness of its performance. It should be properly sized to suit the volume and rates of wastewater that it receives, which are related to the number of people it serves. The tank volume must be big enough to allow for the minimum of 24 hours residence time for the average daily waste of 150-180 litres per person in the tank (EPA, 2000; Gill et al., 2004; Defra, 2011; The Environment Agency, UK, 2012; British Water, 2012). An over-sized tank is not cost effective, while an under-sized tank reduces effluent residence time and discharges insufficiently treated effluent to the soakaway system causing soil blockage and flooding (Seabloom et al., 2005). Eventually, the untreated sewage effluent reaches surface waters through surface runoff causing a threat to human health, ecological and environmental impacts (Withers et al., 2012; The Environment Agency, UK, 2012). Canter and Knox (1985) stated that one third of the tank space is designated to storing wastes while two third of tank volume is for sludge and scum accumulation. Therefore, the tank volume should equal to 2-3 times the daily flow volume it receives (Seabloom et al., 2005; US EPA, 2002).

The rate of sludge accumulation is an important factor to consider when designing ST volumes and is directly related to the number of occupants and bedrooms in the household and the volume of water used per person per day (Canter and Knox, 1985; EPA, 2000; Seabloom et al., 2005; Environment Agency UK, 2012), (Table 2.1). The stated daily sewage volumes produced per person varied in the literature. The Environmental Agency in the UK reported daily domestic sewage volume production per capita of 200 litres (Environment Alliance, PPG4, 2006) and US EPA (2002) reported the volume of wastewater introduced to a STS ranged from 150-180 l/person/day. Therefore, when designing STS, it is important to consider the maximum potential number of occupants rather than the present septic tank users in a dwelling, (Payne and Butler, 1993; EPA, 2000).

EPA (2000) and Gill et al., (2004) reported that a tank volume can be calculated using the equation:

$$C = 180 \times P + 2000$$

Where: (C = the capacity of the tank in litres) and (P = number of ST users).

Table 2.1: Estimated minimum ST size in litres depending on the number of people in relation to no of rooms in a house, based on daily water use of 180 l/person/day (Gill et al., 2004; EPA, 2000; British Water, 2012; Crystal Tanks, 2012).

No of bedrooms	No. of occupants	Estimated volume of water use l/day	Septic tank capacity in litres
1-2	2-4	720	2700
3	5	900	2900
4	6	1080	3080
5	7	1440	3260

2.2 Physical, chemical and microbiological processes within the tank

Processing of waste material inside the tank is a key to the quality of effluent discharged to the soakaway or to the environment. Septic tanks can be considered as reactors in which physical settling and stratification take place and complex biochemical processes are performed by microorganisms under anaerobic condition (Metcalf and Eddy, 1991; Seabloom et al., 2005; Beal et al., 2005) during effluent retention time inside the tank.

Septic tanks provide the following processes, which are reviewed in the following sections:

- Storage, settling and separation of domestic wastes
- Digestion of solids (biochemical processes)
- Transformation of organic P and N into reactive soluble P and ammonia (NH₃)

2.2.1 Physical settling and consolidation of solid particles

Inside the tank, heavier solid particles are physically settled out and accumulate at the bottom of the tank, while floatable fat, oil and greases rise and accumulate at the top of the tank. This initial separation process is driven by gravity and density of waste material and in itself improves wastewater quality prior to any further processing within the tank (Canter and Knox, 1985; Seabloom et al., 2005). D'Amato et al. (2008) described solid settlement as particles settle independently, governed by gravitational force and particle density, and/or particles collide with each other, consolidate and increase in mass before settling. The authors also suggested that suspended solids may be captured and adhere to fats which cause them to be buoyant and accumulate at the top of the tank. However, Seabloom et al. (2005) suggested that gases produced through the biological decomposition of the accumulating sludge rise up to the clear zone causing the re-suspension of the settled material and help the circulation of anaerobic bacteria in the water. These authors also suggested that tank design was key to performance, as a tank with greater settling area tends to provide more efficient settling than a tank with equivalent volume and smaller area.

2.2.2 Microbiological and chemical processes inside the septic tank

The enteric bacteria inside the tank play vital roles in sewage material digestion and sludge volume reduction since they break down much of the organic matter in sewage solids into simpler compounds and gases (Figure 2.4). Processing of sewage solids material (sludge and fats) inside the ST is achieved partly by a short lived aerobic decomposition but mostly by anaerobic digestion (Seabloom et al., 2005; Beal et al., 2005).

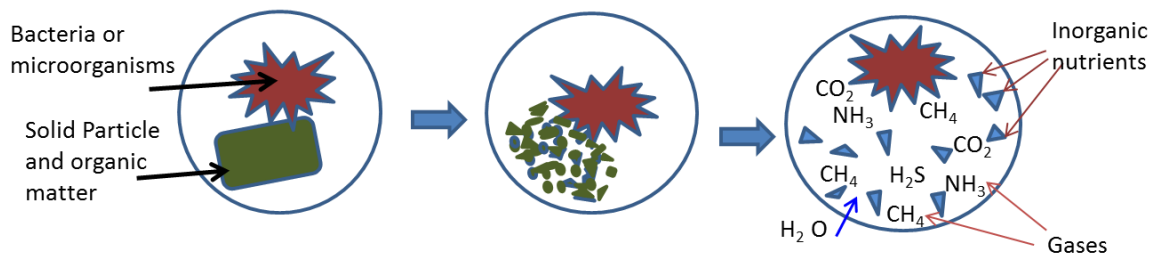


Figure 2.4: The biodegradation of organic matter in septic tank effluent by bacteria or microorganisms into smaller molecules first then into gases (carbon dioxide and methane), water and inorganic nutrients.

Aerobic decomposition occurs when large flows of relatively clean wastewater such as fresh kitchen waste containing dissolved oxygen enters the tank and encourages the growth of microorganisms and bacteria that digest organic matter in the presence of oxygen. However, this is a very short lived process as the respiratory requirement of these aerobic microorganisms soon depletes the dissolved oxygen supply in the wastewater (Seabloom et al., 2005).

Anaerobic decomposition is a complex process that takes place in two stages in the absence of oxygen inside the tank, as explained by Wilhem et al. (1994); Beal et al. (2005); Seabloom et al. (2005) and D'Amato et al. (2008):

The first stage (acid forming phase) occurs when acid-forming bacteria hydrolyse complex organic molecules to simple soluble compounds and produce organic acids. During this stage, starches and proteins are broken down into sugars and amino acids, respectively, while fats remain unchanged.

Thus, the production of organic acids reduces the pH condition in the tank and hinders further bacterial decomposition at this stage.

The second stage (methane phase) occurs when enteric methane-forming bacteria present in the waste hydrolyse organic acids to water, carbon dioxide (CO₂) and methane (CH₄). In this process, amino acids are broken down to ammonia (NH₃) which neutralises the acidic condition and raises the pH to an optimum level for methane-forming bacteria to attack fat molecules (D'Amato et al., 2008). Consequently, fatty acids are decomposed into simpler compounds that are then broken down to water, CO₂ and CH₄. Thus, anaerobic decomposition of organic sludge inside the tank results in a considerable reduction in the accumulated sludge volume (Wilhem et al., 1994; Gross et al., 2005). This process is often accompanied by the emission of unpleasant smelling gases such as hydrogen sulphide (H₂S) which can escape through the plumbing system to the house, or through ST's risers to the drainage field.

2.2.3 Nutrient processing inside the tank

The anaerobic environment within the tank is ineffective in reducing the overall concentrations of nutrients such as N and P in wastewater. Heterotrophic bacteria in the tank convert most of the organic N and P in the waste to ammonium (NH₄⁺) and soluble orthophosphate, respectively, while the total N (TN) and total P (TP) remain unchanged (Van Cuyk et al., 2001; Dudley and May, 2007; Lowe et al., 2009). A typical N and P concentration in the effluent to the soakaway, without considering the sludge fraction, is about 40-100 and 5-15 mg/l, respectively, (Gold and Sims, 2001; Lowe et al., 2009).

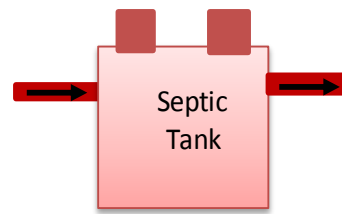
2.3 Characterisation of Septic Tank Effluent (STE)

Domestic waste materials that enter the tank is termed septic tank influent (STI) and is generally comprised of kitchen wastes, toilet flushing, shower and bathtub washings, washing machine and dishwasher wastes, all of which contain both water, dissolved and solid waste material. During residence time of waste material inside the tank, the influent undergoes physical, chemical and microbiological processes inside the tank to become septic tank effluent (STE). Despite this primary treatment, the resulting effluent still contain large concentrations of contaminants such as N, P, suspended solid (SS), organic matter (OM), bacteria and pathogens as well as pharmaceutical organic compounds and household detergents and chemicals. Data on the concentration of these contaminants in STE is limited and largely dated, while comprehensive characteristics data currently is lacking. Most recent literature data are focusing on STS in US, Canada, Australia and others (Brandes, 1978; USGS, 1991; Gross et al., 2005; Seabloom et al., 2005; Carroll et al., 2006; Lowe et al., 2007; Tomaras et al., 2009; Toor et al., 2011; Lusk et al., 2011; Siegrist, et al., 2012) where tank management, detergents and water usages may differ and hence may change effluent properties. Table 2.2 summaries STI and STE characteristics in literature.

Domestic wastewater may contain a number of trace organic chemicals such as: household cleaning products and washing detergents, caffeine, artificial sweeteners and pharmaceutical compounds found in drugs products. These chemicals can be released from kitchen sinks or excreted from human body and flushed down the toilet. These organic chemical may reach watercourses and pose a risk to water quality. Hinkle et al. (2009) found traces of caffeine in groundwater within 19 feet from a ST drainage field. There are little data available in the literature on the concentration of these organic chemicals in STE, and their attenuation in soil systems is poorly understood.

Table 2.2: Septic tank influent (unprocessed waste water) and septic tank effluent (after primary treatment) mean concentration and ranges reported in recent literature for key parameters.

Septic tank influent (STI)					Septic tank effluent (STE)			
Authors		EPA, Ireland, 2000	Canter and Knox 1985	US EPA, 2002; Goss et al., 2005	Canter and Knox 1985	Goss et al., 2005	Lowe et al., 2009	Seigrist et al., 2012
Parameter	Unit	Mean Concentration			Mean Concentration	Conc. Ranges		
TN	mg/l	50	50	60	40	60	27-119	40-100
TP	mg/l	10	25	10	15	8.1	0.2-33	5-15
BOD	mg/l	300	300	250	140	120	44-833	140-200
COD	mg/l	400	750				201-944	
Suspended solids	mg/l	200	781	250	75	60	28-192	50-100
Total bacteria	CFU ^a /100 ml	10 ⁸	10 ⁷		10 ⁸			10 ⁶ – 10 ⁸
Total coliforms	MPN ^b /100 ml	10 ⁷ – 10 ⁸	10 ⁶	10 ⁹	10 ⁶			
Feacal coliforms	MPN/100 ml	10 ⁴	10 ⁴	10 ⁷	10 ⁶	10 ⁶		



a Colony formed units

b Most probable number

From Table 2.2, it is clear that STE contain large concentrations of nutrients, pathogens and faecal bacteria, and that effluent treatment inside the tank is not effective in removing N and P or bacteria. The prevailing anaerobic condition and biochemical processes inside the tank convert most organic N and P to ammonium-N ($\text{NH}_4\text{-N}$) and inorganic soluble phosphates (PO_4), however, TN and TP remain unchanged. Total N in septic tank effluent is on average 40-60 mg/l (Toor et al., 2011) while TP concentration is in the range of 5-15 mg/l (Siegrist et al., 2012). Withers et al. (2011) investigated nutrient concentrations in STE that was directly discharged to a stream and found the concentrations of soluble N and P were 8-63 and <1-14 mg/l, respectively, with NH_4 and soluble reactive phosphorus (SRP) being the dominant fractions.

If a ST discharges its effluent directly to a ditch, stream or a river without secondary or further treatment then all these pollutants would readily enter surface water. Therefore, STE requires further and essential treatment and purification through the soakaway soil system before it is released to ground and surface waters (Goonetilleke et al., 1999; Environment Alliance, PPG4, 2006; Siegrist et al., 2012). Drainage fields and soakaway soil systems and effluent treatment in soil are explored in the next section.

2.4 Drainage field (soakaway) area and alternatives

In a well-designed system, STE leaving the tank reaches a distribution box where it is released through a network of perforated pipes to the subsoil in the drainage field (soakaway). Here additional physical, biological and chemical processes occur to further reduce contaminant concentrations (Figure 2.5).

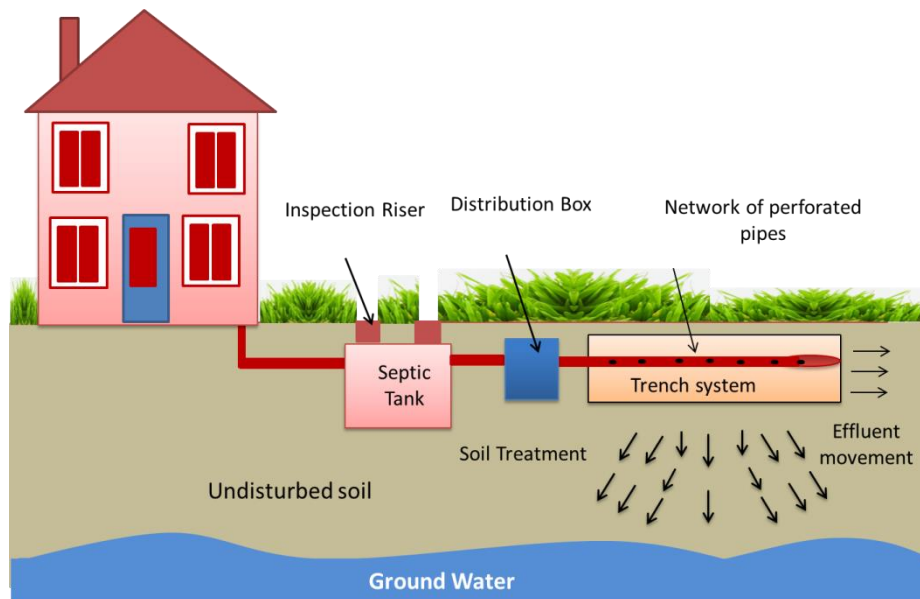


Figure 2.5: Septic tank system and effluent movement while being treated by the subsoil in the soakaway system before reaching ground and surface water.

The design of a drainage field is crucial to the success of STS operation and can be a trench or a bed system (Canter and Knox, 1985; Environment Alliance, PPG4, 2006). When designing a drainage field, three aspects should be observed: 1) the hydraulic characteristics (effluent flow and soil storage capacity to receive effluent); 2) formation of a biomat; 3) protection of groundwater quality (Environment Alliance, PPG4, 2006). All of which depend on the type of subsurface soil and the vertical distance of drainage soil and the top of the highest water table level.

2.4.1 Trench system design

A typical trench system (percolation trench) consists of a series of narrow trenches about 0.8 m to 1.5 m deep and 0.5 m to 0.9 m wide. The bottom of the trench is filled with a 20-30 cm layer of gravel or broken stones followed by the perforated percolating pipe, then another layer of gravel which is covered with geotextile material and finally the top soil layer (Figure 2.6).

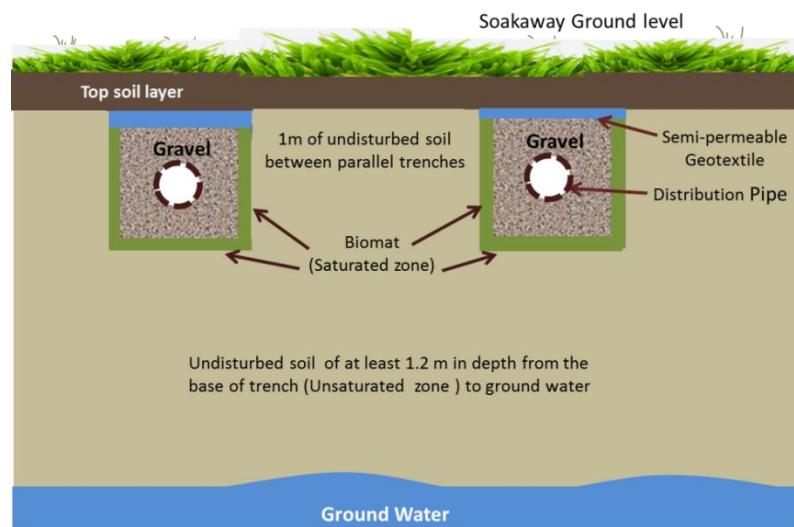


Figure 2.6: A cross section of two adjacent drainage trenches above the unsaturated soil.

The geotextile material is semi-permeable and acts as a filter to prevent top soil clogging the trench system. A minimum of 1m of undisturbed soil should be between parallel trenches and a minimum of 1.2 m of undisturbed soil should be between the base of the trench and the bedrock/or the highest level of water table (EPA, 2000; Gill et al., 2004). The effluent from the ST flows into the soakaway through the perforated pipes which allow the liquid to soakaway beneath the ground level.

A common length of drain field for OSWTS is 20 meters (Patterson, 1994). In sites where conditions do not allow for trenches or bed systems to be constructed, alternative systems can be used such as mound systems, constructed wetlands or reed beds.

2.4.2 Percolation beds

Percolation beds are suitable for relatively level sites with sandy and loamy sand soils. The bottom of the bed systems are the main infiltration surfaces for the effluent. Percolation beds cost less to construct and require less total area than trenches. On the other hand, percolation trenches provide much larger percolation area (sides and base of trenches) than bed system with similar land area (Canter and Knox, 1985).

2.4.3 Septic tank-mound system

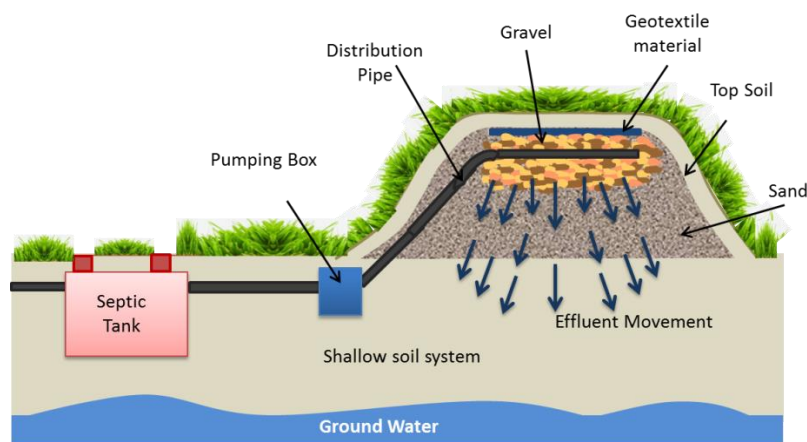


Figure 2.7: Septic tank-mound system.

In cases where site and soakaway soil characteristics are not suitable for ST conventional wastewater disposal, an alternative system such as ST-mound system is used. Mound system can be used in shallow sites that do not meet setback distance between STS and water table or in sites that have low or high soil permeability rates. A ST-mound system is an elevated soil system which comprises: a ST unit, a pumping chamber and the mound itself (Figure 2.7). The mound itself is comprised of a layer of sand as a filling material on top of the natural soil, followed by gravel layer which engulfs and supports the distribution pipes. A layer of geotextile fabric is placed to cover the gravel followed by top soil over the entire mound (EPA, Ireland, 2000). The effluent is elevated by a pump from the tank to flow through the fill material where it is processed before entering the natural soil. The total depth of the natural soil and the sand together should equal the required setback distance from percolation pipes to groundwater of 1.2 m.

2.4.4 Reed bed treatment systems (RBS)

Reed bed systems (Figure 2.8) are considered to be effective and of low operational cost as alternative treatment for secondary or tertiary treatments. They require large area for effective effluent treatment and they are not recommended as standalone secondary treatment systems. The principle of reed treatment is the ability of reed plants to survive in waterlogged conditions and to transfer oxygen from leaves through their root systems to a gravel bed, promoting the growth of bacteria and microorganisms (Defra, 2011). Septic tank effluent is allowed to seep through the gravel bed for pollutant removal by physical filtration, chemical precipitation and aerobic and anaerobic bacterial digestion (Antony Merritt, 1994). Reed beds are designed to detain the wastewater for 5 to 7 days allowing sufficient time for the settling and filtering of suspended solids, nitrification/denitrification to occur, breakdown of organic matter and nutrient removal by micro-organisms and plant uptake. RBS are more effective at nitrifying effluents, converting effluent ammonia into nitrates, nitrites and nitrogen gas than most package sewage treatment plants. RBS are effective in the removal of SS, BOD, TN, faecal coliforms and TP (Davison et al., 2001). However, they are often criticized for their low performance particularly in winter months and the unreliable long term performance. RBS that receive effluent with a high level of suspended solids are susceptible to block up more rapidly, diminishing their ability and their effectiveness of contaminants removal with time. Davison et al. (2001) reported P saturation and reduction in P removal by reed bed system after eight years of operation.

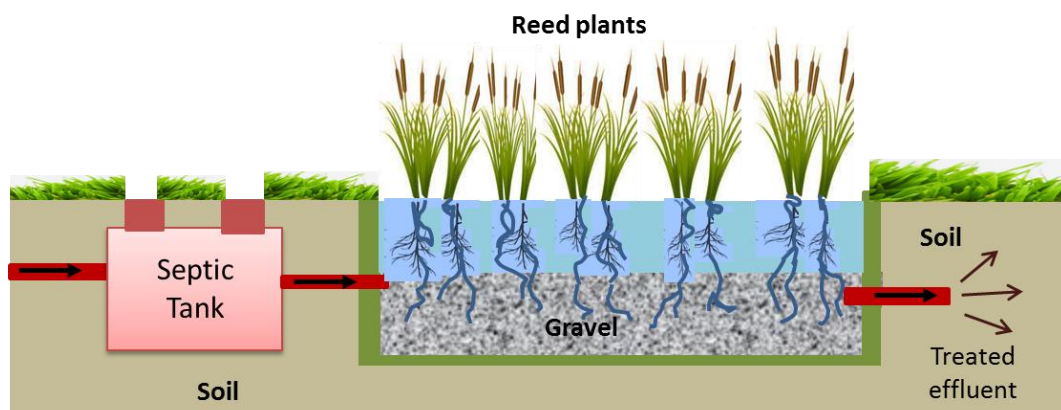


Figure 2.8: Reed bed treatment system.

2.4.5 Deep borehole soakaway

A deep borehole soakaway is often a deep hole in the ground where STE flows for disposal over a small area of soil. For this reason, deep borehole soakaways are often clogged causing ponding that threatens surface waters. Moreover, when the soil within a deep borehole soakaway becomes saturated and reaches its limit of treatment capacity, the untreated effluent travels further and becomes a threat for the contamination of groundwaters. Therefore, deep borehole soakaways are less effective in effluent treatment and should not be used (SR:6, 1991; SEPA, 2000). UK Building Regulations (2008) stated that deep borehole soakaways are illegal.

2.4.6 Alternating bed systems

Effluent hydraulic overload is the most common factor for STS drainage field failure. To prevent this, a construction of a backup drainage area (site permitting) is often required with the ability to direct tank effluent to either field (Figure 2.9). This allows the alternating use of one of drainage field while the other field is resting to recover for 6 months (Canter and Knox, 1985; Goonetilleke et al., 1999).

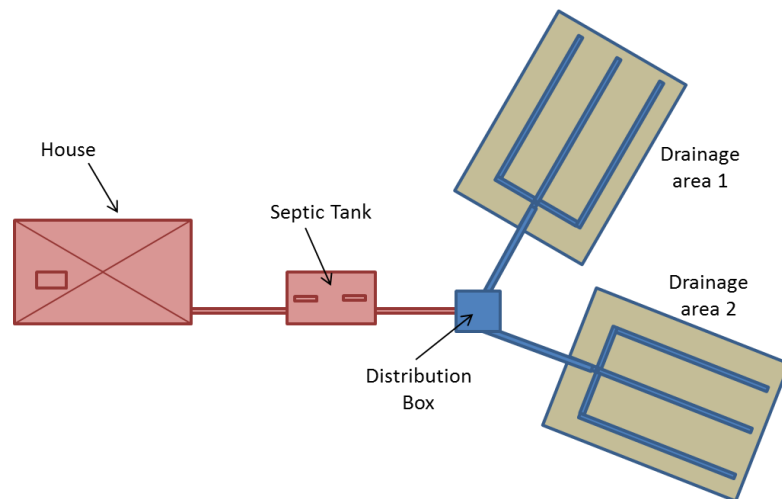


Figure 2.9: Illustrating alternating drainage system in which effluent distribution is switched to the backup area every 6 months allowing drainage area to recover before the next cycle.

2.4.7 Soakaway criteria and design

In the UK, under The Building Regulations, 2010; section H2 and BS 6297: 2007 and amendment 1 2008, a site is not considered suitable for absorption of STE before conducting three mandatory tests:

The first test is to determine that the groundwater beneath the soakaway is not classified by the Environmental Agency or SEPA, as a “Groundwater Source Protection Zone” that is used for drinking water and hence would be polluted if effluent from a ST soakaway reached it (Environment Alliance, PPG4, 2006).

The second test is the “Trial site assessment hole” which is a 2 m deep large hole dug to determine that the maximum level of water table is not within 1m (England, Wales and Scotland) and 1.2 m (Northern Ireland and most countries) of the bottom of the soakaway pipes (Environment Alliance, PPG4, 2006). This test is a deciding one and if it fails, there is no point in performing the third test: the percolation test.

The third test is the “Percolation Test” in which the porosity of the soil is determined by measuring the time it takes for water to drop 1mm. A standard amount of water is poured into a standard size dug hole in the soil then timing the change in the level of water within the hole. If the water soaks away too fast or too slowly, then the construction of the soakaway will not be permitted (Canter and Knox, 1985; Environment Alliance, PPG4, 2006; Building Regulation, 2007; Wastewater solution, 2012). A moderate flow through soil pores that is neither too rapid nor too slow ($15-100 \text{ s mm}^{-1}$) allows for physical, chemical and biological processes to take place to further improve the effluent in the soil (Dawes and Goonetilleke, 2003; Environment Alliance, PPG4, 2006).

2.5 Effluent treatment through soakaway soil system

The soakaway's soil quality is a crucial factor in the failure/success of any STS and the level of effluent treatment it provides (Seigrist et al., 2000; Dawes and Goonetilleke, 2003; Eveborn et al., 2012; Dubber et al., 2014). In poorly structured soils (heavy clay soils), effluent ponding may occur which promotes anaerobic conditions and reduces effluent treatment. A study by Withers et al, 2011 reported that heavy clay soils were inefficient in treating and retaining septic tank effluent. Equally, in coarse textured soils (coarse sandy soils), wastewater effluent movement is rapid and soil-effluent contact time is greatly reduced resulting in insufficient biological and chemical processes to occur. Fine textured soils (clay and silty soils) have greater surface area which is ideal for dissolved pollutants removal by chemical processes such as sorption (Van Cuyk et al., 2001). However, the presence of discontinuities such as fissure and cracks in the subsoil can provide preferential flow paths for percolating liquids (Gill et al., 2004) which reduce treatment contact time between effluent and soil particles (EPA, 2000).

Secondary treatment processes of effluent in the soil system are reviewed next and comprises of removal of suspended solids by physical filtration, increase in biological activity through biomat formation, reduction of N by nitrification and denitrification, removal of P by sorption, biodegradation of organic matter by microbial processes and removal of bacteria and viruses (Gill et al., 2004; Beal et al., 2005; Lusk et al., 2011; Seigrist et al., 2012; Eveborn et al., 2012).

2.5.1 Physical filtration and straining in soil system

Soil is an excellent medium for the treatment and the removal of STE contaminants. As effluent enters the soil system, it filters and infiltrates the soil system by two processes described by Canter and Knox (1985):

- **Surface filtration:** As large particles in the effluent do not penetrate soil particles and accumulate at the soil surface. These large particles themselves may act as a filter and trap finer suspended particles.

- **Straining:** When effluent particles are small enough and able to enter soil pores as the effluent and the dissolved pollutants percolate through the subsoil.

Thus, physical filtration of effluent in soil systems produces effluent with reduced pollutants. Jenssen and Siegrist (1990) declared that soil filtering and straining of the effluent has the ability to reduce 75-90% of effluent suspended solids (SS) and biochemical oxygen demand (BOD).

2.5.2 Biomat formation (the saturated zone)

Effluent secondary treatment in soakaway soil systems relies on the massive increase in biological activity in the subsoil of the percolation trenches. As STE enters the soil system, effluent suspended solids and organic material infiltrate the soil and gradually clog soil particle pores as effluent loading rate exceeds its infiltration rate (Gill et al., 2004; Beal et al., 2005). As a result a saturated zone at the base of percolation trenches is created (approximately 5 mm) that promotes massive growth of bacteria and microorganisms (the biomat) (Figure 2.10). Bacteria in the biomat provide much of the decomposition of the suspended material and OM of the effluent through biological processing (Siegrist, 1987; Beal et al., 2005; Dudley and May, 2007; Onsite Sewage Treatment Program, 2011). The biomat is also crucial in providing an even distribution of wastewater within the soakaway and prolonging soil-effluent retention time to maximise effluent treatment. Gill et al. (2009b) concluded that STE treatment is restricted in drainage areas where the biomat is underdeveloped. If STE is too highly treated in the tank and contains less OM and suspended solids, the biomat may not form sufficiently to optimise effluent filtration, chemical and biological treatment (Dudley and May, 2007; Siegrist, et al., 2012).

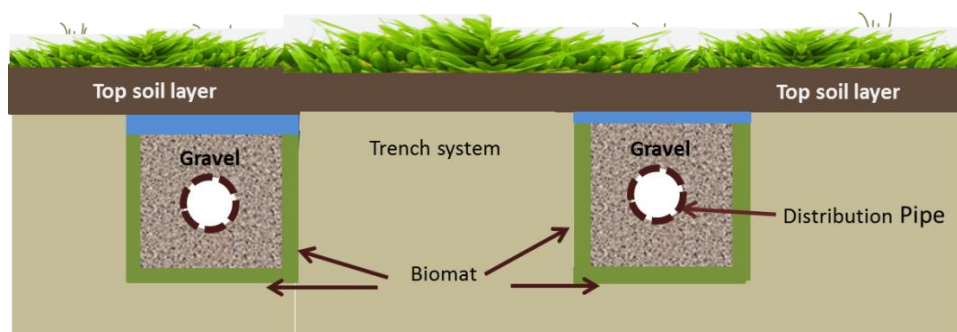


Figure 2.10: Representation of biomat in a trench system.

The biomat (saturated zone) maintains an anaerobic state due to the prevailing high moisture and the increase in biological activity and oxygen consumption within the zone (Gill et al., 2004; Dudley and May, 2007). As the biomat is established, the infiltration of the effluent becomes sufficiently reduced to keep the soil beneath percolation trenches unsaturated (unsaturated zone). Eventually a steady state is reached between the saturated zone and the unsaturated zone beneath it which allow the effluent to slowly flow through the unsaturated soil (Van Cuyk et al., 2001). Meanwhile, the soil in the unsaturated zone contains oxygen which allows oxidation of nutrients and the removal of effluent pathogenic organisms by soil aerobic bacteria (Onsite Sewage Treatment Program, 2011).

Magdoff et al. (1974) investigated P removal from wastewater in soil columns in the presence and the absence of a biomat. The authors observed a decrease in P concentration as ponding conditions started to occur in soil columns where a biomat was present (2–6 mg/l) allowing sufficient soil-effluent contact time for P adsorption, compared to (11–14 mg/l) in soil columns with no biomat. Postma et al. (1992) declared that the infrequent use of STS (e.g. during occupants prolonged absence) influences biomat development and may impair its formation altogether. The authors revealed that seasonal occupancy of dwellings relying on STS may promote groundwater contamination due to the incomplete formation and sometimes the absence of the biomat in drainage trenches. On the other hand, excessive biomat growth causes hydraulic failure which results in ponding (Figure 2.11) and leads to the failing of the drainage field (Potts et al., 2004). Repairing failing drainage areas is often costly, can involve removing and disposing of contaminated soil and the construction of a new drainage area (Canter and Knox, 1985). Siegrist and Boyle (1987) concluded that aeration of STE before releasing to soakaway trenches improves the longevity of STS through preventing excessive biomat growth.



Figure 2.11: Representation of effluent ponding caused by soil clogging and hydraulic failure. Photo was taken during PhD field work.

2.5.3 Reduction of organic-N and ammonium-N

Septic tank effluent contains TN concentration (40-100 mg/l) of which (70-90%) is in the form of $\text{NH}_4\text{-N}$ and (10-30%) is in organic-N form (Toor et al., 2011; Siegrist et al., 2012). Ammonium ions (NH_4^+) present in STE must come in contact with soil surfaces for removal by processes such as adsorption, cation exchange, incorporation into microbial biomass or released as ammonia gas to the atmosphere by nitrification process (Siegrist et al., 2012). Effluent organic-N is converted to $\text{NH}_4\text{-N}$ in ammonification processes in which biochemical degradation of organic-N into NH_3 or NH_4^+ occurs in both aerobic and anaerobic soil conditions, as described by Canter and Knox (1985):

Organic-N + heterotrophic bacteria $\rightarrow \text{NH}_3$ or NH_4^+ (Ammonification Process)

In the saturated zone of the soakaway soil, the positively charged ammonium ions (NH_4^+) are readily adsorbed to the negatively charged soil particles or OM in the soakaway under anaerobic condition. When the adsorption capacity limit of the saturated soil is reached, NH_4^+ ions travel further down through the unsaturated zone until reaching new unoccupied soil adsorption sites.

Ammonium ion can be detained by the unsaturated soil cation exchange capacity (CEC) where soil particles exchange their positively charged ions such as H^+ , Na^+ , K^+ , Ca^{2+} , Mg^{2+} and Al^{3+} that are held by the negatively charged soil particles with effluent (NH_4^+) positive ions. As cation exchange sites of the unsaturated soil become exhausted, effluent NH_4^+ ions move further towards groundwater unchanged. On the other hand, in basic soil environments, NH_4^+ ions are transformed to ammonia gas (NH_3) which is then released to the atmosphere.

In the upper layer of the soil system (the top 30 cm of the unsaturated soil) where oxygen is present, aerobic reactions occur where NH_4^+ ions are converted first to nitrite ion (NO_2^-) then to nitrate (NO_3^-) in nitrification processes by soil microorganisms (Washington Environmental Health and Safety, 2005; Toor et al., 2011).

Microorganisms + O_2 + NH_4^+ $\rightarrow \text{NO}_2^-$ + O_2 $\rightarrow \text{NO}_3^-$ (Nitrification - aerobic reaction)

2.5.4 Removal of nitrate-N

Nitrate-N removal is achieved by plant uptake and denitrification processes. In soil system, nitrates (NO_3^-) are more mobile than NH_4^+ as the net negative charge of the nitrate ions (NO_3^-) causes them to repel the negatively charged soil particles. As a result, nitrates are highly mobile in the unsaturated zone and often reach groundwater (Katz et al., 2009; Oakley et al., 2010; Toor et al., 2011). Removal of nitrate by soakaway plant uptake (e.g. grass and vegetation) is an effective way to reduce nutrient concentration from STE. A plant that has long growing season and high nitrogen uptake should be selected for drainage fields. Reduction of NO_3^- by denitrification in soil system occurs in anaerobic reactions mediated by bacteria, in which the reduction of (NO_3^-) to nitrite (NO_2^-) occurs first, then to nitrogen gas (N_2) in the absence of oxygen.



2.5.5 Removal of effluent phosphorous (P) in soakaway soil

Total P concentration in STE is in the range of 5-15 mg/l, of which 85% is in the soluble phosphate form and the remainder is in the organic and particulate P form (Siegrist et al., 2012). Phosphorus is removed from STE into subsurface soil through mineralisation, adsorption, precipitation and soil CEC processes. Harman et al. (1996) stated that mineral precipitation dominated P attenuation processes in the unsaturated zone.

Organic P can be adsorbed to soil particles directly or can be converted to inorganic orthophosphate by soil microorganisms in mineralisation processes (Canter and Knox, 1985). Effluent inorganic P that enters soil drainage field is mainly in the form of soluble reactive phosphorus (SRP) which can be readily adsorbed to soil particles. Clay particles have large platy surface areas, which make them ideal adsorption sites for P (Patterson et al., 1994). In acidic condition, phosphate ions (PO_4^-) are adsorbed on the surfaces of soil iron (Fe) and aluminium (Al) cations to form insoluble aluminium and iron phosphate. In alkaline condition, PO_4^- binds to calcium ions (Ca^{2+}) to be slowly converted to a stable calcium phosphate precipitate (hydroxyapatite) (Lusk et al., 2011). The movement of P through a soil column is minimum until soil sorption sites are occupied then P movement through the soil is increased (Siegrist and boyle, 1987). Therefore, P in STE is effectively retained in soakaway soil systems and only a

small concentration reaches groundwater. However, the risks for P leaching can be substantial from P-saturated soakaway soils that are too close to streams or through effluent direct discharge to watercourses.

Canter and Knox (1985) stated that it is possible to reduce P concentration in STE through addition of aluminium sulphate (alum), lime and iron chloride to ST units and that P can be completely removed when aluminium is present in excess to produce aluminium phosphate as a precipitate. The authors criticized this method of P removal as it requires 9.6 g of alum to precipitate 1.0 g of P which also results in increase the volume of sludge accumulation in the tank.

2.5.6 Organic matter and biological contaminants removal

Septic tank effluent contains large concentrations of OM and a large quantity of this OM (60%) is removed during the physical sludge settling process inside the tank (Lee and Coyne, 2012). The remaining 40% of the OM is released with the effluent to soil systems in the form of particulate matter or suspended solids (SS) where break down and degradation processes occur by soil microorganisms and microbial population in the biomat (PPG4, 2006). Biochemical oxygen demand is often used as an indicator of effluent OM degradation which measures the amount of oxygen required by the microorganisms to hydrolyse OM in the effluent.

Septic tank effluent contains faecal coliforms bacteria and viruses in the range of 10^6 - 10^8 and 0 - 10^5 MPN in 100 ml (most probable number in 100 ml), respectively (Siegrist, 2012). Lusk et al. (2011) stated that pathogenic bacteria present in STE such as *E. coli*, *Salmonellae* and *Shigellae* can cause infections in humans in much lower dosage than their actual concentration in STE. Therefore, the removal of these pathogenic bacteria before STE reaches surface and groundwater is essential for public health protection.

Bacterial removal occurs by filtration and straining through soil pores on the top 2 to 6 mm of the soil surface that blocks the physical movement of bacteria (Canter and Knox, 1985; Kouznetsov, et al., 2004). These surface retained bacteria are subjected to ultraviolet light (UV), desiccation and are less likely to survive (Rail, 2000). Clay and silty soil particles have small enough pore sizes to filter out most

bacteria; however, the presence of macropores can provide preferential flow which decreases bacterial filtering. Rail (2000) stated that bacteria survive less in acidic soils (peat) than alkaline soil (limestone) and their adsorption to soil particles is increased with soil acidity. Viruses, comparably, are much smaller than bacteria and are not filtered by the soil system. Some viruses contain positive charges and thus they are adsorbed and held by negatively charged soil particles (Berba et al., 1975). However, bacteria and most viruses hold a net negative charge on their surfaces which prevent their adsorption to soil particles (repelling forces) (Lusk et al., 2011). Effluent cations such as Ca^{2+} , Mg^{2+} , Na^+ and H^+ saturate the surface of bacteria making them suitable for adsorption by the negatively charged soil particles (Canter and Knox, 1985; Stevik et al., 2004). Therefore, adsorption of bacteria and viruses to soil particles can only occur in fluids with high ionic concentration and at low flow rate since rapid movement decreases soil-fluid-bacteria contact time.

Bacteria and viruses present in STE have various die off rates and are eventually killed off in the soil as their survival outside the human body is dependent on soil condition and time. Gerba et al. (1975) reported bacteria and viruses' survival in soil of less than 2-3 months and that viruses can become desorbed from soil particles and travel greater subsurface distance. Soil conditions such as temperature, moisture content, pH and the presence of the soil's own bacterial predators effects the survival of STE bacteria and viruses. Under favourable conditions of high moisture content, low temperature, alkaline pH, and high OM content, bacteria may survive up to 100 days (Stoddard et al., 1998). Conversely, in hostile conditions such as low pH and dry sandy soils with low OM, bacteria may only survive for 1 or 2 days (Stevik et al., 2004). Reneau et al. (1977) reported that the total coliforms population decreased with horizontal distance and depth from the soil percolation system. The removal of effluent major pollutants in soil particles and the reasons for their possible failure is summarised in Table 2.3.

Table 2.3: Methods of major STE contaminants removal in soil and possible reasons for attenuation failure.

Contaminant	Method of attenuation	Reason for failure
Phosphorus	Precipitation, mineralisation, cation exchange, adsorption and plants uptake	Saturation of soil binding sites and P leaching, low soil clay content and low concentration of effluent cations
Nitrogen	Adsorption, cation exchange, microbial assimilation or released as ammonia gas by nitrification and denitrification or plant uptake	Saturation of soil binding sites, absence of biological mat and low concentration of effluent cations
Microbial	filtration and straining, exposure to UV light, die off by low or high pH and adsorption to soil particles	The presence of preferential flow (no straining), low ionic concentration in the effluent and unsuitable soil type
Organic matter	filtration, straining and degradation by microbial activities	Soil clogging, reduction of soil microbial population

2.6 Causes of septic tank system failure

STS continues to have mixed reputation as being unpredictable with variable treatment efficiencies and failure rates (Goonetilleke et al., 1999; Beals et al., 2005). Some STS operate successfully for many years while others fail (e.g. release nutrients and pathogens into the environment) within months or even weeks of installation (Goonetilleke and Dawes, 2001; May et al., 2010). Failed STS (Figure 2.12) produces poorly treated sewage effluent that may enter the natural environment and contaminate ground and surface waters with potential of public health and environmental impact. Failing or poor performing ST are considered to be major sources of contamination of drinking water supplies (Carroll and Goonetilleke, 2005). EPA, Ireland (2006) found that 29% of groundwater was contaminated with faecal indicators and ESB International (2008) indicated that nutrient loading from septic systems to surface water was 3 and 7% for N and P, respectively. Withers et al., 2011 reported that STS were effective in wastewater treatment if they were designed, sited and maintained properly. This mixed reputation questions the capability of STS of being a viable long term option for sewage treatment. A report by WSDH (2003) highlighted that the causes of STS failures were dominantly: age, unsuitable soils, lack of maintenance, high groundwater table and excessive water use.



Figure 2.12: Examples of old tanks that showing signs of failure of broken lid and effluent seeping out of the tank (left), and inadequate cover for the tank (right). Photos were taken during PhD field work.

2.6.1 Unsuitable and old septic tanks

Older septic tanks are susceptible to failure as they were not designed to meet our modern lifestyles of domestic water use: frequent bathing, power showers, washing machines and dishwashers (May et al., 2010). The amount of water used per person 25 years ago was about 90 L/day, far less than today's use of approximately 150-180 L/day, with the average family using 500 L/day (The Environment Agency, UK, 2012). Therefore, many older and undersized STS were not designed to cope with modern lifestyle of water use of frequent bathing and use of appliances, all of which may overwhelm STS and cause hydraulic overloading and failure (May et al., 2010). Hydraulic overloading occurs when too much water enters the septic system at one time, resulting in wastewater backing into drains or effluent surfacing in drainage area. Regulating the use of water or replacing an undersized tank with a larger tank may prevent hydraulic overloading.

In a report by May et al. (2010) it was highlighted that half of all septic tank systems were not operating satisfactorily. A study by Gill et al. (2007) suggested that 95% of STS in some areas of Ireland were failing on the basis of soil hydrological characteristics related to STS age. ESB International (2008) reported that, on sample inspection, the majority of STS were considered sub-standard compared to current standards. Older STS that have not been upgraded did not require a permit to be installed, as the recent legislations (e.g. setback distances from surface and groundwaters, tank size, soakaway soil quality and percolation test) were not in place then. Therefore, many old systems were wrongly sited, under sized and are in need of replacement (Goonetilleke and Dawes, 2001; Gill et al., 2007; May et al., 2010).

2.6.2 Unsuitable soakaway soil system



Figure 2.13: Examples of unsuitable soakaway with signs of effluent ponding, untreated effluent is released to the environment. Photos were taken during PhD field work.

Old STS are often wrongly installed on sites without consideration for soil condition or high water table level. Soakaways are often damaged (compacted) during the installation process (Gill et al., 2009b; O’Keeffe et al., 2014). A study by Laurence Day (2005), on the effectiveness of STS for wastewater treatment, revealed that 80% of soil system characteristics were not suitable for ST function and many existing septic systems were in need of design improvement. Jordan et al. (2004) concluded that a soil’s ability to remove pollutants becomes increasingly exhausted over time and that ST age was a key factor in the deterioration of soakaway soil. As STS ages, the soil system’s capacity to absorb effluent from the tank is exceeded, causing soil clogging and pooling (Figure 2.13) due to limiting infiltration capacity. Consequently, runoff transports effluent contaminants directly to watercourses. Treatment of STE relies also on natural processes below the soil surface in the soakaway area through the sufficiently long soil-effluent contact time (Goonetilleke et al., 1999; Beal et al., 2005). A significant failure occurs when STE passes through soakaway soil with high permeability rate, which allows rapid movement of contaminants to groundwater without sufficient treatment. The presence of discontinuities (e.g. fissure and cracks) in the subsoil can further provide preferential flow paths for percolating effluent, which limits the attenuation capacity of the soil and decreases soil-effluent contact time increasing the chance of contamination (Gill et al., 2004). Effluent insufficient treatment can also occur in heavy clay soils as effluent infiltration rate is too low causing soil clogging and ponding (Goonetilleke et al., 1999; Gill et al., 2004). Withers et al. (2011) reported that heavy clay soils were inefficient in treating STE.

Canter and Knox (1985) confirmed that soil efficiency is influenced by seasonal variations; with greater efficiency observed during summer and autumn when the unsaturated depth of soil was greater (low

water table) and soil efficiency decreased during winter when water tables were high. This raises the question; do STE properties and concentration vary during different seasons? There are few data available in the literature to answer this question as very few studies have been conducted on changes in STE composition over time, or during different seasons and the effect of these changes on stream water quality.

2.6.3 Lack of ST maintenance

Septic tank failure is often caused by lack of regular inspection and maintenance. Inside the tank the sludge is constantly being biodegraded by anaerobic digestion and thus reduced in volume. However, the volume of the sludge does increase with time and requires desludging at regular intervals that are variously reported: 1-4 years (Gill et al., 2004); every 3-4 years (Canter and Knox, 1985) or every 12 months (EPA, 2000; Seabloom et al., 2004; Environment Alliances, PPG4, 2006; UK Building Regulation, 2007). Sludge build up occurs gradually and reduces the tank volume required for effluent retention time needed to complete effluent treatment inside the tank. As a consequence, untreated effluent may exit the tank (Seabloom et al., 2005) leading to environmental impacts, especially in the cases of direct discharges to watercourse. Therefore, ST should be inspected and pumped out regularly; the frequency of desludging depends on the size of the tank and the number of ST users in the household (Goonetilleke et al., 1999; Onsite sewage treatment program, 2011).

2.7 Signs of septic tank system failure

Septic tank system failure means that untreated wastewater directly or indirectly can enter natural environment and contaminate ground and surface water with potential of public health and environmental impacts (UK Building Regulation, 2008). It is essential to identify early signs of ST failure to implement effective measures to reduce their impact.

2.7.1 Early signs of tank failure

There are indicative signs of ST failure (Figure 2.14) which can be easily noticed without detailed analysis investigation:



Figure 2.14: Indicative signs of ST failure: Left: showing broken tank lid exposing the effluent to the environment. Middle: showing effluent discharge (blue colouration) leaking on to the surface. Right: showing effluent flooded on to the surface above the tank lid. Photos were taken during PhD field work.

- Strong, bad odours coming from the ST or drains
- Plumbing back-ups
- Sewage leaking from the ST
- Effluent surfacing in soakaway area
- Lush and greener grass in soakaway area
- Grey cloudy discharge of untreated sewage to nearby ditches and streams
- Excessive algal blooms in nearby streams or lakes
- High concentration in nitrates and coliforms in nearby ditch, stream or lake

2.7.2 Bacteria as an indicator of ST failure

The presence of faecal coliforms bacteria in surface water can indicate ST contamination and is a sign of wastewater treatment failure. Faecal coliforms bacteria are present in the digestive tract of humans and animals as they aid food digestion processes. Faecal coliforms are not necessary pathogens (disease causing organisms), but their presence is an indicator for other pathogenic organisms that cause dysentery, gastroenteritis and hepatitis A (Lusk et al., 2011). The discharge of organic matter that contains faecal coliforms to watercourses can be harmful to the environment. The aerobic decomposition of the organic matter depletes dissolved oxygen, leading to fish kills and deteriorated aquatic environments. Chlorine and other chemicals are often used to reduce pathogens and faecal coliforms in wastewater but they can also kill essential bacteria required for tank processes (Environment Alliance, PPG4, 2006).

2.7.3 Prevention of ST failure

Studies have revealed that causes of STS failures in the past are the same as today and prevention is the best measure to reduce STS failure. US EPA (1980); Environment Alliance PPG4 (2006); EPA (2006); Environment Agency UK (2008) and UK, The Building Regulation (2008) discussed ST failure prevention measures:

- Soil suitability should be evaluated during high water table season and prior to installing STS.
- Maintain a minimum of 1-1.2 m vertical distance from soakaway bed/trench base to highest level of water table.
- Newly installed systems and their components should be approved by competent STS experts, soil scientists and engineers.
- The ST unit must be water tight and made from durable material.
- Tank size should be appropriately proportional to the number of users.
- It is recommended to use multi-compartment ST to minimise SS clogging.
- Maintain regular inspection for STS and removal of sludge and scum from the tank.
- Remove only half of sludge content of the tank when cleaning out to encourage the growth of microorganisms.
- Reduce water use and wastewater entering the system.

- The drainage field should be adequately sized and should be capable of processing maximum hydraulic loading.
- Implementing a resting period for a drainage field by the adoption of a dosing and resting effluent loading technique (site permitting).
- Avoiding the compaction of drainage field/soakaway by not using it for driving on or parking.

Site design plays a key role in preventing STS failure. Literature and regulations emphasise that with careful planning and observing the setback distance required between septic tank system and surface and groundwaters, the risk of contamination is greatly reduced. Sites with steep slopes, impermeable soils, high clay content, or shallow bedrock will not absorb and treat septic effluent readily and need special attention to avoid failure. In order to try to reduce pollutant concentration and bacterial counts before effluent is discharged to the soakaway, new technologies such as an aerobic treatment system with disinfection unit may be used. However, these new technologies are expensive, not widely used and often criticized for the loss in their performances and the need of regular maintenance (Levett et al., 2010).

Soils have the ability to filter bacterial cells by physically straining and by adsorption to soil surfaces to prevent cell transport to groundwaters (Goonetilleke et al., 1999). Pollution from failing STS can be avoided if septic systems are properly constructed and sited. By increasing the distances from drainage field to groundwater, the removal of pathogens are increased and their transport to groundwater reduced (Lusk et al., 2011). Special attention should be paid to items entering STS through flushing down the drain household chemicals and large objects (e.g. sanitary towels and nappies). Excessive use of household cleaning products such as detergents, bleaches and disinfectant may disrupt the natural bacterial development required for wastewater treatment. However, Grant and Moddie, (1995) declared that moderate use of household cleaning products and detergents should not pose a threat to microorganisms in the tank. Septic tank users should regulate water use to avoid hydraulic failure, use eco-friendly detergent and cleaning products and keep their use to the minimum. The potential for household P contributions from detergents through septic tank effluent is discussed in Chapter 3.

2.8 Septic tank impacts on water quality

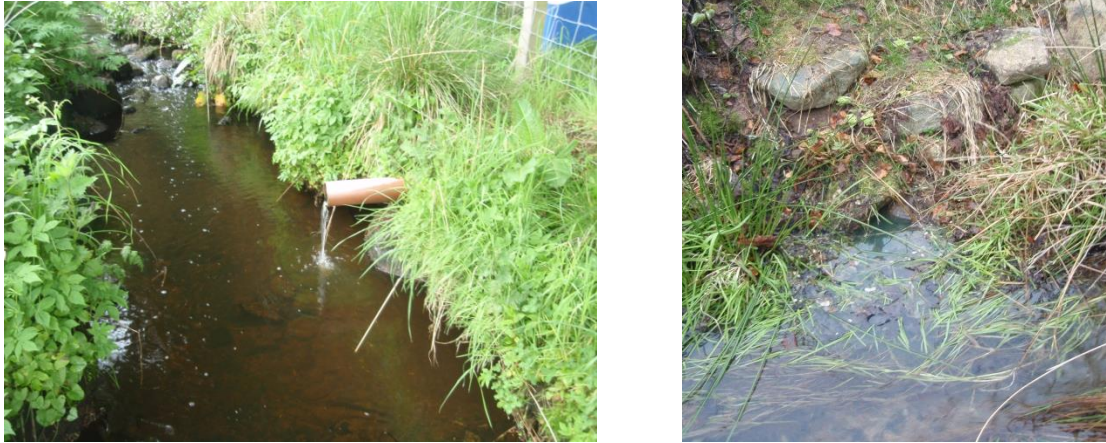


Figure 2.15: Examples of STE direct discharge to stream water. Photos were taken during PhD field work.

Many studies have linked contamination of surface and groundwater to sewage wastes including septic tank system wastes (Goonetilleke et al., 1999; Edwards and Withers 2008; Bowes et al. 2010; Withers et al., 2011). Many STS continue to discharge their effluent directly to ditches and streams, which pose a great threat to local watercourses (Figure 2.15). The likely factors for water contamination by STS are the close siting of ST relative to surface water and high ST density in a given area. Efrogmson et al. (2007) declared that STS that were located within close proximity of watercourses and those with hydraulic failures have direct impact on water quality. Yates (2006) and Ozkan et al. (2007) reported increased disease outbreaks as distance from STS to groundwater wells decreased. A study on the concentration of contaminants from STS at soil depth of 1.5 m by Viraraghavan and Warnock (1976) indicated effluent with high concentrations at this depth (Table 2.4). Hence, if the water table is within 1.5 m from STS, then these concentrations of contaminants would readily enter groundwater.

Table 2.4: Effluent parameter concentrations at soil depth of 1.5 m, (Viraraghavan and Warnock, 1976).

Parameter	Concentration mg/l
SRP	6-9
Ammonium-N	10-78
BOD	28-84
COD	57-142
TSS	18-53
DOC	7-18

The US EPA specified areas that have more than 40 ST per square mile as high density ST areas (Katz et al., 2010). Many researchers have correlated increased disease outbreaks with high ST density in such areas. Ground and surface waters in areas with high density of STS were more prone to bacterial contamination, and have shown deterioration in water quality with high concentrations of NO_3^- , bacteria, P and trace and heavy metals (Canter and Knox, 1985; Harman et al., 1996; Meeroff et al., 2008; Katz et al., 2009). Arnscheidt et al. (2007) found a positive correlation between septic system density and the density of poorly maintained systems, and TP concentration in the catchments. The authors also reported a positive correlation between P fraction and markers of faecal and grey-water contamination. Soils in these areas often reach their saturation limit and provide little time for soil-effluent treatment, which leads to the transport of bacteria and other pollutants to groundwater (Dillon et al., 1999).

2.8.1 Bacterial impact

Bacterial contamination from ST systems to water courses is a major concern and poses risk of disease outbreaks if untreated STE reached drinking water in nearby water wells. Yates (2006) indicated that STS in the USA discharge 800 billion gallons of wastewater to the subsurface every year and if STS are failing, untreated wastewater may reach and contaminate groundwater and cause waterborne diseases outbreaks (Goonetilleke et al., 1999). Many rural communities that rely on STS for domestic waste disposal often also have wells or use surface waters, for drinking water supplies. Reneau et al. (1977) considered total coliforms and faecal coliforms with concentrations of 10,000 and 100 MPN/100 ml, respectively in surface water to be acceptable, while the desirable levels of these organisms are <100 and <20 MPN/100 ml, respectively.

2.8.2 Nitrogen impact

A high concentration of N in surface water contributes to the eutrophication of waterbodies with detrimental impacts on aquatic biodiversity and water quality. Apart from plants uptake of N, the soil system is not capable of retaining $\text{NO}_3\text{-N}$ in the soil column and thus NO_3 can seep into groundwater (Goonetilleke et al., 1999). Withers et al. (2011) reported stream nitrite-N concentrations above that harmful to fish level of 0.1 mg/l originated from the direct ST discharge to streams. Moreover, effluent $\text{NH}_4\text{-N}$ reduction is coupled by nitrification (Canter and Knox, 1985), which leads to $\text{NO}_3\text{-N}$ build up in nearby surface and groundwaters and the depletion of watercourses of their dissolved oxygen, posing potential health and environmental risks. Nitrate is highly mobile and readily travels through soil to ground and surface waters. Water with more than 45 mg/l NO_3 may cause methemoglobinemia in infants while the presence of $\text{NH}_4\text{-N}$ in receiving waters is toxic and have detrimental effect to fish.

2.8.3 Phosphorus impact

Many studies have linked P contamination of surface waters to STS wastes (Edwards and Withers, 2008; Bowes et al., 2010). Withers et al. (2012) reported the potential impacts of STS on water quality in a rural headwater during low flow conditions. Efroymson et al. (2007) declared that ST that were located within close proximity of watercourses and those with hydraulic failures have direct impacts on water quality. These authors also stated that during P transport through the soil system, a significant amount of P was adsorbed to clay soil particles or precipitated with soil iron, aluminum and calcium before reaching surface water. Goonetilleke et al. (1999) declared that soils have fixed capacity for P removal and once this capacity is reached, effluent P move to groundwater.

Studies have shown that P retention in soil can be achieved within 1 m of a drainage pipe by precipitation and adsorption. Robertson et al. (1998) investigated P transport from ST to groundwater and concluded that P migration from STS was <0.3 and 1 m/year in clay-silt and sandy gravel soils, respectively. A study by Lowe and Siegrist (2008) concluded that 99% of P removal from STE was achieved in sandy loam soil percolation system. Another study published by Robertson et al. (2008) confirmed that P adsorbed to soil surfaces can be released by desorption, become mobile and migrate

further to eventually reach surface and groundwater. Many research studies observed that even with STS that are functioning properly, P migration in soil system is 1 m/year (Robertson et al., 1998; Zurawsky et al., 2004) and for old STS P plumes can gradually develop, reaching groundwater or streams with time. In the UK, the setback distance between watercourses and ST soakaway is currently 10 m, and 50 m from a water abstraction point (UK Building Regulation, 2008). Since most STS operate for more than 25 years (Fildes, 2011), this suggests that the recommended setback distance can be insufficient to protect water quality (Scottish Executive, 2001). A study by Laurence Day (2005) revealed that many STS require the horizontal distance to streams of 130 m to provide adequate treatment. In many countries, planning regulations require a minimum of 1.2 m of undisturbed soil between the base of the percolation trenches and either the bedrock below, or the highest level of the water table (EPA, 2000; Gill et al., 2004). In Scotland, this distance is 1m (Scottish Executive, 2001). Many old STS do not meet current regulation of setback distance separation requirement and may contaminate groundwater directly (ESB international, 2008).

2.8.4 Septic tank registration

To regulate ST impact on water quality in the UK, the Controlled Activity Regulations (2005) were introduced. In Scotland, all new and existing ST are required to be registered with SEPA. In Ireland, the Water Services (Amendment) Act 2012 requires owners of all existing domestic ST and sewage treatment systems to ensure that their tanks were registered before February 2013 in order to protect Ireland's ground and surface waters. Septic tank registration regulations in England and Wales were introduced by the Department for Environment, Food and Rural Affairs (Defra) and the Welsh Government in 2010 to implement the European Union Water Framework Directive. However, these registration regulations were reviewed by the UK Government in 2014 and as a result the requirement to register all septic tanks has been removed in England and Wales from 1st January 2015 (SN 06059, 2014).

2.9 Approaches to the evaluation of source pollution

Knowledge of pollution sources to watercourses is important to examine ST impacts relative to other catchment pollutants in order to target and prioritise mitigation measures. Evaluation of ST pollution is often conducted in terms of the annual load of an environmentally targeted element such as P for its contribution to eutrophication of surface waters. It is recognised that a large portion of P annual load to UK waters is derived from agricultural activities (Kurz et al., 2001; Defra, 2004). However, Muscutt and Withers (1996) suggested that point source pollution including ST could be the major source of P for most rivers in England as rural catchments were subjected to low-level but persistent P inputs from domestic sewage systems. Jarvie et al. (2006) stated that the assessment of source contributions was often based on annual fluxes of dissolved and particulate P, which were dominated by diffuse input. However, these authors considered that point source effluent, rather than diffuse agricultural pollution sources of P, posed the most significant risk for eutrophication of waterbodies. These authors also reported that SRP was the dominant fraction in watercourses at low flow periods and that SRP concentration was diluted as the flows increased indicating point source rather than diffuse pollution. Edwards and Withers (2007) described the dynamic of P delivery as “variable” from agricultural diffuse losses and “continuous and direct” from point sources, whilst, the bioavailability of P changes from the less bioavailable particulate form in diffuse to become dominated by the directly bioavailable soluble form in point sources. The authors also considered source apportionment and suggested that unlike small point sources, the locations for large point sources such as effluent from Sewage Treatment Works (STW) were generally known and required consented discharge and regular monitoring for operational efficiencies. The authors also stated that catchments that were dominated by point sources had larger proportion of dissolved P compared to diffuse sources that were associated with particles-bound P.

Mathematical models are created to aid the understanding of P dynamic in both land and river systems to make predictions of future changes in water quality under specific scenarios. Models are often used to estimate fluxes of P from different sources; however, a degree of calculation uncertainties are often unavoidable (Demars et al., 2005). In a catchment P losses study modelled by Matias and Johnes (2011), it was concluded that the dominant source of P loading was from large point source such as STW and diffuse leakage from rural STS. Stutter et al. (2014) revealed that agricultural land inputs (P losses) were mostly present in the form of particulate bound P, while STW and ST P were considered to have a constant level but a smaller load inputs. In the case of STW or ST, the high SRP input has larger

ecological impact than annual TP load, especially considering delivery risk at times of low dilution and low river base-flow. Modelling analyses for source apportionment are often laborious and may be hindered by insufficient information, or simplified data needed to accommodate the lack of field data. A drawback of modelling would be to assume that ST P is expected to be locked up in the soil system as many models do not account for direct discharges to watercourses. Moreover, the disproportionate cumulative impacts of ST are not taken into account when they are at high densities in rural areas.

Phosphorus and sediment yield characterisation in catchments (PSYCHIC) is an example of a P modelling tool developed to quantify diffuse P and SS pollution from agricultural land. However, point sources were also estimated based on the number of people in each 1 km² grid cell. This mathematical model required inputs on soil type, slope, land use and P input from inorganic and organic fertilisers (Strömqvist et al., 2008) to estimate the attenuation and the transport of P and SS from the field via surface pathways and drains to watercourses. However, the authors indicated that the ability of PSYCHIC to predict short-term P and SS transfers required further refinement. Furthermore, this model does not include ST contribution to P transport.

The Integrated Catchment model for Phosphorus (INCA-P) is another mathematical model for assessing the effects of multiple sources of P transport and retention within a river system which is based on land use. The model simulates P dynamics in both the land and stream components of a catchment. This is achieved on three levels: river catchment, sub-catchment and land cover types. The model incorporates daily and annual land use organic and inorganic P fluxes in the soil, groundwaters and surface waters. The model can be applicable at spatial and temporal scales, coupled with field data available in the literature (Wade et al., 2002). The model requires calibration as it includes a variety of input variables such as catchment and sub-catchment boundaries, land management practices (vegetation types and fertiliser application), air temperature, soil hydrology, rainfall, flow rates and SRP concentration of sewage effluent. The model is used on the assumption of the fertiliser, wastewater, slurry and livestock inputs and phosphorus process rates are the same for a particular land use type within the catchment. Septic tank input was a rough calculation of average P exports obtained from literature, multiplied by estimated number of ST within 100 m of the water course (Jackson-Blake et al., 2015). In a study by Baulch et al. (2013), ST P load was estimated based on P excretion and detergents release of 0.5 kg P/ha/year, which was added to agricultural P input (based on the assumption that a proportion of P is retained in septic beds. A criticism of INCA-P is the lack of published uncertainty analysis (Dean et al., 2009).

Sowah et al. (2014) showed a way of identifying sources of P transfer during low-flow periods using biochemical fingerprinting as a method for tracing domestic waste effluent from human and animal sources. The authors reported the presence of a positive relationship between septic system density and faecal indicator organisms (FIO) concentration in watercourses indicating point source potential impact on human health. On the other hand, Arnscheidt et al. (2007) identified the source contributions of faecal contamination from either human or field animals (herbivore) in stream sediments by the sterol ratios (coprostanol:24-ethylcoprostanol), as a long term signal for point and diffuse faecal matter inputs. The authors were able to identify human from field animals, if the sterol ratio was >75 and <30%, respectively. Tracing and identifying effluent sources and pollution mobility in watercourses is discussed in the next section.

2.10 Tracing of STE

The US EPA, 2002 stated that ST process 4 billion gallons of water per day in the USA, and the resulting effluent is released to the subsurface, and that 10-20% of these STS fail annually. Failure of STS increases the risk of contaminants entering drinking water, which poses risks to human health. As part of developing new knowledge to understand risks and manage such pollution, it is beneficial to locate and trace STE pollution sources. This can be especially useful if tools were developed to facilitate the scaling of individual failing tanks to medium catchment scales.

To trace STE in stream water, it is important to choose effective environmental tracer to identify the source and the pathway of contaminants:

- Tracers should be conservative and stable.
- Tracers should be non-toxic to humans or to the environment.
- Tracers' concentration should be high enough and easy to detect.
- Tracers should be transported in a similar way to the target pollutants.

Studies have investigated the use of boron (B) and chloride (Cl) to detect point source impacts on river waters (Neal et al., 1998; Jarvie et al., 2006). Neal et al. (2010) considered B as a good indicator of sewage pollution and used Na, B concentration and river discharge behaviours in river waters to evaluate point source impacts of P associated with effluent sources. Boron is a component of modern detergents as a bleaching agent and its use as tracer for municipal wastewater pollution is attributed to its conservative behaviour in natural waters (Neal et al. 2010). Bundschuh et al. (1993) stated that elevated B concentrations are indicative of anthropogenic inputs; conversely Verstraeten et al. (2005) called for caution when relying solely on B alone in tracing sources of catchment pollution, as B has multiple source: natural source (parent rock, rainwater, soil erosion), agricultural runoff (fertilizers) and anthropogenic (detergents). Furthermore, Verstraeten et al. (2005) suggested that additional indicators should be implemented before assuming contamination. Alhajjar et al. (1989) used Cl concentrations and electric conductivity (EC) in STE and groundwaters to imply P transport to groundwater from domestic ST using P-based detergents. Vengosh and Pankratov (1998) used Cl/Br ratios to distinguish water impacted by sewage from urban runoff (high ratio) from agriculture runoff (low ratio). Others used added chemical tracers such as sulphur hexafluoride (SF_6) and dichlorobenzene to investigate STE attenuation and contamination in wells and groundwaters (Robertson, 1994; Dillon et al., 1999). It is clear that the use of tracers is a useful tool to determine pathway of pollutants in natural waters, the source and the impact. Effectively, there is no comprehensively-studied natural tracer or set of tracers

for STE discharge. It is crucial to provide composite, cost-effective tracer approaches to aid current environmental impacts and future policy benefits evaluation.

Substances that are normally found in domestic wastes such as caffeine and artificial sweeteners may be explored for their use as STE discharge potential tracers. These trace organic compounds originate solely from anthropogenic sources such as food, drinks, medicines, toothpaste, and are therefore present in sewage waters through human consumption then excretion often un-hydrolysed (Arnalud, 1993; Spoelstra et al., 2013). The concentration of artificial sweeteners in sewage treatment plant effluent (Table 2.5) was determined by Scheurer et al. (2009). The authors reported that saccharin and cyclamate are readily degraded in sewage treatment plant processes, while Soh et al. (2011) reported sucralose' resistance to degradation through water treatment processes. Caffeine concentration from 20-300 µg/l in sewage effluent was reported in the USA and Canada (Umari et al., 1995; Rogers et al., 1986). Not many data are available on the concentration of these substances in STE, and their attenuation/degradation in soil particles is poorly understood.

Table 2.5: Concentration of caffeine and artificial sweeteners found in sewage effluent (Rogers et al., 1986; Umari et al., 1995; Scheurer et al., 2009)

Indicator	Concentration µg/l
Cyclamate	190
Acesulfame	34-50
Saccharin	34-50
Sucralose	1
Caffeine	20-300

2.11 Research gaps and key questions

Throughout the literature, there is generally a lack of comprehensive data on the concentrations of contaminants in STE. The data available are limited to just a few parameters, and largely dated, while comprehensive data on multipollutant characteristics are currently not available. Most recent literature data are focusing on STS in the USA, Canada, Australia and other parts of the world where tank management, detergents and water usage differ from the UK and hence may change effluent properties. Thus, an investigation of ST outputs (discharges) to surface waters in terms of effluent fingerprinting, characterisation, enrichment to watercourses and the effects of tank management factors (e.g. design, management, detergents use etc.) on effluent quality is necessary.

The hypothesis is: The relative high concentration of STE discharges have the potential capability to enrich surface waters adjacent to the tank input and can pose risks as small inputs of multiple pollutants. This work addresses the following questions:

- What are the current physical, chemical and microbial properties of STE?
- What are the enrichment potentials of STE compared to stream waters?
- Does STE composition change with tank design, maintenance or number of users?

The consistency of STE throughout the year is another area of little consideration in literature. There are very few studies that have been conducted on changes in STE composition over time, or during different seasons and the effect of these changes on stream water quality. Therefore, a study is required on the consistency of STE quality in terms of its properties in different seasons and the potential consequential effect on adjacent stream water.

The hypothesis is: STE compositions vary in different seasons and thus may have different potential ecological impact on water quality during different seasons, for example during the low flow ecologically sensitive periods. This work addresses the following questions:

- Are STE properties consistent throughout the year or vary during different seasons?
- Does stream water show seasonal variation associated with that of STE?
- What are the impacts of STE discharges on downstream waters?

Detergents and household cleaning products may contain large quantities of P as human input to STE, despite manufacturers' voluntary agreements and potential legislation to reduce P concentration. Human input of P from detergents to STE is not sufficiently quantified and P load from detergents is poorly understood in literature. Therefore, an investigation to evaluate detergents' P contribution to STE may be necessary.

The hypothesis is: Detergents and household cleaning products contain large quantities of P despite manufacturers' voluntary agreements and potential legislation to reduce detergents P. This work addresses these questions:

- What are P concentrations in household detergents?
- What are P loading scenarios if only regular or reduced-P detergents were used?
- Can trace elements found in detergents act as a tracer for effluent discharges?

Septic tank effluent contains trace organic compounds that if traced can be indicator of environmentally targeted element such as P. The concentration and the attenuation of these organic chemicals in soils are poorly understood. It is beneficial to evaluate the nature of the degradation or attenuation (biotic or abiotic) of effluent P and trace organic compounds found in STE (caffeine and saccharin) by soil as well as to evaluate the rate and effectiveness of their attenuation in soil system.

The hypothesis is: For P and other STE organic molecules, it is expected to be locked in the soil system, and P attenuation in soil is dominated by sorption, while the attenuation of organic compounds may be dominated by microbial degradation. This work addresses these following questions:

- Can these substances found in STE be removed or reduced by soil treatment?
- Is the attenuation behaviour of these substances similar in STE and in aqueous solution?
- Does a complete degradation of these substances occur in soil?
- What is the dominant process of the degradation/attenuation?
- Can compounds found in STE (caffeine and saccharin) be indicators for an environmentally targeted element such as P?

It is important to understand nutrient contribution of ST in terms of P annual loadings to prioritise and target mitigation measures to control nutrient enrichment and reduce the risk of eutrophication of surface waters. An estimation of P annual loading from STE is required based on monitoring data/empirical evidence.

The hypothesis is: STE phosphorus annual loading can be considerable, and the long term release of sewage effluent to soakaway soil may cause the soil to become enriched in P. This work answers the following questions:

- What are the annual P loadings from STE discharge?
- What is the effect of effluent irrigation on soakaway soil?

It is clear that the use of tracers is a useful tool to determine the pathway of pollutants in natural waters, the source and the impact. It is beneficial to provide composite, cost-effective tracer approaches to aid current environmental impacts and future policy benefits evaluation. To date, there is no comprehensively studied, naturally present tracer or set of tracers for STE discharge. Thus, an investigation to assess the potential of naturally occurring effluent constituents' caffeine and artificial sweeteners (Acesulfame K, Saccharin, Sodium Cyclamate and Sucralose) as well as effluent fluorescence, microbial and chemical indicators to be used as tracers of discharges contamination may be necessary.

The hypothesis is: Effluent natural constituent's concentrations are much higher compared to stream waters and thus may be used to quantify effluent discharge and may enable source tracing.

This study answers the following questions:

- Can effluent in-situ indicators be used to trace effluent discharge?
- Are these potential in-situ tracers effective in different flow scenarios?
- Can detection of tryptophan-like peak downstream from the source indicate of effluent discharge?
- Can STE caffeine and artificial sweeteners be used as tracking tools for effluent discharge?
- Does the presence of these trace organics in stream waters act as surrogate tracers for effluent P?

Chapter 3

The contribution of household chemicals to environmental discharges via effluents: combining chemical and behavioural data



This work was published in Journal of Environmental Management, 2015.

Richards, S., Paterson, E., Withers, P.J.A., Stutter, M., 2015. The contribution of household chemicals to environmental discharges via effluents: combining chemical and behavioural data. Journal of Environmental Management 150, 427-434.

Author Contributions:

SR designed and performed the experiment, analysed the data, wrote the paper and all co-authors reviewed and commented.

Abstract

Increased concentrations and loads of soluble, bioavailable forms of phosphorus (P) are a major cause of eutrophication in streams, rivers and lakes in many countries around the world. To implement P control measures, it is essential to identify P sources and their relative load contributions. A proportion of P loading generated from household wastewaters is derived from detergents yet the P composition of the range of domestic detergents is poorly understood. To quantify P loads from household detergents, we analysed a large range of detergents and cleaning products commonly available in the UK and Europe, comparing regular and eco-labelled products. Chemical data were coupled with survey results on typical household detergents preferences and usage (n=95 households). We also determined whether the major and trace element signatures of these household detergents could potentially be used as anthropogenic tracers in watercourses. The greatest P concentrations were found for regular dishwasher detergents (43-131 mg P/g detergent) whilst the range of P in eco-labelled dishwasher detergents was much lower (0.7-9.1 mg P/g detergent). Other household cleaning groups contained relatively smaller P concentrations. Considering the survey results, detergents' total P loading generated from one household using either regular or eco labelled products, was 0.414 and 0.021 kg P/year, respectively. Given a household occupancy of 2.7, the P load from all detergent use combined was 0.154 kg P/person/year of which the dishwasher contribution was 0.147 kg P/person/year. In terms of elemental signatures, (DWD) dishwasher detergents were significantly (P-value <0.001) different from other household cleaning products in their As, Na, TP, Si, Sr, SRP, Ti, Zn and Zr signatures. Na, P and B were all positively correlated with each other, indicating their potential use as a tracer suite for septic tank effluent in combination with other indices. We conclude that forthcoming legislation for reducing P contents in domestic laundry detergents will not address the dominant environmental P load from DWD and studies such as this are important in promoting and allowing scenarios of benefits from future legislation for DWD.

Keywords: Eutrophication, Detergents P, Tripolyphosphate, Zeolite A, Wastewater, Bioavailable P

3.1 Introduction

Phosphorus (P) is a key nutrient causing eutrophication in surface waters around the world (Smith et al., 1999; Wind et al., 2007; Withers and Jarvie, 2008). An increase in P concentration under certain conditions of ambient temperature, dissolved organic carbon and nitrogen concentrations in watercourses with long retention time, causes blooms of algae and harmful bacteria (cyanobacteria), (Hilton et al., 2006). This leads to oxygen depletion in fresh waters, discolouration and the unpleasant odour with subsequent threats to fish and aquatic biodiversity (Correl, 1989). Besides agricultural diffuse pollution, P can enter watercourses from municipal Waste Water Treatment Works (WWTW) and septic tanks (ST) that are used as onsite wastewater treatment systems. Since ST are highly variable in P removal rates and are not regulated for P discharges (unlike WWTW, which may include P stripping technologies), they constitute potential routes for delivery of P from household sources to surface waters (Zurawsky et al., 2004; Withers et al., 2011) adversely affecting water quality (Ahmed et al., 2005). Jarvie et al. (2006) indicated that point sources such as septic tank effluents represent more significant risk to river eutrophication than agricultural diffuse pollution particularly during low flow periods of spring and summer. Despite recent improvements in water quality following P reductions at major WWTPs (Neal et al., 2010), many watercourses are still subject to pollution from municipal wastewater and agricultural runoff (Rothwell et al., 2010; EA, 2012; Withers et al., 2014).

Septic tanks specifically are not designed to remove phosphorus from wastewater. Apart from the initial sludge settling process which removes particulate P and organic P, most soluble P in ST effluent are discharged to the environment without treatment. Failing tanks pose even greater risk as all fractions of P including particulate P are released to the environment causing a threat to human health and environmental ecological impacts (Jarvie et al., 2006; Withers et al., 2012).

Household detergents are a source of bioavailable P (phosphate) present in municipal wastewater that if not removed, may eventually reach surface and groundwaters (Pattusamy et al., 2013). Phosphates and sodium tripolyphosphates are important components of modern synthetic detergents which consume ~5% of total mined phosphate rock, (Gilbert and Dejong, 1997; Prud'homme, 2010). Approximately, 80% of phosphate rock is mined for manufacturing fertilizers and the remaining 20% are used for detergents, animal feeds and other industries. However, the world reserves of the non-renewable resource of phosphate rock are declining in quality and economic-viability, leading to P being added to a European list of critical materials in May 2014 (EC, 2014). Although reserve estimates

for phosphate rock are contested as based only on commercial data sources it remains clear that this fundamental resource vital to food production and nutrition is safeguarded for future generations, especially considering global projected population rise (Cordell and White, 2011; Edixhoven et al., 2013).

Detergent phosphates are used as builders to decrease the hardness of water by binding to calcium and magnesium ions present in hard waters which otherwise reduce the effectiveness of the surfactant. This then allows a reduced amount of surfactant to be used. They act by loosening mud, fats, oils and greases from fabrics and surfaces, breaking them into small particles, keeping them suspended in solution and preventing their re-attachment to the cleaned surface (Duthie, 1972).

Many studies have used boron (B) as a tracer for wastewater (Neal et al., 1998; Jarvie et al., 2006). Boron in the form of borate is also used in modern detergents as a bleaching agent and its use as a tracer for municipal wastewater pollution is due to its conservative behaviour in natural waters (Neal et al., 2010). Borate is best suited to hot water washing and since there is a shift in public preference to low temperature washing in the recent years, many detergents manufacturers have substituted oxygen-based bleaching agents instead of borate. The effect of this shift was highlighted by Metzner et al. (1999) who reported a decrease in B concentration in municipal wastewater as a result of replacing B with other bleaching agents. A reduction in the sale of sodium perborates in Europe and UK from 1997 has been reported (RPA, 2008; RIS, 2006) that is expected to lead to lower B concentrations in surface water. While Bundschuh et al. (1993) stated that elevated B concentrations are indicative of anthropogenic effect, Verstraeten et al. (2005) recommended not to rely solely on B alone in tracing sources of catchment pollution.

Attempts to reduce the environmental impact of detergents have been made by the production of compact powders and tablets. Some alternative builders have been used but were found to have low performance, be less effective or too costly (Kohler, 2006). An alternative builder to sodium tripolyphosphates is Zeolite A which is an artificial zeolite derived from aluminium oxide. It is a relatively inert substance, insoluble in laundry detergents and hence separates from laundry waters. It has a reasonable performance but has limitations as a builder, requiring a co-builder (polycarboxylic acids) to fully substitute for phosphates (Morse et al., 1995; Kohler, 2006).

Many countries in Western Europe, US, Canada and Japan regulate the use of detergent products containing sodium tripolyphosphate as a measure to control eutrophication through reduction of P loading to WWTP and subsequent discharge to streams and rivers. In the UK, The Detergents Regulations 2010 (SI 2010 740) restricts the amount of phosphates in domestic laundry detergents from January 2015, stating: "It is an offence to place on the market a detergent intended for use in domestic laundry if the weight of phosphorus as inorganic phosphate contained in the detergent is greater than 0.4% of the weight of the detergent". This is derived from the 2013 amendment to the EU detergents regulation (684/2004), (EU Parliament Regulation, 2004). It is being discussed that similar restrictions will be placed on dishwasher detergents from 2017 and so studies are needed as evidence for the current situation with P in detergents and allow for benefits scenarios for upcoming policies.

In this study 80 laundry products and household detergents available on supermarket shelves, and widely used in the UK and Europe, were tested for P and trace elements concentrations. A survey was devised and distributed in 4 catchments to gain real information on the different types of detergents and household cleaning products that are normally used and the frequency of their use. Detergent products were in a variety of forms (condensed tablets, powders, gels and liquids) of different classes and uses: Laundry detergents (LD), dishwasher detergents (DWD), fabric softeners (FS), washing up liquids (WUL), general cleaning products (GCP) and hand soaps (HS). The aims were: 1) to examine P concentrations in these household chemicals across different usage categories including those determined as 'eco-products' compared to regular products; 2) to combine concentration data with survey data on household product usage and cleaning habits to produce household P loading scenarios for regular and eco-product use, and 3) to investigate whether the major and trace element signatures of these household chemicals could be used as an indicator for anthropogenic wastewater input to watercourses.

3.2 Materials and Methods

3.2.1 Questionnaire on household detergents usage

To gain an informed knowledge of typical household detergent preferences and their usage, we surveyed household detergent use (Appendix 1) in four catchments in the North East of Scotland as representatives of many catchments in the UK and Europe. The catchments varied from intensive agricultural (Rivers Dee, Don and Lunan) to peri-urban (River Ythan), (Figure 3.1) with no demographic discrimination, having been selected on the basis of estate tenanted farms, rented accommodation, catchment focus groups and local house to house distribution. The purpose of the survey was to gather real information on detergents use and habits, product preferences and the frequency of their use. The survey was intended to gain information relevant to assessing environmental impacts of ST but also included those discharging effluent to WWTWs. All respondents were questioned whether eco or low P products were considered as viable options as a substitute to regular products and, for those who use eco-products, to comment on their performance, price and availability. Additional questions focussed on ST system condition and management. The response rates to the survey were 58%, yielding 95 responses using ST as wastewater disposal systems and 24 using WWTWs.

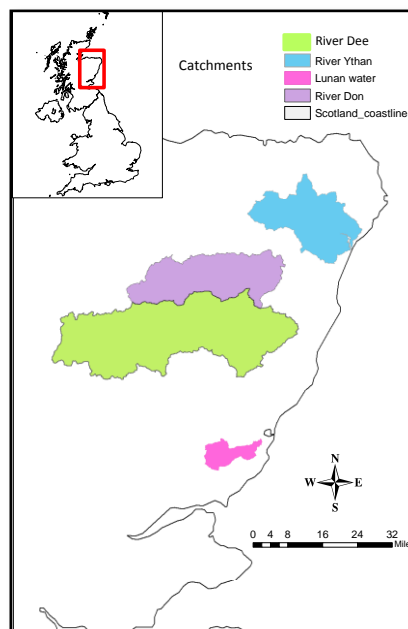


Figure 3.1: Location map of surveyed catchments in North East of Scotland (ArcMap 10).

3.2.2 Classifying detergent products and preparation for analysis

To quantify the amount of P that household detergents and cleaning products contained, eighty products in all forms (tablets, powders, gels and liquids etc.) that were widely available on British supermarkets shelves during 2013 were examined. These detergents and cleaning products were categorised in eight product types: 27 regular laundry detergents (RLD), 5 eco laundry detergents (ELD), 12 regular dishwasher detergents (RDWD), 3 eco dishwasher detergents (EDWD), 12 washing-up liquids (WUL), 7 fabric softeners (FS), 9 general cleaning products (GCP) and 5 hand soaps (HS). Solid form of detergents (powders and tablets), were milled (IKA Labortechnik, type A10S9 miller) for 60 seconds then stored in airtight polyethylene containers until analysis.

3.2.3 Chemical characterisation of detergents

To convert all forms of polyphosphate in detergents to soluble orthophosphate, the detergents were oxidized using an acidified persulphate digestion process (Environment Canada, 2013). Digestion was conducted in duplicate for each product and eight blanks (Millipore water 18.2 MOhm-cm) for quality control were included. The digestion was carried out using 1 g of milled or liquid detergent dissolved in 90 ml of Millipore water, 4 g ammonium persulphate and 10 ml of 2.5 M sulphuric acid. The mixture was digested at 180 °C for 90–120 minutes and the solutions were reduced to 40 ml in volume. The reduced mixture solutions were made up to 100 ml again with Millipore water. A subsample of the mixture was diluted and analysed for major metal concentrations by ICP-OES (inductively coupled plasma-optical emission spectrometry; Agilent 7500ce, Tokyo, Japan). Following the digestion, total P (TP) was detected as dissolved orthophosphate by colorimetry using the molybdate reaction (Standard methods for the examination of water and wastewater, 1992) and using Shimadzu UV Probe UV-1800 Spectrophotometer and UV Probe 2.33 software (880 nm wavelength).

As well as a digestion for total P, a weaker extraction was used to simulate conditions of product solubility when used in the home. Detergent's SRP fraction was determined by dissolving one g of each milled powdered and liquid detergent in 100 ml of Millipore water. The dissolved solutions and eight blanks (Millipore water) were shaken on orbital shaker at 200 rpm for 30 minutes and heated at 60 °C for 45 minutes to mimic washing machine or dishwasher action. Subsamples of the dissolved mixtures were diluted and 0.1 ml of a silicon-based antifoaming agent (Skalar Analytical B.V. Antifoam B) was added to all samples and blanks. Samples were then analysed for trace element concentrations by ICP-

MS (Inductively Coupled Plasma Mass Spectrometry; Agilent 7500i, Shield-Torch System). SRP concentrations were determined in solutions by molybdate colorimetry as for TP.

3.2.4 Data Handling and Statistical Analysis

Total P and SRP contents were expressed as mg P in one gram of detergent in original form (powder or liquid). Statistical analyses including descriptive statistics (average, minimum, maximum, standard deviation and range) were conducted using Minitab 16 and GenStat 16th edition. Data were transformed where necessary using natural log (Ln) transformation according to the results of Anderson-Darling normality tests. Principal component analysis (PCA) on Ln data and a biplot for the scores and loading in the first two PC were used to evaluate the complex major and trace element signatures. One-way Analysis of Variance (ANOVA) with P-value <0.05 was used to determine the difference between mean populations, then pairwise comparisons (Tukey Tests) were deployed to evaluate which groups were significantly different. Box and whisker plot of total P of detergent groups were used to illustrate the distribution of data with the median values and confidence intervals.

The survey data was used to determine the average occupancy, the number of bedrooms, average laundry and dishwasher usage per week. Total P per one gram of detergent was scaled up to per household use according to the manufacturer's recommended dosage recorded on each box or bottle of detergent. Survey data were combined with TP concentration data to scale up to weekly and then annual use. Total P load from detergents for an average household and per person for regular and eco labelled detergents were then estimated.

3.3 Results

3.3.1 Phosphorus chemistry of detergent products

The range and means of SRP and TP are expressed as mg P per one gram detergent (in original form: powder or liquid) of all classes of products tested (eco and regular) are listed in Table 3.1. In general, eco-advertised products contained less TP than regular products; this was mainly observed in DWD. Comparison of TP and SRP in all 8 classes of household detergents showed that RDWD were significantly different ($P < 0.001$) from other groups of cleaning products and contained the highest amount of P (Figure 3.2). A positive correlation between SRP and TP in dishwasher products was determined with correlation coefficient (r) of 0.82. The average TP (95 ± 9 mg P/g) in RDWD was nearly 100 times greater than RLD (Table 3.1). Although there was a significant difference between TP in RLD and ELD products ($P < 0.001$), there was only a small absolute difference between their average concentrations. However, the difference between average TP in regular and eco products were greatest in DWD (20x for TP; Table 3.1), with the supermarket own brands of RDWD containing the highest values of TP. For most cleaning products (WUL, FS, GCP and HS) the TP and SRP concentrations were generally below detection limits, but reached up to 3 and 4 mg P/g for SRP and TP, respectively, for GCP (Table 3.1).

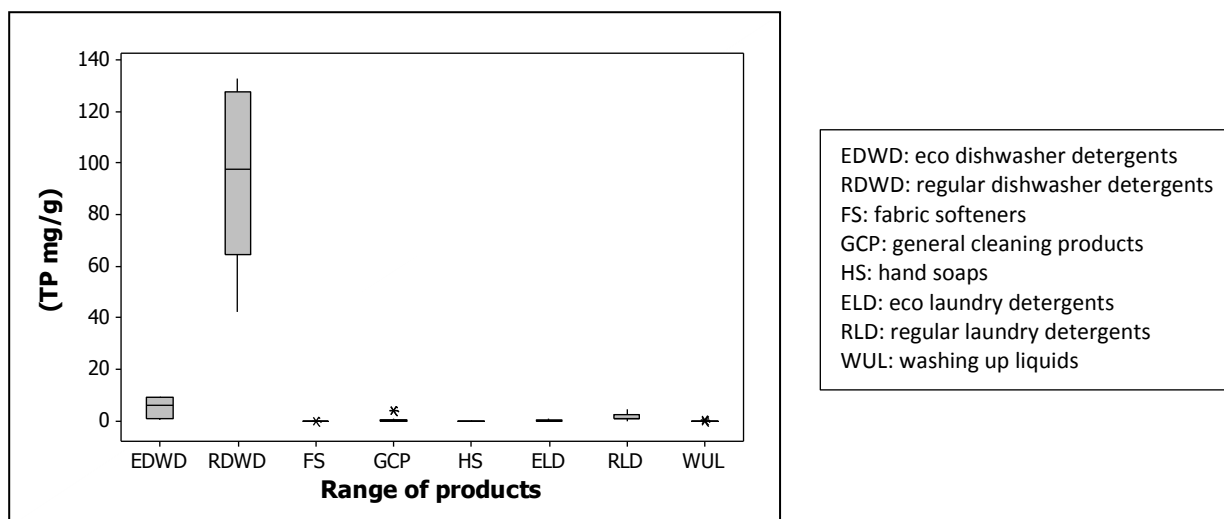


Figure 3.2: Boxplot of total P (TP) concentrations in one gram of all household detergents and cleaning products tested, showing that dishwasher detergents have the highest TP contents.

Table 3.1: Major elements, SRP (soluble reactive P) and TP (total P) in household detergents and cleaning products in average mg/g \pm 1s.e. (with range). Values denoted '<' are below stated detection limit. The superscripts A, B, C, AB, BC, ABC describes Tukey Test as means that do not share letter are significantly different P-value <0.05.

Products	LD		DWD		WUL	FS	GCP	HS	P-value
	Reg. LD	Eco LD	Reg. DWD	Eco DWD					
No	27	5	12	3	12	7	9	5	
Element									
SRP	0.13 \pm 0.03 (<0.03-0.61) ^B	0.12 \pm 0.08 (<0.03-0.43) ^B	1.23 \pm 0.14 (0.55-1.97) ^A	0.30 \pm 0.08 (0.22-0.46) ^B	<0.03 \pm 0.00 (<0.03) ^B	<0.03 \pm 0.01 (<0.03) ^B	0.48 \pm 0.44 (<0.03-3.02) ^B	<0.03 \pm 0.00 (<0.03-0.05) ^B	<0.001
TP	1.61 \pm 0.30 (0.03-4.61) ^B	0.17 \pm 0.08 (0.03-0.62) ^B	95.36 \pm 9.46 (43.05-130.94) ^A	5.22 \pm 2.46 (0.66-9.10) ^B	0.03 \pm 0.00 (<0.03) ^B	0.03 \pm 0.00 (0.03-0.05) ^B	0.65 \pm 0.42 (0.03-3.96) ^B	0.03 \pm 0.00 (<0.03) ^B	<0.001
Al	4.61 \pm 1.3 (<0.001-22.76) ^A	7.80 \pm 7.7 (0.02-38.72) ^{AB}	0.15 \pm 0.04 (0.04-0.54) ^{AB}	0.11 \pm 0.06 (0.06-0.23) ^{AB}	0.10 \pm 0.00 (0.08-0.13) ^B	0.09 \pm 0.01 (0.07-0.12) ^{AB}	0.11 \pm 0.00 (0.09-0.12) ^B	0.10 \pm 0.0 (0.08-0.11) ^{AB}	<0.005
Ca	0.35 \pm 0.1 (0.03-2.00) ^{CD}	0.07 \pm 0.0 (0.05-0.10) ^D	0.21 \pm 0.05 (0.04-0.65) ^C	0.30 \pm 0.16 (0.10-0.65) ^{CD}	0.04 \pm 0.00 (0.02-0.06) ^A	0.12 \pm 0.04 (0.04-0.28) ^B	0.05 \pm 0.01 (0.01-0.13) ^C	0.06 \pm 0.0 (0.04-0.08) ^{AB}	<0.001
K	0.45 \pm 0.1 (0.02-1.67) ^B	6.54 \pm 4.6 (0.02-24.04) ^A	0.72 \pm 0.29 (0.02-3.36) ^B	0.10 \pm 0.01 (0.09-0.13) ^B	0.07 \pm 0.02 (0.02-0.31) ^B	0.02 \pm 0.00 (<0.02) ^B	0.28 \pm 0.24 (0.02-2.19) ^B	0.03 \pm 0.0 (0.02-0.06) ^B	<0.001
Na	126 \pm 25 (2.80-283.27) ^B	111 \pm 65 (6.06-333.68) ^{BC}	251 \pm 17 (118-319) ^C	256 \pm 5 (246-262) ^C	16.12 \pm 1.80 (4.06-26.12) ^C	0.33 \pm 0.03 (0.23-0.46) ^C	3.07 \pm 1.05 (0.39-10.09) ^C	13.57 \pm 0.96 (11.47-16.10) ^C	<0.001
Si	7.95 \pm 1.7 (0.01-24.64) ^C	9.69 \pm 7.5 (0.01-38.70) ^{BC}	16.61 \pm 8.35 (0.08-80.34) ^A	4.27 \pm 2.38 (0.05-8.28) ^{AB}	0.17 \pm 0.01 (0.08-0.22) ^C	0.18 \pm 0.02 (0.12-0.27) ^C	0.17 \pm 0.01 (0.14-0.20) ^C	0.16 \pm 0.0 (0.10-0.20) ^{BC}	<0.001

3.3.2 Major and trace metal concentrations

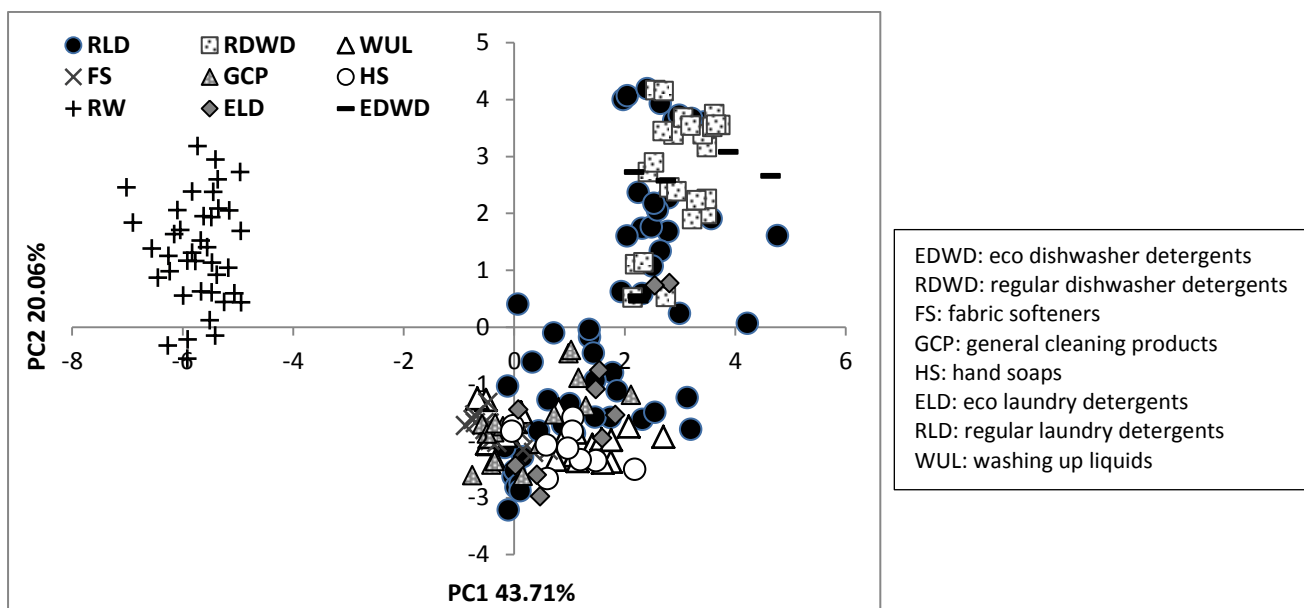
In general, WUL, FS, GCP and HS had low concentrations of major and trace elements (Table 3.1 and Table 3.2). EDWD and RDWD had the highest mean concentration in zinc (Zn), titanium (Ti), B, sodium (Na), arsenic (As), tungsten (W) and niobium (Nb). Tungsten was detected in all detergent classes with concentrations (9-175 $\mu\text{g/g}$). Other elements such as Ti, B, Nb and zirconium (Zr) were detected in detergents with highest concentrations of 211, 210, 72 and 15 $\mu\text{g/g}$, respectively.

A sample score plot (Figure 3.3a) was used to evaluate the relationships between detergent groups and river waters, (groups that are close have positive correlation with each other while groups that are far apart have no correlation with each other). WUL, FS, GCP and HS positively correlate with each other and negatively correlate with dish washer detergents. The properties of laundry products showed positive correlation with WUL, FS, GCP and HS with positive PC1 and negative PC2 values as well as positive PC1 and PC2 with dishwasher detergents. The loading scatter plot (Figure 3.3b) represented all products variables in terms of major and trace elements which showed a strong positive correlation between TP, B, SRP, Na and collectively have weak correlation with Ca, Mg, Sr and Cd. It also showed that K, Fe, Ca and Cu stood out with the lowest values, whilst Al, Mg and Sr stood out with the highest value. ANOVA pairwise (Tukey test) revealed that DWD are significantly different than other detergents for TP, SRP, Na, Si, Ti, As, Sr, Zn and Zr with P-value <0.001 . It also revealed that laundry detergents were significantly different than other classes for Na, K and Ti ($P<0.001$) while there was no significant difference between GCP, WUL, FS and HS ($P>0.05$).

Table 3.2: Trace elements in household detergents and cleaning products in average $\mu\text{g/g} \pm 1\text{s.e.}$ (with range). Values denoted '<' are below stated detection limit. The superscripts A, B, C, AB, ABC describes Tukey Test as means that do not share letter are significantly different.

Products	LD		DWD		WUL	FS	GCP	HS	P-value
	Reg. LD	Eco LD	Reg. DWD	Eco DWD					
No Element	27	5	12	3	12	7	9	5	
As	0.49 \pm 0.1 (0.27-1.73) ^B	0.51 \pm 0.2 (0.27-1.46) ^{AB}	1.28 \pm 0.5 (0.27-2.95) ^A	0.55 \pm 0.2 (0.27-0.91) ^{AB}	0.29 \pm 0.0 (0.28-0.47) ^B	0.27 \pm 0.0 (0.27-0.28) ^B	0.28 \pm 0.0 (0.27-0.28) ^B	0.31 \pm 0.0 (0.28-0.46) ^B	<0.005
B	181.84 \pm 46.5 (1.34-653.58) ^A	22.06 \pm 11.9 (1.35-55.42) ^{AB}	210.61 \pm 59.0 (4.40-672.03) ^A	169.36 \pm 57.3 (85.77-278.99) ^{AB}	10.87 \pm 1.2 (5.14-19.42) ^B	11.60 \pm 0.6 (9.29-13.78) ^B	13.07 \pm 02.5 (6.06-28.98) ^B	10.17 \pm 1.3 (6.46-13.73) ^B	<0.001
Ba	8.79 \pm 1.6 (0.55-37.51) ^{ABC}	3.64 \pm 1.3 (0.55-7.23) ^C	10.78 \pm 1.5 (3.16-17.73) ^{AB}	16.74 \pm 6.3 (7.47-28.83) ^A	4.98 \pm 0.7 (2.10-10.90) ^C	5.64 \pm 0.4 (4.71-6.58) ^{BC}	5.45 \pm 1.2 (2.11-13.20) ^{BC}	5.44 \pm 1.1 (2.28-7.72) ^{BC}	<0.001
Cd	1.24 \pm 0.5 (0.07-12.44) ^{ABC}	0.18 \pm 0.1 (0.07-0.64) ^{BC}	0.12 \pm 0.0 (0.07-0.58) ^C	0.25 \pm 0.2 (0.07-0.60) ^{ABC}	2.42 \pm 0.7 (0.07-8.00) ^{AB}	0.63 \pm 0.4 (0.07-2.34) ^{ABC}	0.83 \pm 0.4 (0.07-2.74) ^{ABC}	3.52 \pm 1.3 (0.07-6.60) ^A	<0.001
Co	1.51 \pm 0.5 (0.08-8.30) ^A	0.90 \pm 0.5 (0.08-2.68) ^A	1.47 \pm 1.3 (0.08-15.33) ^A	2.83 \pm 2.7 (0.08-8.32) ^A	2.73 \pm 1.0 (0.08-11.76) ^A	0.47 \pm 0.3 (0.08-1.93) ^A	0.60 \pm 0.4 (0.07-3.48) ^A	0.764 \pm 0.3 (0.09-1.83) ^A	0.3
Cr	2.55 \pm 0.6 (0.45-10.76) ^{AB}	2.24 \pm 0.2 (0.45-6.04) ^{AB}	0.79 \pm 0.1 (0.45-1.36) ^B	3.79 \pm 2.6 (1.04-8.91) ^{AB}	4.71 \pm 1.4 (0.46-16.26) ^A	1.26 \pm 0.5 (0.45-4.23) ^{AB}	1.02 \pm 0.4 (0.45-3.79) ^B	4.53 \pm 1.3 (0.46-7.76) ^{AB}	0.002
Cu	1.73 \pm 0.2 (0.44-4.34) ^A	0.92 \pm 0.2 (0.28-1.39) ^A	1.54 \pm 0.2 (0.65-3.15) ^A	1.48 \pm 0.4 (0.98-2.30) ^A	1.71 \pm 0.2 (0.94-3.90) ^A	1.47 \pm 0.2 (1.03-2.17) ^A	1.21 \pm 0.1 (0.82-1.64) ^A	1.41 \pm 0.2 (0.91-2.26) ^A	0.464
Fe	112 \pm 31 (27-560) ^A	30.92 \pm 3.3 (27-44) ^{AB}	36.03 \pm 6.9 (27-110) ^B	44.07 \pm 16.5 (27-77) ^{AB}	27.67 \pm 0.0 (27-27) ^B	27.50 \pm 0.1 (27-27) ^{AB}	27.61 \pm 0.1 (27-27) ^B	27.62 \pm 0.1 (27-27) ^{AB}	<0.001
Mg	284 \pm 83 (4-1212) ^A	24.40 \pm 8.2 (4-47) ^B	81.72 \pm 13.9 (23-161) ^B	43.08 \pm 9.2 (25-55) ^{AB}	19.10 \pm 3.5 (9-52) ^B	26.82 \pm 7.5 (16-71) ^B	13.33 \pm 1.0 (7-18) ^B	19.53 \pm 6.5 (8-40) ^B	<0.001
Mn	1.84 \pm 0.7 (0.09-13.90) ^A	0.15 \pm 0.0 (0.09-0.24) ^A	28.17 \pm 27.4 (0.24-329.61) ^A	0.42 \pm 0.2 (0.09-0.67) ^A	0.10 \pm 0.0 (0.09-0.24) ^A	0.12 \pm 0.0 (0.09-0.26) ^A	0.14 \pm 0.0 (0.09-0.32) ^A	0.10 \pm 0.0 (0.09-0.15) ^A	<0.001
Nb	50.32 \pm 19.1 (5-3765) ^A	27.45 \pm 18.1 (5-995) ^A	30.28 \pm 9.8 (5-128) ^A	72.43 \pm 47.6 (19-167) ^A	11.80 \pm 3.7 (5-43) ^A	4.57 \pm 0.0 (4.5-4.6) ^A	10.63 \pm 5.0 (5-50) ^A	15.08 \pm 3.2 (7-24) ^A	0.09
Sr	0.23 \pm 0.0 (0.06-0.91) ^B	0.13 \pm 0.0 (0.6-0.24) ^B	0.77 \pm 0.1 (0.35-1.62) ^A	0.68 \pm 0.2 (0.30-0.96) ^A	0.11 \pm 0.0 (0.06-0.41) ^B	0.09 \pm 0.0 (0.06-0.18) ^B	0.08 \pm 0.0 (0.06-0.24) ^B	0.16 \pm 0.0 (0.06-0.29) ^B	<0.001
Ti	70.68 \pm 13.1 (5-206) ^B	55.82 \pm 37.6 (5-199) ^{BC}	211 \pm 19 (82-292) ^A	203 \pm 25 (162-247) ^A	5.45 \pm 0.6 (5-12) ^C	4.58 \pm 0.0 (4.55-4.61) ^C	7.26 \pm 1.8 (5-175) ^C	5.75 \pm 1.1 (5-10) ^C	<0.001
W	92 \pm 28 (9-592) ^{AB}	32 \pm 14 (9-70) ^{AB}	53 \pm 14 (9-159) ^B	117 \pm 63 (51-244) ^{AB}	40.04 \pm 14.1 (9-168) ^B	9.17 \pm 0.0 (9.1-9.2) ^B	22 \pm 9.0 (9-68) ^B	175 \pm 21.0 (134-249) ^A	<0.001
Zn	2.30 \pm 0.4 (0.55-5.81) ^B	0.96 \pm 0.3 (0.55-1.87) ^B	262 \pm 104 (0.55-1138.43) ^A	259 \pm 170 (0.55-578.83) ^A	2.38 \pm 0.8 (0.55-8.33) ^B	0.61 \pm 0.1 (0.55-0.97) ^B	0.83 \pm 0.1 (0.55-1.50) ^B	0.80 \pm 0.1 (0.56-1.03) ^B	<0.001
Zr	9.35 \pm 1.2 (3.65-24.46) ^B	6.13 \pm 2.4 (3.65-15.92) ^B	15.84 \pm 2.1 (3.65-29.77) ^A	13.37 \pm 4.1 (6.61-20.91) ^{AB}	7.41 \pm 1.9 (3.69-21.81) ^B	3.67 \pm 0.0 (3.64-3.69) ^B	4.23 \pm 0.6 (3.65-8.66) ^B	5.13 \pm 1.4 (3.67-10.88) ^B	<0.001

a)



b)

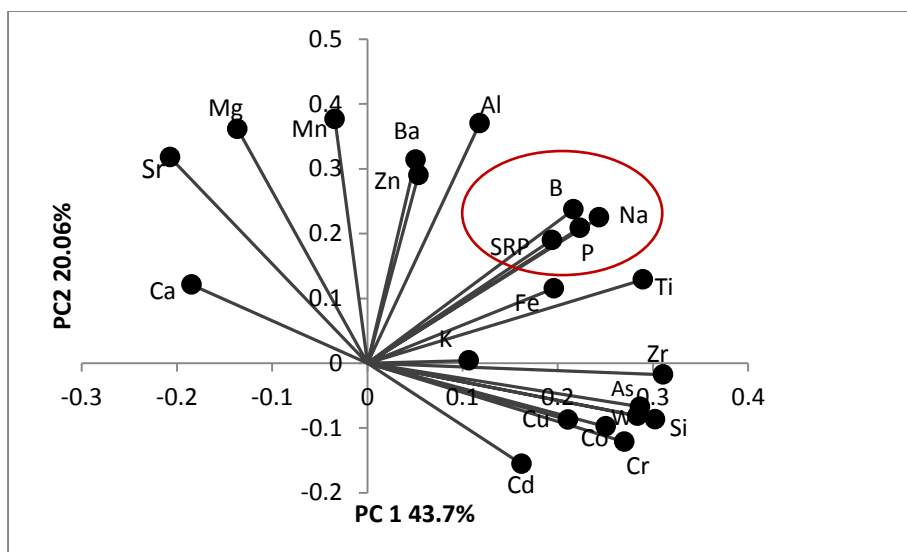


Figure 3.3: a) Plot of the score of PC1 and PC2 of variance explain 64% of all detergents samples and river water (RW). It shows the relationship, correlation and differences among samples. b) Loading plot of weights assigned to individual major and trace elements variables.

3.3.3 Survey results

Survey results revealed that ST users' (n=95) choices of detergent products do not differ from those connected to WWTW (n=24) in terms of type of products and the frequency of their use. For example, ST users did not preferentially choose eco-products over regular products in general. The choices of products in many cases were governed by prices as consumers favoured low prices products (what is on offer or a deal) compared to the more expensive eco-labelled products, with supermarket own brand offers being most favourable to 28% of all users. Only 14% were using eco-advertised products, while 48% had used eco products in the past, but then switched back to regular products because of poorer performance. Also, 68% of ST users surveyed use DWD contained >30% phosphate. The survey also revealed that 100% of users had washing machines, while 78% of households used dishwashers (Appendix 2). The average occupancy and number of bedrooms were 2.7 and 3.5, respectively, while average laundry usage per week was 4.6. For households with dishwashers, average use per week was 5.2 washes. The survey revealed that 30% of septic tank users have had or have a problem with their tank or soakaway/drainage field while 22% of septic systems were located within 30m or less from watercourses. Only 35% of septic tanks were registered with the Scottish Environmental Protection Agency (Appendix 2). Although registration is not mandatory for existing septic systems until the property is sold, however, registration is required for septic systems installed in newly constructed buildings in Scotland.

3.3.4 P load scenarios from detergents per year

Total weekly P load scenarios for a typical household were calculated by combining the data received from the households' questionnaire (type and frequency of detergents use) with detergent composition data. The average weekly usage of laundry and dishwasher products was 4.6 and 5.2 times, respectively, therefore, the average annual load of total P from regular laundry and dishwasher detergents alone per household was 0.414 kgP/year. While the average annual load of total P produced by the same size of household using only eco-labelled laundry and dishwasher detergents was 0.021 kgP/year. Thus the use of regular laundry and dishwasher detergents (n=39) result in environmental TP loads over 19 times greater than the equivalent use of eco-labelled products (n=8), and the supermarkets' own brands (n=16) containing 11% more P than other regular products. Based on the survey data, the estimated TP load combined from regular and eco detergents were calculated to be

0.154 kgP/person/year (0.417 gP/person/day). This was dominated by the TP load from dishwashers which was calculated as 0.147 kgP/person/year (0.401 gP/person/day).

The P load contributions from WUL, FS and HS were insignificant by virtue of their low P concentrations when compared to DWD and LD products, therefore their small P contributions were not included in the TP load calculations. The survey results also revealed that GCP are used infrequently and in small quantities, thus their P contribution was not included in the TP load calculations.

3.4 Discussion

Although national legislation now targets wastewater point sources, it is recognized that the largest source of P input into surface waters in many countries, including the UK, continues to be wastewater discharges (White and Hammond, 2009; Withers et al., 2014). This includes numerous small point sources (ST) in rural areas that are hard to regulate. The link between municipal wastewater P and the eutrophication of surface waters is well documented (Jarvie et al., 2006; Wei et al., 2008; Neal et al., 2010; Withers et al., 2012). Since discharges of P from WWTW and ST remain high due to limited P control measures, detergent P has a considerable contribution to the ongoing problems in attaining water quality under the Water Framework Directive. This is particularly the case due to point source ecological P impacts at low flows and since many septic tanks in headwater catchments are directly connected to waters or have insufficient set-back distances from waters for functioning soakaways/drainage fields.

In this work, we focused on the detergent P contribution to wastewater and estimated detergents' TP load to be 0.154 kgP/person/year of which dishwasher detergents contributed 0.147 kg P/person/year. The survey data (Appendix 2) highlighted the percentage of households that use dishwashers (78%) and revealed the major role that dishwasher detergents play in P load. This finding is in agreement with Foy et al. (1995) who reported an increasing trend in dishwasher detergent contributions to P loads (from 0.004 kgP/person/year in 1980 to 0.099 kgP/person/year in 1991). While Gilmour et al. (2008) estimated the total P load from dishwashers to be 0.095 kg P/person/year; this is substantially less than the calculated value from this current work of 0.147 kgP/person/year. Our results indicated that P load of dishwasher detergents are 20 times greater than that of laundry detergents and this is particularly of concern since 78% of dwellings use dishwashers and the number of dish washes per week is high (5.2). The percentage of dwellings in the catchments surveyed using dishwashers of 78% is much higher than previously reported and dishwasher use is likely to increase in the future.

In comparison the P load from laundry detergent is relatively small (0.007 kgP/person/year). This is because in many countries around the world including the UK, many detergent manufacturers entered a voluntary agreement to reduce detergent phosphates, or to use alternatives such as zeolite A as a builder, or a combination of the two approaches (Morse et al., 1995; Glennie et al., 2002; Defra, 2008) to reduce P in some laundry detergents. This low P content for laundry detergents was confirmed in our study and product labels indicated that half of laundry detergents tested contained zeolite A as a

builder as opposed to sodium tripolyphosphate, or a mixture of zeolites and phosphates. The study also revealed that both P-based and non-P-based detergents are available (though with limited choices for the latter) on large supermarkets' shelves. Glennie et al. (2002) reported similar findings on laundry detergents in European Union (EU) countries of France, Greece, Portugal and Spain. In Canada, phosphorus concentration regulations came into effect in 1989 for laundry detergents and they already have P limits for dishwasher detergents from 2008 (Government of Canada; Water Canada, 2010).

Contents labelling for detergents was not always clear in terms of composition, particularly for P and can be confusing to consumers. The exact quantity of P in laundry and dishwasher detergents was seldom reported on the product packaging. Product labels listed phosphate contents by categories with coarse differentiation as (<5%->30%), and for 4 products there was no mention of phosphate on the label, while our analysis revealed phosphate contents of 0.2% (RDWD), 1.1% (RLD), 2.8% (EDWD) and 34.6% (RDWD), respectively. Dishwasher detergent phosphate contents exceeded 40% (>130 mg P/g detergent) while regular laundry detergents contained <5% phosphate as stated on most packages, which ranged from 0.2%-1.4% phosphate (up to 4 mg P/g detergent). The high P level in DWD is of concern, as 68% of people surveyed use dishwasher detergents contained >30% phosphate with P contribution up to 0.294 kg/person/year from dishwasher use alone.

In Europe, 50% of the non-fertilizer P import is used for detergents, which contribute 25% of the P in wastewaters (Glennie et al., 2002). This large point source P contribution from WWTW has caused major public concern in many countries and warranted calls for the reduction of P load from household and industrial wastewaters. A main driver for this is continuing difficulty to attain water quality goals under the Water Framework Directive (UK Technical Advisory Group, 2008), which has river phosphate concentrations as a key parameter. Discharges from WWTW in the UK have recently been calculated as 55 kt/year P wastewaters with 24 kt/year presently being delivered to waters (Cooper and Carliell-Marquet, 2013).

A combination of legislation and the manufacturers' voluntary agreement to reduce detergents' sodium tripolyphosphate has already resulted in a decrease in detergents P contribution in wastewater from 50% to 16% since the 1970s (Glennie et al., 2002; Defra, 2009). In a report by Glennie et al. (2002) to EU Environment Directorate, it was estimated that a 40% decrease in P load to EU surface water would result from a ban on P use in detergents. The authors also noted the decrease in TP

concentration in Lake Geneva from 0.9 mg/l to 0.4 mg/l that coincided with both improved wastewater treatment and the restrictions on detergents' P.

In our work, we estimated a reduction of >90% of detergent P load could be achieved if only non-P-based detergents were used including dishwasher detergents. This is a 50% further decrease than Glennie et al. (2002) estimation of 40%. On the other hand Defra (2008) suggested that a ban on P in domestic laundry cleaning products could result in 11% reduction in P load to the water environment from WWTP and the savings to the water industry were estimated to be between £7-13 M per year. However, the probability of all households switching to and continuously use non-P-based detergents is low as the survey reported that 48% of consumers switched back to P-based detergents after having tried eco-labelled low P ones. It was also revealed that 83% of those who tried eco-labelled products believe that they were not as effective as P-based products, were more expensive and not widely available in most shops.

Environmental tracing of components of wastewaters helps evaluate poorly understood loading factors for target pollutants such as P. These factors include ecosystem exposure to pollutants at sensitive periods and proliferation of impacts from ST sources. Many studies have investigated the use of certain elemental concentrations such as B and Cl to detect point source impacts on river waters (Neal et al., 2010). This present investigation illustrated a positive correlation between Na, B and P in detergents, which suggests that concentration of Na and B combined in surface waters may be used as tracers for detergent inputs to surface waters. With consideration to their natural abundance from the environment, these elements may be used with other indices as an indicator for P from septic effluent. The clustering of B, Na, Fe and Ti loadings in direction with SRP and total P in the PCA biplot (Figure 3.3) suggests that these elements may also have the potential in tracing domestic wastewaters using composite fingerprinting approaches in the future and warrant further work.

Legislative controls on P in domestic laundry cleaning products are imminent in the EU (EU, 2012). In the UK, The Detergents Regulations 2010 (SI 2010 740) which comes into force in the 1st January 2015 restricts phosphate content in domestic laundry detergents to no greater than 0.4% of detergent's weight (The Detergent Regulations 2010) which does not include DWD. It was found in this work that laundry detergents contained phosphate ranging from 0.2-1.4%, and in 11 out of 32 cases evaluated here, require phosphate reduction up to 2.5 times their current existing phosphate content to meet the Detergent Regulation 2010. The purpose of the regulation is to protect the environment from the

release of P from certain products that could contribute to eutrophication of surface waters. The findings of this work suggest that dishwasher detergents contribute a much higher impact on P load than laundry detergents. It is planned in the future to extend detergent legislations to dishwasher detergents from 2017. We provide evidence here to support such future legislation. The methods combined here show not only that the P concentration of dishwasher detergents are much greater than laundry detergents and other product classes, but also that dishwasher usage is surprisingly high; together these explain fully how our load estimations are greater than earlier work. So, the restriction of P content should extend to dishwasher detergents as well as laundry detergents in order to reduce P load in sewage and STE and improve surface and groundwater quality. In addition we showed general dissatisfaction with low P eco-brands, so to realise future legislation eco and low phosphate based detergents need be made more attractive to consumers by increasing their cleaning efficiency, availability and affordability.

Not only is it important to reduce P usage in the full range of detergents to ease environmental impacts there are important contributions to P resource use. As the world population continues to grow, there is an increasing global demand for phosphate rock use in fertilizers to maintain global food security. Although the quantities of current global reserves of phosphate rock are widely contested (Cordell and White, 2011), importantly these reserves are decreasing in economic-viability and quality and need to be conserved for food production. The concern over the long term availability of phosphate rock has stimulated the demand to find more sustainable alternatives to current manufactured P inputs including detergents.

3.5 Conclusion

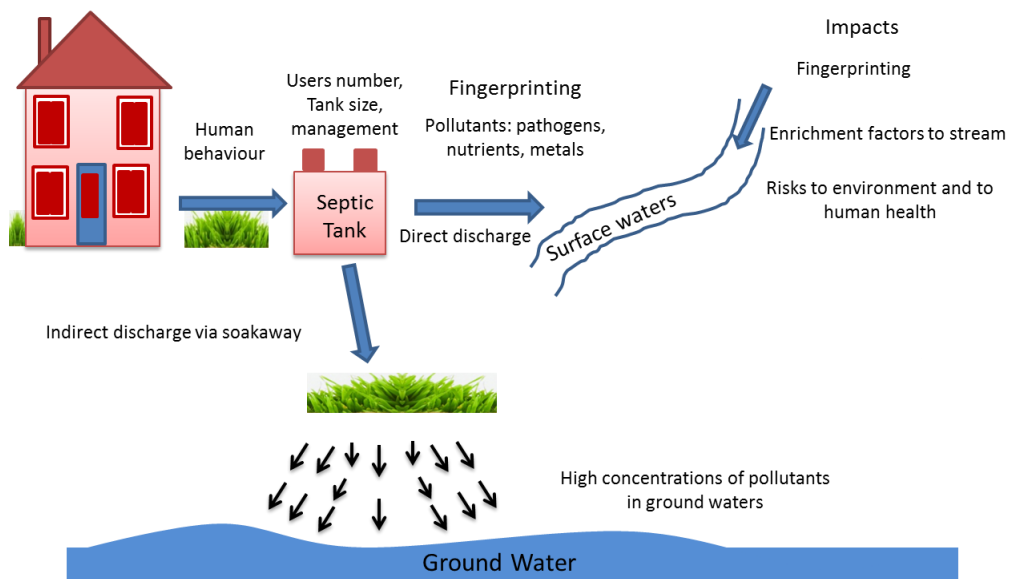
Using a combination of analytical screening of a range of detergent and household cleaning products coupled with a survey approach into consumer choices and behaviours we have made P loading estimates for domestic wastewaters. The calculated P loads from detergents (0.154 kgP/person/year) were greater than previously reported values and were dominated by contributions from dishwasher detergents (0.147 kgP/person/year). This is of major concern as >75% of dwellings in the catchments surveyed used dishwashers and the most regularly used dishwasher detergents contain >30% phosphate. Washing-up liquids, fabric softeners, general house cleaning products and hand soaps were found to have little or no P. Eco-advertised products were generally found to contain less P than regular detergents but were not popular with consumers for reasons of price and performance.

Metals identified in this study may have promise in providing composite tracer approaches to aid current environmental impacts and future policy benefits evaluation. It is crucial that cost-effectiveness of actions such as dishwasher detergent P legislation is judged alongside actions for diffuse pollution with the farming industry. Therefore, our study provides evidence of the limited impacts of the forthcoming legislation concerning only laundry detergents phosphate reduction. It is vital to extend this legislation to dishwasher detergents to reduce detergents environmental impact.

Chapter 4

Septic tank discharges as multi-pollutant hotspots in catchments

Graphical Abstract



Septic tank discharges; as multi-pollutant hotspots in catchments

This work was published in Science of the Total Environment, 2016.

Richards, S., Paterson, E., Withers, P.J.A., Stutter, M., 2016. Septic tank discharges as multi-pollutant hotspots in catchment. Science of the Total Environment 542, 854-863.

Author Contributions:

SR designed and performed field work and the experiment. SR also analysed the data, wrote the paper and all co-authors reviewed and commented.

Abstract

Small point sources of pollutants such as septic tanks are recognised as significant contributors to streams' pathogen and nutrient loadings, however there are little data in the UK on which to judge the potential risks that septic tank effluents (STE) pose to water quality and human health. We present the first comprehensive analysis of STE to help assess multi-pollutant characteristics, management-related risk factors and potential tracers that might be used to identify STE sources. Thirty-two STE from residential households located in North East of Scotland were sampled along with adjacent stream waters. Biological, physical, chemical and fluorescence characterisation was coupled with information on system age, design, type of tank, tank management and number of users. Biological characterisation revealed that total coliforms and *Escherichia coli* concentration ranges were: 10^3 - 10^8 and 10^3 - 10^7 MPN/100 ml, respectively. Physical parameters such as electrical conductivity, turbidity and alkalinity ranged 160-1730 μ S/cm, 8-916 NTU and 15-698 mg/l, respectively. Effluent total phosphorus (TP), soluble reactive P (SRP), total nitrogen (TN) and ammonium-N (NH_4 -N) concentrations ranged 1-32, <1-26, 11-146 and 2-144 mg/l, respectively. Positive correlations were obtained between phosphorus, sodium, potassium, barium, copper and aluminium. Domestic STE may pose pollution risks particularly for NH_4 -N, dissolved P, SRP, copper, dissolved N, and potassium since enrichment factors were >1651, 213, 176, 63, 14 and 8 times that of stream waters, respectively. Fluorescence characterisation revealed the presence of tryptophan-like peak in the effluent and downstream waters but not detected upstream from the source. Tank condition, management and number of users had influenced effluent quality that can pose a direct risk to stream waters as multiple points of pollutants.

Keywords: Septic tank effluent, Water quality, Nutrients and metal concentrations, Bacteria, Tracers

4.1 Introduction

Septic tank systems (STS) are the most widely used collection systems for onsite treatment and disposal of domestic wastewater around the world. Their use is particularly common in rural areas where connection to main sewerage network system is not available or impractical and costly (Dudley and May, 2007). In the UK, only 4% of the population are served by small private treatment works or septic tanks (ST), (Defra, 2002), but over one third of dwellings in Ireland (400,000) use them (Gill et al., 2004). Approximately 13% of the Australian population and 25% of households in the United States are served by onsite systems (Dawes and Goonetilleke, 2003; D'Amato et al., 2008). The efficiency of these systems is reflected in the quality of septic tank effluent (STE) and the functioning of the soakaway. STE poses potential risks to human health and aquatic ecosystems if it reaches surface or groundwaters without effective treatment (Withers et al., 2014) which depends on tank performance, effluent retention time and the physical, biological and chemical processes inside the tank. Effluent quality also depends on wastewater organic matter content and use of chemicals in the household, which affects bacterial growth and activity in the tank (Brandes, 1978).

Historically, ST were made from bricks or concrete and comprised of one rectangular chamber connected with an inlet pipe (receiving influent from the house) and an outlet pipe (discharging effluent to the soakaway) (May et al., 1996). Septic tanks should be designed to accommodate vertical soil pressure and should be large enough to provide a minimum effluent retention time of 24 hours (Seabloom et al., 2005). The primary functions of ST are solids removal from wastewater, accumulation and storage of sludge and scum, breakdown of solid material in an anaerobic digestion process and finally discharge the partially treated effluent to soakaway soil for further treatment (D'Amato et al., 2008). Most STS are capable of treating domestic wastewater effectively at low cost if situated, designed, constructed and maintained appropriately (Environmental Alliance PPG4, 2006).

Septic tank effluent is thought to have negligible or less impact on water quality compared to diffuse pollution (Sharpley et al., 1993; Haygarth et al., 2005). However, domestic wastewater contains a wide variety of potential pollutants including pathogens, faecal bacteria, organic matter (OM), phosphorus (P), nitrogen (N), ammonia (NH₄-N), biochemical oxygen demand (BOD) and suspended solids (SS) as well as pharmaceutical organic compounds and household detergents and chemicals (Gill et al., 2004; Wilhelm et al., 1994; Siegrist et al., 2012) that pose a risk that may contaminate fresh waters. Many studies have linked P contamination of surface waters to STE (Bowes et al., 2010; Edwards and Withers,

2008). Bacterial contamination of watercourses from untreated STE is of major concern and poses a risk of disease outbreaks if it contaminates drinking water in nearby water wells (Harris et al., 2013). Lusk et al. (2011) stated that pathogenic bacteria present in STE such as *Escherichia coli* (*E. coli*), *Salmonella* and *Shigella* can cause infections in humans (diarrhoea, nausea, dysentery and hepatitis) in much lower dosage than their actual concentration in STE. Domestic wastewater may contain a number of trace organic chemicals derived from cleaning products, washing detergents and other human activities including caffeine, pharmaceutical compounds, hormones and endocrine disrupting compounds contributing to environmental and human health risks from STE (Kusk et al., 2011).

Although most ST discharge their effluents to soil soakaways for secondary treatment, some ST discharge their effluents and contaminants directly to surface waters or to soakaways that are sited too close to watercourses, (Dudley and May, 2007). Efrogmson et al. (2007) declared that the ST that are located within close proximity of watercourses and those with hydraulic failures have direct impacts on water quality. Withers et al. (2011) considered that effluent discharges during low flow periods in summer would have the greatest ecological impact and risk to human health. There is little data on the composition of STE in the UK with which to assess the risk to both water quality and human health, or the variability in effluent quality between different types of tanks and due to effects of management factors is currently poorly known. For example, very few studies have looked across a range of nutrient, metal and microbiological parameters, yet the knowledge of these combinations of contaminants will inform impact, tracing techniques to quantify STE emissions and future control.

In the UK, onsite waste water treatment systems are unregulated and not monitored for performance. In the absence of this knowledge of their true impact, we propose that STE enrichment to freshwaters can pose significant risks at catchment scales, acting as small inputs of multiple pollutants. The current study examined the effluent composition of thirty two STE from residential households located in the North East of Scotland. The main hypothesis is that STE compositions indicate they are a major environmental source of physical, chemical and microbial pollution. Knowledge is required on ST management and landscape factors that may control effluent composition and potential pollution impact. Therefore, we further hypothesise that 1) STE composition, and hence impact on receiving waters, can be related to tank management factors that may provide risk descriptors and 2) composition factors can be identified to inform development of future environmental tracing methodologies to quantify STE risks.

4.2 Materials and Methods

4.2.1 Study sites

Thirty two conventional residential STS serving permanently occupied dwellings located in four rural river catchments in the North East of Scotland were selected for effluent sampling and analysis. Site location, tank management and catchment information is reported in supplementary material (Table S4.1) and (Figure S4.1): Lunan water (n=5), River Dee (n=14), River Don (n=8) and Ythan River (n=5). Selection of sites was based on a survey (Appendix 1) previously sent to ST users to gain information on their STS and to acquire permission and agreement to participate in the study. Sites were visually assessed for tank access and for signs of system failure before sampling. Twenty one sites had individual conventional concrete ST and eleven sites were reinforced fibre glass/polyethylene tank type. Five sites were within 2-10 m from watercourses. Three tanks discharged their effluent directly without soakaway secondary treatment to watercourses, five discharged the effluent through an undersoil surface soakaway and eventually to streams, and two discharge their effluent to ditches, while others discharged their effluents to surface soil beds or to fields. The ages of the tanks varied from 1 to over 100 years. Management of the tanks also varied; from being emptied yearly to never having been emptied, whilst some users did not know the history of their tanks. Six of the 32 sites did not use dishwashers. The number of people served by individual ST in this study varied from 1 to 7 people in a household and sampling occurred between February and June 2014.

Table S4.1: The 32 septic tank sites of this study, locations, tank information and number of people served by each tank.

Site No	Catchment	Type of tank	National grid reference	Tank age ^a	Users no _b	Last Emptied ^a
1	Lunan water	Polyethylene	NO4160	8	2	Yearly
2	Lunan water	Concrete	NO4159	Not known	3	Not known
3	Lunan water	Polyethylene	NO7974	3	3	New tank
4	Lunan water	Concrete	NO4655	60	2	Yearly
5	Lunan water	Concrete	NO4655	Not known	4	Not known
6	River Dee	Concrete	NJ5750	45	4	Not known
7	River Dee	Polyethylene	NJ3351	4	2 ^c	New tank
8	River Dee	Concrete	NJ2851	Not known	2	Not known
9	River Dee	Polyethylene	NJ1550	19	1	6 years ago
10	River Dee	Polyethylene	NJ7346	12	2	Every 2 years
11	River Dee	Concrete	NJ2757	12	4 ^c	Every 2 years
12	River Dee	Concrete	NJ4149	60	1	One year ago
13	River Dee	Concrete	NJ4650	50	2	One year ago
14	River Dee	Concrete	NJ5847	65	2	20 years ago
15	River Dee	Concrete	NJ1444	100	3	Every 2 years
16	River Dee	Concrete	NO9957	40	2 ^c	6 years ago
17	River Dee	Concrete	NJ3147	Not known	2	Yearly
18	River Dee	Polyethylene	NJ5146	1	2 ^c	New tank
19	River Dee	Concrete	NJ3648	78	2	Not known
20	River Don	Polyethylene	NJ1960	10	2	Every 2 years
21	River Don	Polyethylene	NJ3260	10	4	4 years ago
22	River Don	Polyethylene	NJ1888	15	2	8 years ago
23	River Don	Concrete	NJ1862	50	3	Every 3 years
24	River Don	Concrete	NJ1860	70	2 ^c	One year ago
25	River Don	Concrete	NJ1762	60	2	Not known
26	River Don	Concrete	NJ1765	Not known	2	Not known
27	River Don	Concrete	NJ3356	85	2 ^c	18 years ago
28	River Ythan	Concrete	NJ3993	23	2	Not known
29	River Ythan	Polyethylene	NJ3295	17	3	Every 2 years
30	River Ythan	Concrete	NJ5780	70	3	Never
31	River Ythan	Polyethylene	NJ2094	20	7	Never
32	River Ythan	Concrete	NJ2390	25	3	6 years ago

a Estimated by householders

b Taken from survey data by householders

c Household do not use dishwasher

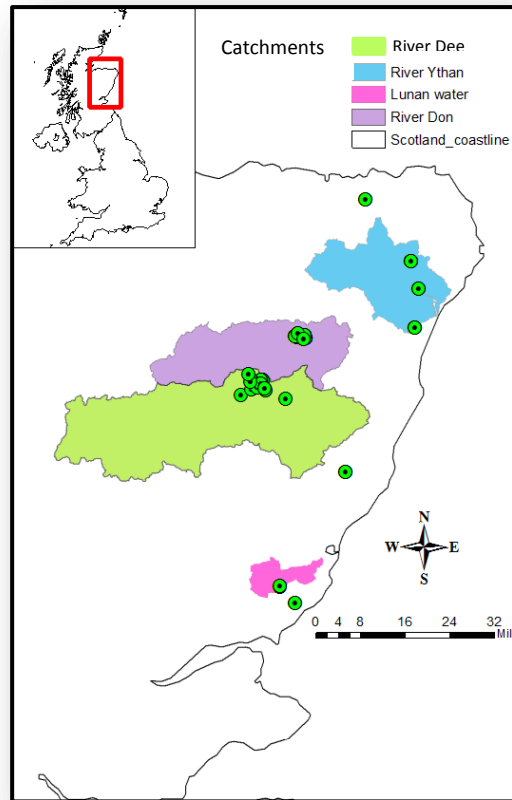


Figure S4.1: Septic tank sampling sites within the four major river catchments in North East Scotland (ArcMap 10).

4.2.2 Effluent sampling and analyses

Two separate effluent samples were collected from each site: 40 ml was sampled into a sterile vial for microbial, chemical oxygen demand (COD) and biochemical oxygen demand (BOD) characterisation; 1 L was sampled into a polyethylene bottle for physical and chemical characterisation. Where possible, upstream and downstream water samples of the study sites were also collected (n=10). Effluent and water samples were kept in a cold box during transportation to the laboratory then in a cold room at 4°C until processing. Microbial, BOD and COD analyses were performed within 12 h while processing for physical and chemical analyses were within 36 h. Total viable counts (TVC) of heterotrophic bacteria were performed using a spread plating technique. Serial dilution was made and diluted samples were spread aseptically on top of solidified nutrient agar, (Standard Methods for Examination of Water and Wastewater, 1999). Plates were incubated at 37°C for 24 h then bacterial colonies were counted and colony formed units (CFU) were calculated in 1 ml of effluent or water.

For total coliforms, faecal coliforms and *E. coli* detection, effluents were diluted appropriately using sterilised saline phosphate buffer (pH 7.3) and the diluted effluents were screened using IDEXX Colilert-18 kits and Quanti-Tray/2000 (IDEXX Laboratories, Westbrook, ME, USA). Samples were mixed with Colilert substrate then poured into Quanti-Tray, sealed and incubated for 18-22 h at 37°C for total coliforms and *E. coli* and at 44°C for faecal coliforms. The number of positive yellow wells was counted for coliforms enumeration and ultra violet (UV) blue fluorescence for *E. coli* and then converted into most probable number (MPN) according to manufacturer's instructions.

Five day BOD (BOD₅) was determined using Hach Lange cuvette tests with a nitrification inhibitor. Appropriate dilutions of STE were prepared using aerated buffer solution and added to BOD cuvette tests before incubating for 5 days at 20°C. BOD₅ was detected at 620 nm wavelength (DR2800 spectrophotometer, Hach, Colorado, USA). COD was performed using Hach Lange cuvette tests by oxidizing the effluent with sulphuric acid and potassium dichromate (Cr²⁺) solution for 2 h at 150°C including blanks. The detection of the green chromic ion (Cr³⁺) was quantified at 605 nm wavelength (DR2800 spectrophotometer, Hach, Colorado, USA).

Turbidity was determined using a turbidity meter (Hach 2100P, Turbidimeter, Camlab) and calibration standards measured in nephelometric turbidity units (NTU). Electric conductivity (EC) was determined using a Hanna HI-98312 conductivity tester. Alkalinity, NH₄-N and SRP were determined in triplicate

with appropriate blanks using automated colorimetry (Konelab Aqua 20, Thermo Scientific, Vantaa, Finland). Bromide, Cl, F, NO₃ and SO₄ were determined by ion chromatography (Dionex DX600, Dionex, California, USA). Total dissolved nitrogen (TDN) was determined using automated colorimetry (TOC-VCSH analyser, Shimadzu, Japan). Effluent pH was measured using Hanna pH 210 meter.

Total suspended solids (TSS), was determined gravimetrically on prewashed GF/F (0.7 µm) filters which were dried at 105°C for 18 h and reweighed. To investigate total particulate phosphorus (TPP) and nitrogen (TPN) retained on the filter papers, a persulphate digestion was used with subsequent colorimetric analyses (Methods for Chemical Analysis of Water and Wastes, U.S. EPA, 1983). Effluent and water samples were filtered through 0.45 µm cellulose membrane and the filtrates were scanned for carbon species between 200-700 nm wavelengths using Shimadzu UV Probe, UV-1800 Spectrophotometer, Shimadzu, Japan and UV Probe 2.33 software. The filtrates were also analysed for dissolved organic carbon (DOC) concentration using automated total organic carbon analyser (Shimadzu TOC-VCSH, Tokyo, Japan). Specific UV absorbance at 254 nm (SUVA₂₅₄) was normalised for DOC concentration and reported in l/mgC/m. Effluent and water filtrates were also analysed for OM fluorescence (Gilden Photonics Fluorimeter, fluoroSENS1.88.7, Glasgow, UK). Excitation emission matrices (EEMs) were obtained at wavelength intervals ranged Ex 200-450 nm at 2 nm increments Em 270-500 nm at 5 nm increment, band pass width was 5 nm and 0.1s integration time to cover both UV and visible fluorescence regions. Effluent spectra were Raman normalised against Millipore water (18.2 MOhm) at 397 nm. Dissolved OM peaks were picked and determined using a Gilden Photonics Contour Visualizer (V.1.0) to provide the relative intensity of fluorescence at various wavelengths for tryptophan-like fluorophores (amino acids) and fulvic and humic-like fluorophores peaks in fluorescence intensity units (FIU).

The filtrates' major elements (Al, Ca, Cu, Fe, K, Mg, Na, P as TDP, S, Si and Zn) were determined in triplicate by ICP-OES (Agilent 7500ce, Tokyo, Japan). Trace elements concentrations (As, B, Ba, Co, Cr, Li, Mn, Nb, Pb, Sn, Sr, Ti, W and Zr) were also analysed by ICP-MS (Agilent 7500i, Shield-Torch System).

4.2.3 Statistical analysis

Effluent and water data were subjected to descriptive statistical analysis using GenStat 17 and Minitab 17 and Anderson-Darling normality tests applied with log 10 transformations where necessary. One

way analysis of variance (ANOVA) was performed ($P < 0.05$) to examine the significance of ST management/categorised factors. Tanks were categorised as: Compromised $n=5$ (tanks with broken or no lids, do not maintain anaerobic condition, leaking and effluent is exposed to the environment) vs Intact tanks $n=27$ (no obvious sign of broken structure); Receive $n=6$ (tanks that receive roof runoff) vs Not receive $n=26$; Dishwasher $n=26$ (tanks that receive dishwasher waste) vs No dishwasher $n=6$; Concrete tanks $n=21$ vs Polyethylene tanks $n=11$; Desludging < 2 years $n=14$ (tanks reported desludging every 2 years or less) vs > 2 years $n=18$ (desludging frequency is more than 2 years or never been emptied); No of users ≤ 2 People $n=20$ (tank serves up to 2 person) vs More $n=12$ (tank serves more than 2 person). Multifactor analysis was not applied due to the unbalanced data in some categories. The enrichment factor of STE was calculated based on the mean STE concentration ($n=10$) divided by the mean of upstream water concentration ($n=10$) from the source. Box and whisker plots were used to illustrate the distribution of data and to evaluate the difference between the two levels of each grouping factor. Principal component analysis (PCA) based on the correlation matrix was performed on the data and a biplot of the loading in the first two PCs for STE indicators and metals were used to evaluate major and trace element fingerprints.

Tank residence time calculations were made to understand the impact of receiving roof runoff on ST processes. It was not possible to determine ST volumes accurately or to distinguish volumes between categories of older concrete and modern polyethylene tanks. Therefore, in the calculation of residence time (t_{res}) for a typical household of 2.7 persons ($t_{res} = \text{tank volume} / \text{flow in, out}$) the local building standards recommended 2720 l was applied. Flow was assumed by calculation of 150 l/day/person to be 405 l/day/household, giving $t_{res} = 6.7$ days without the tank receiving roof runoff. In the case of roof runoff the average annual regional rainfall of 1126 mm on a modelled roof of 100 m² gave an additional average daily flow of 308 l/day/household (Water Catchment Calculator) and a reduced $t_{res} = 3.8$ days. The worst case scenario for accelerated flushing from rain was based on a 24 h 1 in 5 years modelled regional rainstorm (FEH, 1999) prediction of 48 mm (4800 l/day on the 100 m² roof) giving $t_{res} = 0.5$ days.

4.3 Results

4.3.1 Effluent quality and enrichment factor

Means, concentration ranges and degree of skewness for the physicochemical, microbial parameters and metals of STE including stream waters are shown in Table 4.1 and Table 4.2. STE contained large concentrations of $\text{NH}_4\text{-N}$, SRP, DOC, TSS and very little $\text{NO}_3\text{-N}$ and Br (Table 4.1). The pH of STE was generally neutral with mean of 7.01 and range 6.37-7.68. STE were also high in EC, BOD, COD, turbidity and alkalinity with means 866 $\mu\text{S/cm}$, 234 mg/l, 655 mg/l, 198 NTU and 303 mg/l, respectively. The effluents contained large bacterial concentrations (mean total coliforms, faecal coliforms, *E. coli* and TVC (2.3×10^7 , 3.2×10^6 , 1.3×10^6 MPN/100 ml and 2.7×10^8 CFU/100 ml, respectively). Trace metals such as B, Ba, Cu, Fe, Mn, Sr, W and Zn were found to have concentrations that ranged from 45-366 $\mu\text{g/L}$ (Table 4.2).

The enrichment factors (EF) of STE relative to upstream water ($n=10$) are listed in Table 4.1 and 4.2. The highest EF were shown for $\text{NH}_4\text{-N}$ (1651), faecal coliforms (1340), *E. coli* (691), total coliforms (312), TVC (234), TDP (213), SRP (176) and TSS (103), whereas, TP, Turbidity, Cu, TPP, BOD and COD had only moderate to high EF (40-100). A moderate EF (10-39) suggests that TDN, TN, TPN, F and DOC were of lesser risk to stream waters. A low EF (2-10) was obtained for alkalinity, K, W, Ti, B, EC, Zn, Na, Al, Mn, Ba, Co, Cr, Cl, Fe, Nb, Pb and Zr. The loading scatter plot (Figure 4.1) represented STE variables in terms of indicators, major and trace metals. The indicators in Figure 4.1a, showed a strong positive correlation between TN, TDN, Cl, $\text{NH}_4\text{-N}$, SRP, TDP, TP, EC, DOC and alkalinity which collectively have no correlation with TSS, TPN and negative correlation with SUVA_{254} and $\text{NO}_3\text{-N}$. Total coliforms have positive correlation with pH, weak correlation with turbidity, TPP and negative correlation with SUVA, TSS and $\text{NO}_3\text{-N}$. Figure 4.1a, also showed that TP, EC, alkalinity, TDP, TDN, $\text{NH}_4\text{-N}$, TPP and TSS hold the highest values while Br, TVC, SO_4 , total coliforms and *E. coli* hold the lowest values. The major and trace metals biplot (Figure 4.1b) showed a strong positive correlation between K, P, Na, Ba, Cu, Al and Zn which are collectively have negative or no correlation with Fe, Mn and Ca. Phosphorus, Na and K hold the highest values followed by As, Ba, B, Cr, Li, Nb, Zr and Ti.

Table 4.1: STE parameter ranges, mean, standard of errors and skewness for all tanks (n=32), compared with the mean of upstream waters and calculated STE enrichment factors (EF) (n=10).

Parameter	Unit	STE	STE		Skewness ^e	Stream waters ^g		STE EF ^d
		Range	Mean	±1 s.e.		Mean	±1 s.e.	
pH		6.37-7.68	7.01		N	7.26		1
EC	µS/cm	160-1730	866	±69	N	259	±56	4
Turbidity	NTU	8-916	198	±34	Sk+	3.42	±0.69	76
TSS	mg/L	14-3895	384	±167	Sk++	6.10	±0.78	103
COD	mg/L	48-5514	655	±164	Sk++	15.18	±5.37	40
BOD	mg/L	16-565	234	±26	N	6.33	±3.06	41
Alkalinity	mg/L	15-698	303	±27	N	42	±11	9
DOC	mg/L	5-179	48	±7	Sk+	6.06	±1.34	11
SUVA ₂₅₄	L/mg/m	0.39-4.28	1.70	±0.13	Sk+	4.24	±0.96	0.4
TP	mg/L	1.13-32.49	14.55	±1.46	N	0.16	±0.05	98
TDP	mg/L	0.22-26.43	9.46	±1.18	N	0.05	±0.02	213
SRP	mg/L	0.15-25.68	8.37	±1.06	N	0.05	±0.03	176
TPP	mg/L	0.59-22.25	4.77	±0.69	Sk++	0.10	±0.05	53
TN	mg/L	11-146	68	±6	N	5.77	±1.02	13
TDN	mg/L	5-125	59	±6	N	4.61	±1.082	14
NH ₄ -N	mg/L	2-144	55	±6	N	0.04	±0.01	1651
NO ₃ -N	mg/L	0.01-3.85	0.44	±0.15	Sk+	4.40	±1.01	<0.1
TPN	mg/L	0.01-12.46	4.80	±0.57	N	0.26	±0.04	12
SO ₄	mg/L	0.53-20.78	6.21	±0.89	Sk+	8.07	±4.16	0.7
Br	mg/L	0.018-0.062	0.02	±0.00	N	0.07	±0.02	0.4
Cl	mg/L	18-94	51	±4	N	27	±5	2
F	mg/L	0.02-7.37	0.36	±0.23	Sk++	0.08	±0.01	12
Total coliforms	MPN/100 ml ^a	10 ³ -10 ⁸	2.3x10 ⁷		Sk++	2.3x10 ⁴		312
Faecal coliform	MPN/100 ml ^a	10 ³ -10 ⁷	3.2x10 ⁶		Sk++	9.8x10 ²		1340
<i>E.coli</i>	MPN/100 ml ^a	10 ³ -10 ⁷	1.3x10 ⁶		Sk++	1.7x10 ³		691
TVC	CFU/100 ml ^b	10 ⁷ -10 ⁸	2.7x10 ⁸		N	1.1x10 ⁶		234
Tryptophan	FIU ^c	6.6x10 ³ -1.8x10 ⁵	7.6x10 ⁴		—	1.7x10 ^{3f}		—

a Most probable number in 100 ml

b Colony formed unit in 100 mL

c Fluorescence intensity unit

d Enrichment Factor = $\sum([STE_{n=10}]/[upstream_{n=10}])/n$

e Skewness:(-1 to +1) is N, (1 to 3) is Sk+, (>3) is Sk++

f Only detectable in downstream waters

g n=10 as only possible where receiving watercourse present

Table 4.2: STE major and trace metals ranges, mean, standard of errors and skewness for all tanks (n=32), compared with the mean of upstream waters and calculated STE enrichment factors (EF) (n=10).

Parameter	Unit	STE	STE		Skewness _e	Stream waters ^g		STE
		Range	Mean	±1 s.e.		Mean	±1 s.e.	E F ^d
Al	mg/L	<0.01-0.20	0.06	±0.01	Sk+	0.02	±0.01	4
Ca	mg/L	6-67	21	±3	Sk+	24	±6	1
K	mg/L	3-42	24	±2	N	3.31	±1.71	8
Mg	mg/L	1.40-27.72	6.60	±0.86	Sk+	8.08	±2.12	1
Na	mg/L	17-113	53	±5	N	17	±3	4
P	mg/L	0.27-26.43	9.30	±1.16	N	0.05	±0.02	215
S	mg/L	2.42-35.63	9.13	±1.14	Sk+	10.90	±6.44	1
Si	mg/L	1.36-15.72	6.58	±0.57	N	7.27	±0.82	1
As	µg/L	0.50-5.00	1.20	±0.24	Sk+	0.50	±0.00	3
B	µg/L	19-244	111	±10	N	27	±3	5
Ba	µg/L	26-925	366	±38	N	165	±44	3
Co	µg/L	0.05-3.95	0.45	±0.13	Sk++	0.14	±0.07	3
Cr	µg/L	0.25-3.49	1.05	±0.15	Sk+	0.40	±0.07	3
Cu	µg/L	5-637	109	±29	Sk+	1.85	±0.53	63
Fe	µg/L	<1-1486	198	±49	Sk++	188	±159	2
Li	µg/L	1.00-10.00	2.21	±0.45	Sk+	2.95	±0.87	1
Mn	µg/L	10-312	74	±13	Sk+	31.36	±21	3
Nb	µg/L	2.50-25.00	5.38	±1.10	Sk+	2.50	±0.00	2
Pb	µg/L	0.50-6.67	1.68	±0.31	Sk+	0.57	±0.07	2
Sn	µg/L	2.50-25.00	5.05	±1.09	Sk+	2.50	±0.00	1
Sr	µg/L	27-236	89	±10	Sk+	119	±21	1
Ti	µg/L	2-65	11	±2	Sk+	2.50	±0.00	5
W	µg/L	5-346	45	±13	Sk++	5.46	±0.46	7
Zn	µg/L	18-287	150	±13	N	32	±6	4
Zr	µg/L	2.00-20.00	3.81	±0.80	Sk++	2.00	±0.00	2

d Enrichment Factor = $\sum([STE_{n=10}]/[upstream_{n=10}])/n$

e Skewness: (-1 to +1) is N, (1 to 3) is Sk+, (>3) is Sk++

g n=10 as only possible where receiving watercourse is present

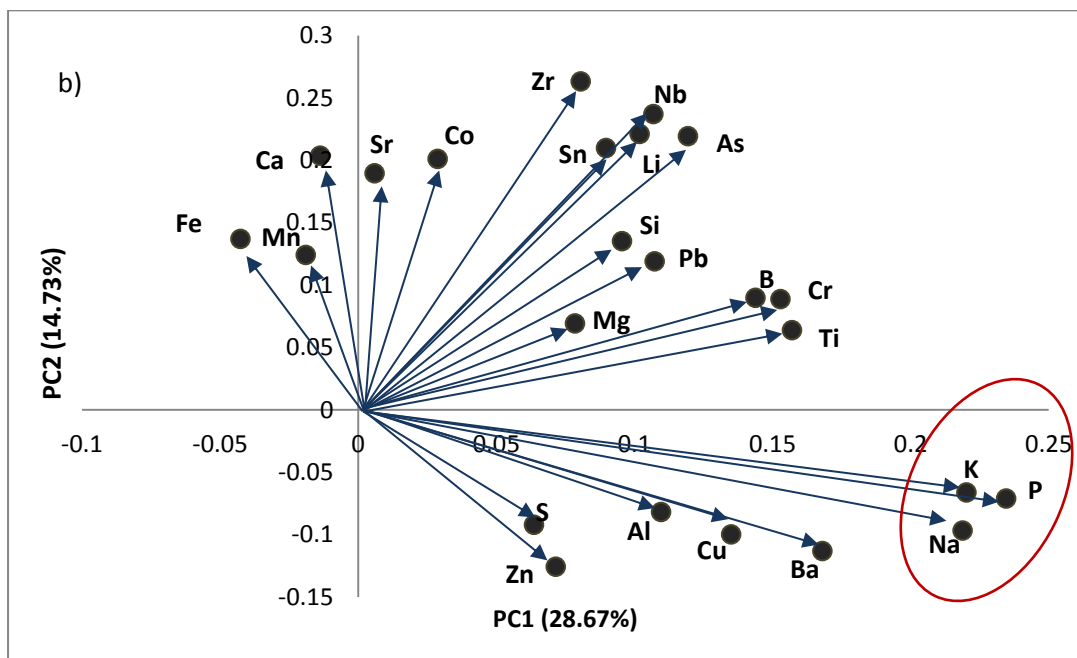
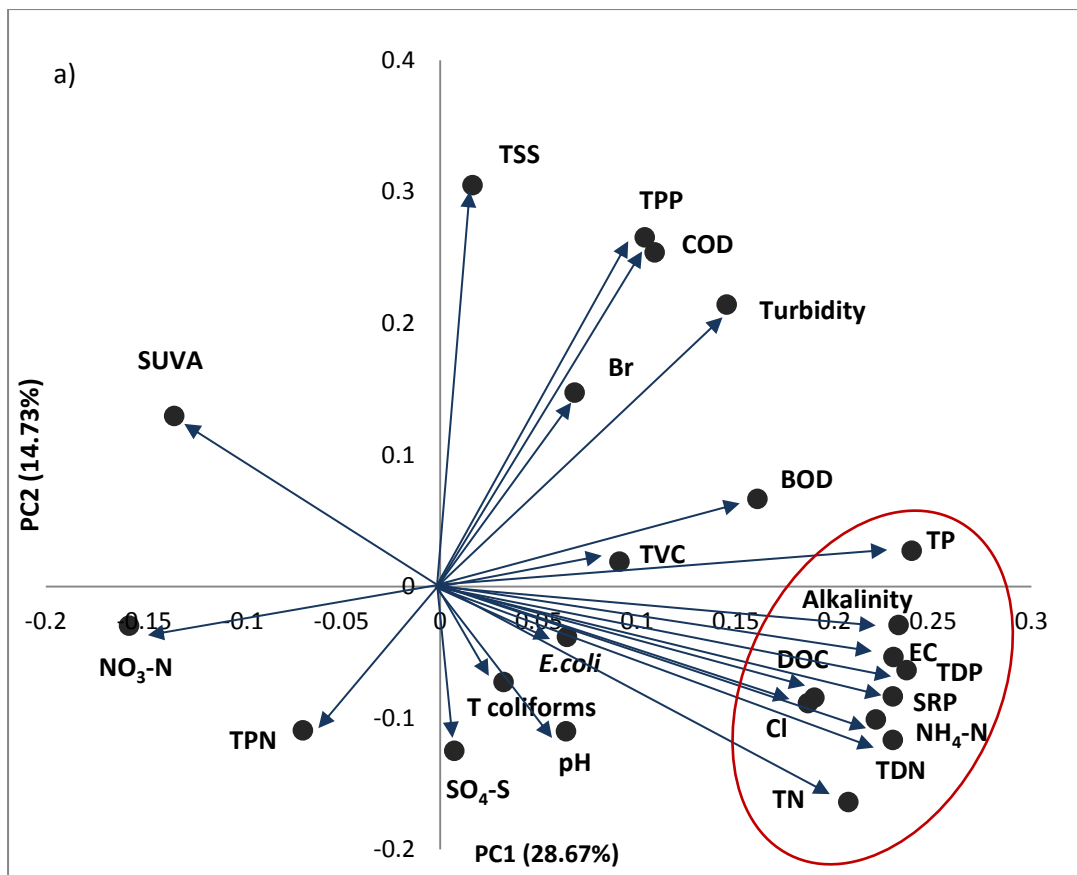


Figure 4.1: a) Loading plots of weights assigned to each of STE indicator variables and, b) specifically to STE major and trace metal variables. Points show loadings positions, length of lines and arrows represent the strength and the direction of loading of each parameter in relation to others.

4.3.2 Tank management factors

The significant effects of tank and system design and management on STE composition are given in Table 4.3. Figure 4.2, box plots shows some of the major differences in effluent composition between the two levels in each group factor. The results revealed that STE quality varied according to system design (ie. Receiving roof water) and management. Tanks that received roof runoff exhibited significantly ($P < 0.05$) reduced concentrations for a large number of parameters (Table 4.3). Effluent pH, alkalinity, EC, turbidity, COD, BOD and DOC, total coliforms and nutrients concentrations with the exception of NO_3 were all much higher in tanks that did not receive roof runoff (Figure 4.2). Systems that received dishwasher wastes, had effluent properties with significant difference ($P < 0.05$) in TVC, TN, TPN, TSS, COD and TPP concentrations (Table 4.3). Metal concentrations also exhibited significant differences ($P < 0.05$) in As, Sn, Li, Nb and Zr. Effluent from frequently desludged systems (<2years) exhibited a significant difference ($P < 0.05$) in pH and TPN concentrations with high pH, EC, coliforms and *E. coli* populations, while nutrient concentrations were much higher in effluents from tanks that were not frequently desludged.

In the *Tank Type category* (Concrete vs polyethylene), no significant difference was found between the two types of tanks ($P > 0.05$). However, STE from concrete tanks ($n=21$) exhibited high pH, alkalinity, TSS, EC and BOD. Nutrient concentrations (TP, TDP, TPP, TN and $\text{NH}_4\text{-N}$) and metal concentrations (Na, Ca, Fe, Ba and Sr) were also high in effluent from concrete tanks. *Number of Users category*, exhibited a significant difference ($P < 0.05$) in total coliforms and Si (Table 4.3). Total coliforms and *E. coli* concentrations were much higher in effluent that served > two people (Figure 4.2). The same trend was observed in pH, EC, alkalinity, DOC, Na and Ca concentrations. There were no significant differences in *compromised/intact category* ($P > 0.05$), although generally TVC, TN, $\text{NH}_4\text{-N}$ concentrations were higher in intact tanks. Anions in STE such as SO_4 and F showed no significant difference ($P > 0.05$) in all grouping factors and ranged between 0.53-20.78, 0.03-7.37 mg/l (Table 4.1).

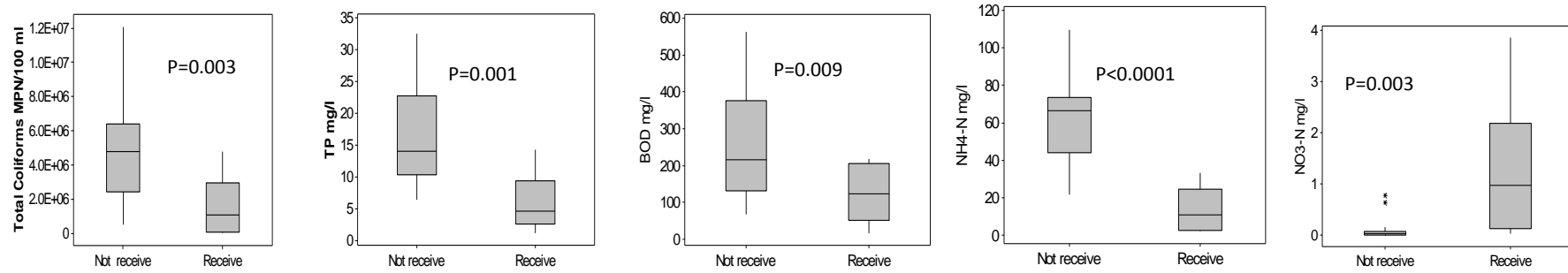
Table 4.3: Number of tanks in each factor and parameters ANOVA results of significant differences ($P \leq 0.05$). Parameters with no significant difference ($P > 0.05$) not included.

Factor A	Receive ^a (n=6)	Dishwasher (n=26)	Desludging <2 years (n=14)	No users ≤ 2 (n=20)
Vs Factor B	Do not receive (n=26)	No dishwasher (n=6)	Desludging >2 years (n=18)	No users > 2 (n=12)
Parameter	ANOVA results P-value			
PH	0.015		0.017	
EC	0.002			
Alkalinity	0.001			
TVC		0.028		
TP	0.001			
TN	<0.0001	0.026		
TDN	<0.0001			
TDP	0.001			
TPN		0.051	0.001	
SRP	0.001			
NH ₄ -N	<0.0001			
Cl	0.001			
SUVA	0.001			
K	<0.0001			
P	0.001			
Si				0.034
Fe	0.048			
As		0.009		
Ba	0.022			
Sn		0.001		
Turbidity*	0.008			
TSS*		0.007		
COD*	<0.0001	0.014		
BOD*	0.009			
T coliforms*	0.003			0.047
TPP*		0.015		
NO ₃ -N*	0.003			
DOC*	<0.0001			
Al*	0.02			
Na*	<0.0001			
S*	0.012			
Cu*	0.02			
Ba*	0.001			
Cr*	0.012			0.004
Li*		0.007		
Nb*		0.01		
Ti*	0.006			
Zr*		0.004		
PC1	<0.0001			
PC2	0.08	0.005	0.08	

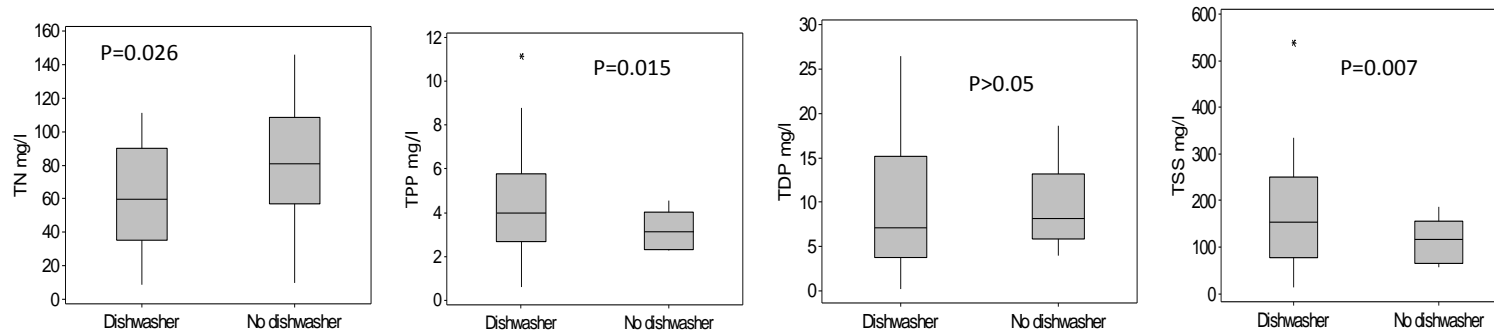
* Transformed data

a Receive roof runoff vs Do not receive roof runoff

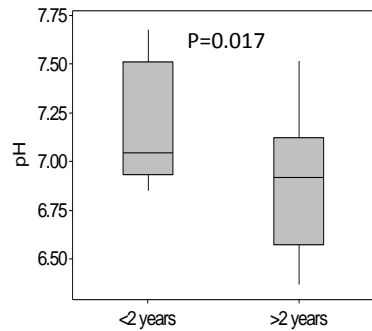
a) Receiving roof runoff (n=6) vs not receiving (n=26)



b) Dishwasher (n=26) vs no dishwasher (n=6)



c) Desludging <2 years (n=14) vs >2 years (n=18)



d) No of users <2 people (n=20) vs >2 people (n=12)

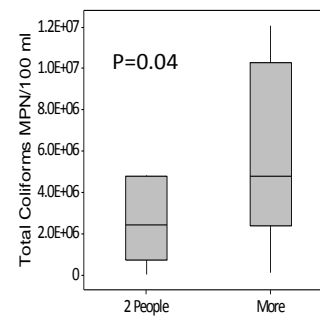


Figure 4.2: STE indicators grouped as a) Receiving roof runoff, b) Dishwasher, C) Desludging , d) No of users. P-values for variable are <0.05 except for dishwasher TDP, P>0.05.

4.3.3 Effluent fluorescence

Effluent OM characterisation by fluorescence excitation emission matrices (EEMs) produced a three dimensional contour map of STE and showed a tryptophan-like peak (T) in the UV region present in all STE at excitation range 260-290 nm and emission range 290-370 nm, (Figure 4.3). Anthropogenic input in the form of tryptophan-like fluorophores intensities ranged between 6.6×10^3 - 1.8×10^5 and the average was 7.6×10^4 fluorescence intensity unit (FIU). A tryptophan peak was also present in downstream but not detected in upstream waters (Table 4.1). A fulvic-like peak (C) was also detected in effluent from *compromised* tanks and those that *received roof runoff* categories at excitation emission ranges of 300-350 nm and 390-450 nm, respectively, (Figure 4.3) with average intensities of 4.29×10^4 FIU.

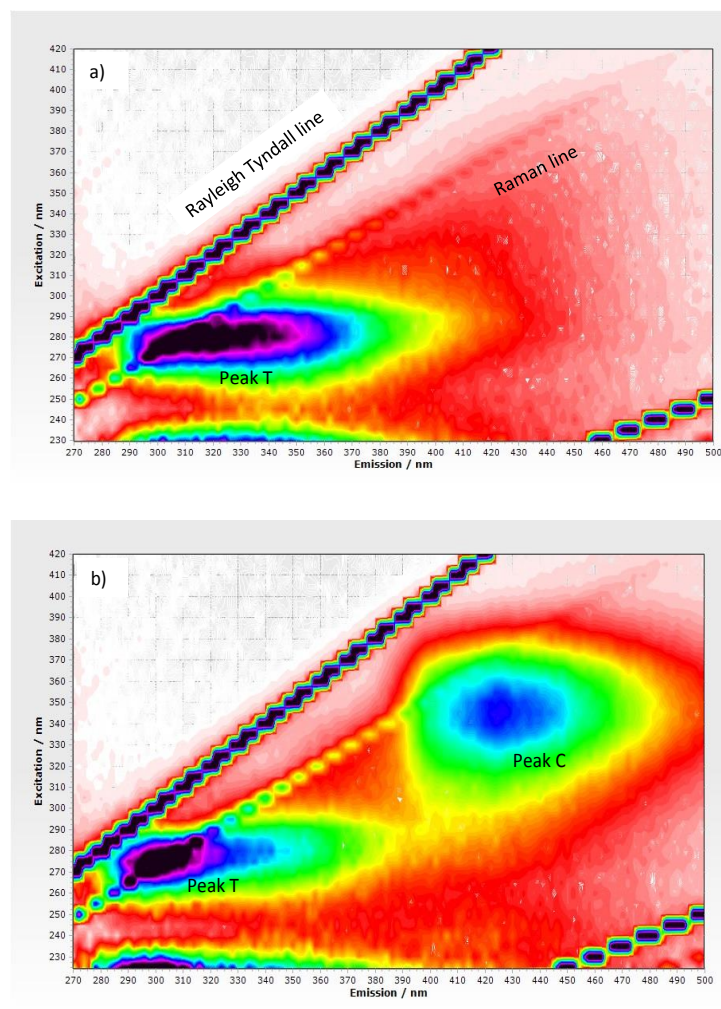


Figure 4.3: a) Fluorescence excitation emission matrices (EEMs) for septic tank effluent with the dominant protein like peak attributed to tryptophan-like fluorophore (Peak T). b) An extra peak attributed to the fulvic-like fluorophore (Peak C) in tanks that receive roof runoff or have broken lids.

4.4 Discussion

This study provides the first comprehensive analysis of STE in the UK, combining physical, chemical and microbial compositions of effluent from households across North East of Scotland. The 32 sites covered a range of different tank type, age, condition, size, number of users and tank management and were considered representative of the wider population of tanks in use. Septic tank effluent is rich in nutrients, metals and microbial populations which can pose great risk to stream waters. Although most onsite waste water treatment systems discharge their effluent to soil soakaways for contaminant removal, it should be noted that 25% of STS tested in this study discharged their effluent directly to surface waters or to soakaways which are too close to watercourses and therefore may pose a risk to water quality and human health (Dudley and May, 2007).

4.4.1 Effluent impacts and tank management

4.4.1.1 Nutrient composition

The analysis showed that most ST have high concentrations of inorganic N, P and C in their effluent (Table 4.1). The anaerobic condition that functional tanks should maintain allows the heterotrophic bacteria to convert organic N and P to $\text{NH}_4\text{-N}$ and SRP, while the TN and TP remain unchanged (Canter and Knox, 1985; Seabloom, 2005). The study showed that tank design and management play a critical role in effluent quality and may reduce effluent residential time in the tank with the risk of discharging unprocessed effluent to the environment. Although TN exhibited a similar range (11-146 mgN/l) to the values found by Lowe et al. (2009) and Gross (2005), the mean TN concentration across all sites of 68 mgN/l was lower than 107 mgN/l reported by O'Luanaigh et al. (2012). This may be associated with dilution from roof runoff or broken lids exposing effluent to the rainfall. Tank management effects on effluent quality was also apparent when considering only STE not receiving roof runoff which increased the mean TN concentration to 80 mgN/l. Ammonium range in the effluent was increased when considering tank management (not receiving roof runoff and with intact lids). An opposite trend was observed on nitrate concentrations which were three times greater in effluents that were exposed to the environment. Tank management (*Receiving roof runoff*) created an association between high concentrations of $\text{NO}_3\text{-N}$ /low $\text{NH}_4\text{-N}$ which can be explained by nitrification of $\text{NH}_4\text{-N}$ to $\text{NO}_3\text{-N}$ in the presence of oxygen. High $\text{NO}_3\text{-N}$ levels and the nitrification of $\text{NH}_4\text{-N}$ as the effluent is discharged from the tank are of environmental concern, due to the high mobility of nitrate and its role in eutrophication

of surface water, contamination of groundwater and public health concern for drinking waters (Ward et al., 2005).

This study revealed that STE may continue to pose a risk on stream water health, as most organic P and polyphosphate in STE are converted to soluble phosphate (TDP) by microorganisms. Effluent TDP levels in this current work constitute 65% of TP concentration; however, controlling P discharge from onsite waste water treatment system is crucial to combat eutrophication of the receiving stream since the effluent is dominated by soluble reactive forms of P. Moreover, STE are discharged persistently throughout the year and their risk to water quality can be greater during critical summer periods when ecology is most sensitive to elevated nutrient concentrations (Withers et al., 2011). Total P concentration of STE in this study (range 1.13-32.49 mgP/l, mean of 14.55 mgP/l), (Table 4.1) are greater than (10-20 mg/l) reported by Wilhelm et al. (1994); EPA, Ireland (2000); Gross (2005) and Idaho, Department of Environmental Quality (2012), but agree with the values reported by Lowe et al. (2009). Tank management (*receiving roof runoff*) influenced P concentrations as TP range and mean were greater (6.37-32.49 and 16.54 mgP/l) when we consider only tanks that do not receive roof runoff and with intact lids. It is well recognised that, with legislation on P contents of some household cleaning products, dishwasher detergents remain a key domestic source of phosphates, (Chapter 3, Richards et al., 2015), alongside human sewage. Notably, effluent from tanks that do not receive dishwasher wastes exhibited relatively low TDP concentration (ranged 4.01-11.40, mean 7.26 mgP/l) and significantly decreased TPP ($P < 0.05$), (Table 4.3).

Most literature reports BOD and COD rather than dissolved organic carbon (DOC) and associated $SUVA_{254}$ as a measure of C content of STE. In this work, DOC concentrations, (Table 4.1) can be compared with values reported by Lowe et al. (2009) and by Robertson et al. (1998; 1991). Although OM (colloids or particles) can settle within the sludge layer, considerable concentrations of DOC can be transported with effluent discharges. These dissolved and particulate organic C discharges, form part of effluent BOD load with resulting impacts on decreasing dissolved oxygen in receiving waters where effluent is discharged directly. Despite the fact that there are not many literature data on STE ($SUVA_{254}$) the value reported by this current work 1.7 l/mgC/m agrees with the mean value reported by Conn and Siegrist (2009) of 1.5 l/mgC/m.

The enrichment factors (EF) of BOD and COD are 41 and 40 times greater than stream waters, and most tanks tested in this study had high BOD and COD concentrations, which is an indication of the high proportion of OM content of the effluent. Human behaviour on effluent quality was evident in the high COD values from tanks that did receive dishwasher wastes ($P=0.014$), (Table 4.3). The implication of high BOD and COD and their associated OM of STE is of concern for water quality since if these parameters were not reduced in soakaway soil system, they may reach surface waters and may result in reduction of dissolved oxygen in watercourses.

4.4.1.2 Effluent physical composition

Physical properties such as turbidity, TSS, EC, alkalinity and pH are useful indicators for effluent characterisation and can indicate tank failure and effluent discharge to watercourses. Effluent turbidity is an indicator of the suspended matter and the relationship between turbidity and TSS is highlighted by the positive correlation; Person correlation coefficient of 0.627 ($P=0.001$). Surprisingly, there are not many STE turbidity values reported in the literature, however, Mandal (2014) and Igbinosa and Okoh (2009) reported wastewater turbidity levels of 43 and 159 NTU, respectively, being lower than the mean turbidity value of 198 NTU found in STE of this current work. The EF of STE turbidity is 76 times of stream waters and when discharged directly to watercourses, it can cause increase in stream turbidity affecting stream sunlight level and its associated stream habitats (Lloyds et al., 2011). Effluent pH influences its chemical and biological interactions as low or high pH reduces the ability of the microorganisms to break down OM. Excess of hydrogen ions can cause the denaturing of a key enzyme protein and excess of hydroxide ions exert toxic effect on microorganisms. In this current work, typical pH of 7.0 is comparable to Patterson (2003) and the optimum pH range for bacterial growth reported by Rowe and Abdel-Magid (1995) of 6.8-7.7 agrees well with this current data.

4.4.1.3 Effluent microbial concentrations

This work showed that STE have large microbial abundances, the mean abundance of both faecal coliforms and *E. coli* are one and two order of magnitude higher than that reported by Low et al. (2009), respectively. TVC of STE in this work of 10^8 CFU/100 ml agrees with that reported by Toor et al. (2011). The large microorganism populations in ST discharges such as faecal coliforms and *E. coli* are of concern as their EF are 1340 and 691, respectively, and their survival periods in groundwater are 20-30

and 90-110 days, respectively, (Crites and Tchobanoglous, 1998; Flint, 1987). The effect of human behaviour on STE was evident in the significantly increased total coliforms concentrations ($P=0.04$) as number of tank users increased to >2 people, (Figure 4.2). This can be an indication of unsuitable tank size for the household.

4.4.1.4 Metal concentrations

There are limited data available in the literature on trace metals in STE, however, in this current study the major and trace metal EF for P, Cu, K, W, Ti, B, Na, Al and Zn (Table 4.2) were 215, 63, 8, 7, 5, 5, 4, 4 and 4 times of stream waters, respectively. Effluent mean concentrations of Cu (0.11 mg/l) and Zn (0.15 mg/l) were double the values reported by Whelan and Titamnis (1982). Elevated levels of Cu are toxic in aquatic environments and in drinking waters. The presence of other elements in STE such as Br, Ca, Li, Mg, S, Si, Sn and Sr are of no concern as their mean concentrations were below or equal to that of upstream waters (Table 4.1 and 4.2). It is clear that STE is enriched in most major and heavy metals and if discharged untreated, it poses a threat to water quality and aquatic ecosystems due to their persistence and accumulation (Edem et al., 2008). A possible source of these metals is food products and household chemicals that were previously reported to contain high concentration in trace metals (Richards et al., 2015).

4.4.2 Effluent compositional indicators as potential tracers of impact

The use of tracers is a useful tool to determine pathway of pollutants in natural waters, the source and the impact. The fluorescence EEMs is a novel tool that was utilised to detect STE discharge. Excitation emission matrices of STE showed a distinct high intensity for the tryptophan-like (peak T), (Table 4.1 and Figure 4.3) which is a known marker in environmental samples for contamination with STE or sewage effluent (Hudson et al., 2007). The presence of a tryptophan-like peak in the receiving surface water downstream from the source that was also undetectable upstream is an indication of effluent discharge. Thus, fluorescence EEMs may be used as a potential tracer for effluent contamination to watercourses. This work also highlighted the presence of humic substances (peak C) in some STE (Figure 4.3b) associated with tanks that receive roof and/or field runoff. Therefore, EEMs may also be used to detect tank failure or poor tank management.

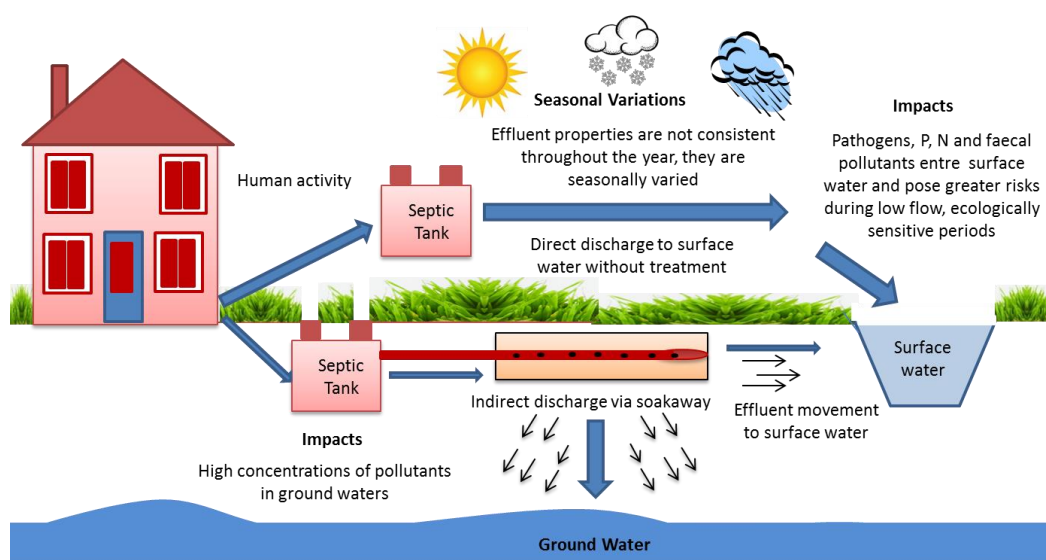
4.5 Conclusion

The composition of residential STE was characterized to provide full and integrative data to provide the knowledge of their impact with respect to ST type, management and user behaviours. The characterisation of domestic effluent revealed that not only are STE rich in nutrients, organic matter and metals, but also high proportions of these parameters are present in the soluble reactive forms and pose great risk to stream waters. Factors such as tank condition, management in terms of frequent desludging and maintenance, use of dishwasher and number of tank users, significantly influenced the quality of STE, in turn affecting risk to stream eutrophication and water quality especially during periods of ecological sensitivity. Receiving roof runoff was linked to reduction in effluent retention time in the tank. Infrequent desludging was linked to increased organic matter, bacterial abundance, alkalinity and phosphorus. Dishwasher use caused increased suspended solids and particulate phosphorus, while tanks that served larger number of users had effluent with high dissolved phosphorus, nitrogen and microbial abundance. The presence of tryptophan-like fluorescence peaks in receiving water downstream from STs indicated effluent discharge and potential for future source loading tracing approaches. There is a need for better tank management through possible legislation (possibly to remove direct connections to streams) and/or to consider an additional treatment for STE before discharge to surface waters or reaching groundwaters. This would be beneficial in protecting and improving stream water quality and guarding against human health impacts.

Chapter 5

Temporal variability in domestic point source discharges and their associated impact on receiving waters

Graphical Abstract



Temporal variability in domestic point source discharges and their associated impact on receiving waters

This work was published in *Science of the Total Environment*, 2016.

Richards, S., Withers, P.J.A., Paterson, E., McRoberts, C.W., Stutter, M., 2016. Temporal variability in domestic point source discharges and their associated impact on receiving waters. *Science of the Total Environment* 571, 1275-1283.

Author Contributions:

SR designed and performed the experiment and field work. McR performed instrument analysis for caffeine and artificial sweeteners. SR also analysed the data, wrote the paper and all co-authors reviewed and commented.

Abstract

Discharges from the widely distributed small point sources of pollutants such as septic tanks contribute to microbial and nutrient loading of streams and can pose risks to human health and stream ecology, especially during periods of ecological sensitivity. Here we present the first comprehensive data on the compositional variability of septic tank effluents (STE) as a potential source of water pollution during different seasons and the associated links to their influence on stream waters. To determine STE parameters and nutrient variations, the biological and physicochemical properties of effluents sampled quarterly from 12 septic tank systems were investigated with concurrent analyses of upstream and downstream receiving waters. The study revealed that during the warmer dryer months of spring and summer, effluents were similar in composition, as were the colder wetter months of autumn and winter. However, spring/summer effluents differed significantly ($P < 0.05$) from autumn/winter for concentrations of biological oxygen demand (BOD), arsenic, barium (Ba), cobalt, chromium, manganese, strontium (Sr), titanium, tungsten (W) and zinc (Zn). With the exception of BOD, Ba and Sr which were greater in summer and spring, the concentrations of these parameters were greater in winter. Receiving stream waters also showed significant seasonal variation ($P \leq 0.05$) in alkalinity, BOD, dissolved organic carbon, sulphate, sulphur, lithium, W, Zn and *E. coli* abundance. There was a clear significant influence of STE on downstream waters relative to upstream from the source ($P < 0.05$) for total suspended solids, total particulate P and N, ammonium-N, coliforms and *E. coli*. The findings of this study found seasonal variation in STE and place effluent discharges as a factor affecting adjacent stream quality and call for appropriate measures to reduce or redirect STE discharges away from watercourses.

Keywords: Water quality, Septic tank effluent discharge, Phosphorus, Microbial populations, Eutrophication

5.1 Introduction

Septic tank systems (STS) are widely used all over the world in rural areas for onsite wastewater treatment, where there is no connection to a main sewage network. Details on STS design, function, management and effluent retention time were studied in Chapter 4 and in Richards et al. (2016a). Septic tanks are considered to be cost effective; require low energy and minimal maintenance. However, septic tank effluent (STE) discharges to watercourses are considered as one potential source of water pollution. Their discharges are persistent and unregulated, and they can impact on adjacent water quality during ecological sensitive periods of low flow and high temperature (Withers et al., 2011 and 2012). Many studies have linked nutrient and pathogen contamination of surface waters to sewage treatment works discharge including ST discharges (Jordan et al., 2007; Edwards and Withers, 2008; Bowes et al., 2010; Macintosh et al., 2011; Withers et al., 2014) leading to concerns over eutrophication and human health (Smith and Schindler, 2009). Dodds et al. (2002) reported that a change from oligotrophic to eutrophic status in streams can lead to highly undesirable changes in ecosystem structure and function. Small point sources such as STS play their role in stream nutrient enrichment through the persistent direct discharge of effluents (Macintosh et al., 2011; Withers et al., 2014), or more diffusely through soakaway discharges (Dudley and May, 2007). Septic tanks are not always designed and sited correctly and often fail (US EPA, 2002; Day, 2004). Failure of STS due to physical damage and poor maintenance increases the risk of contaminants entering stream waters, with several studies linking disease outbreaks with ST density and discharges (Borchardt et al., 2003; Katz et al., 2010 and 2011; Lusk et al., 2011). The potential enrichment factor of STE contaminant concentrations relative to those in stream waters is large for some contaminants, notably, ammonia (NH_4), dissolved phosphorus (DP), *Escherichia coli* (*E. coli*), total and faecal coliforms (Richards et al., 2016a).

The high abundance of microorganisms and high concentrations of metals and nutrients (P, N and C) normally present in STE are expected to be attenuated by filtration, absorption and adsorption to soil soakaway systems, thereby minimising any environmental risk. However, Day (2004) stated that many ST in USA were sited on unsuitable soils for effluent treatment. Moreover, Canter and Knox (1985) suggested that soakaway soil efficiency is influenced by seasonal variations; with greater efficiency observed during summer and autumn when the unsaturated depth of soil was greater (low water table) and soil efficiency decreased during winter when water tables were high. Therefore, the concentration of contaminants in STE and how efficiently they are attenuated in soil systems may also vary throughout the year. This can arise due to environmental factors such as rainfall and temperature

effects, or due to household factors; for example, use of water and detergents in a household may change from season to season. As a consequence, effluent retention time (minimum requirement of at least 24 h) in the tank may vary or shorten and untreated effluent may be released to the soil and stream systems. Furthermore, the ability of many soil systems to remove pollutants becomes increasingly exhausted over time (Jordan et al., 2005) causing these contaminants to move further away from the soakaway and may reach ground and surface waters (Robertson et al., 1998 and 2008; Katz et al., 2011).

US EPA (2002) reported the volume of wastewater introduced to a STS ranged from 150-180 litres/person/day that are treated by soil systems. On the other hand, soakaway soils exhibited seasonal variation in the efficiency of removal of ST pollutants (Canter and Knox, 1985). This raises the question whether STE composition is varied or consistent throughout the year and in what parameters the variations are? Very limited data are available on changes in STE composition over time, or during different seasons and the effect of these changes on stream water quality. A better understanding of the seasonal composition of point source discharges from ST is required to influence policies and actions to control stream nutrient enrichment and to achieve good ecological status in fresh watercourses as required by the European Water Framework Directive (OJEC, 2000). This study investigated STE from 12 residential households and their associated stream waters (where possible), with the aims to: 1) examine seasonal variation in effluent concentrations for a range of potential contaminants, including novel chemical markers for use as tracers, 2) evaluate the corresponding seasonal variation of stream waters, and effluent influence on downstream relative to upstream samples for a subset of 6 sites with either, direct pipe effluent discharge to streams or within close proximity to surface waters.

5.2 Materials and Methods

5.2.1 Study sites

Twelve conventional residential STS serving permanently occupied houses in the North East of Scotland were selected for effluent monitoring. Septic tank sites covered three rural catchments (supplementary material Figure S5.1): River Dee (n=5), River Don (n=4) and Ythan River (n =3). Selection of sites was based on accessibility and sampling permission following a wider survey approach (Appendix 1) to gain data on ST management. Six of the twelve ST sites were located within 10 m from watercourses, of which three tanks discharged their effluent directly to watercourses without soakaway soil treatment, and three tanks discharged their effluent to soakaways and eventually to streams (Figure S5.2). Of the remaining six tanks, one tank discharged its effluent to a ditch and five tanks discharged their effluents to a soakaway or soil bed and eventually to fields. The sub-catchments of ST sites that were associated with watercourses and the number of ST users are described in the supplementary material (Table S5.1). Sampling of effluent and stream waters took place in spring, summer, autumn and winter between 2014 and 2015. Spring and summer are characterised as being relatively warmer and dryer periods (mean long-term temperature 6.7 and 13.4°C, respectively and mean long-term rainfall 200 and 233 mm, respectively). Autumn and winter are characterised as being colder and wetter months (mean long-term temperature 8.3 and 2.5°C, respectively and mean long-term rainfall 292 and 262 mm, respectively). The long-term monthly rainfall, temperature and daily stream discharge data within the three river catchments of the study and the sampling times are illustrated in Figure 5.2. Seasonal average atmospheric temperature data was collected from Glensaugh weather station, (NO66473) altitude 120-450 m above sea level while the sum of monthly, seasonal rainfall and stream discharge was collected from 5 locations within the studied catchments (Ythan: NJ9468430370, Don: NJ88771419, Don: NJ5681817072, Don: NJ3298510480 and Dee: NO7973998317). The distances of sampling up and downstream from the tanks were constrained by the presence of a safe access to the watercourses and the presence of a secondary nearby source or neighbouring tank. These constraints limited up and downstream distances to <50 m each side from the tank, and was considered to be sufficient distance for effluent mixing with stream waters.

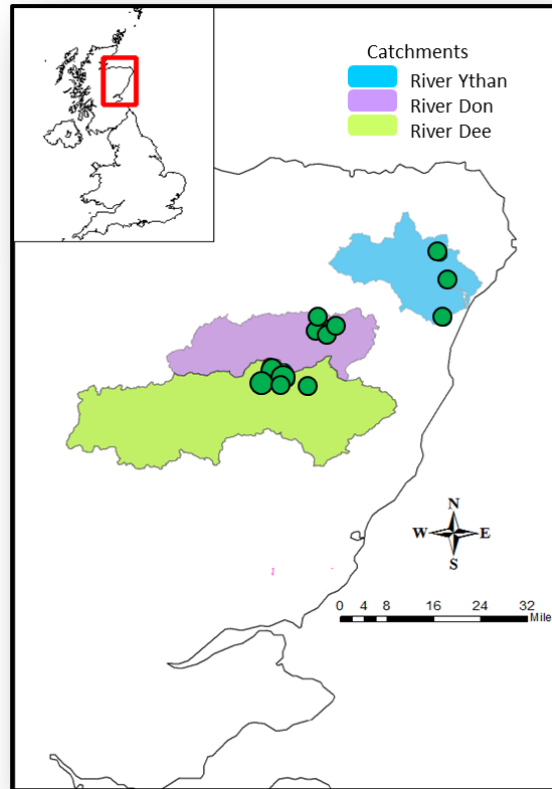


Figure S5.1: Septic tank sampling sites within three river catchments in North East Scotland (ArcMap 10).

Table S5.1: Septic tank sites associated with watercourses including their sub-catchment details.

Site No	No of users	Catchment	Sub-catchment size (km ²)	Forestry %	Moorland %	Arable / grassland %	Sub-catchment septic tanks no
1	2	River Dee	0.46	30	25	45	3
3	2	River Dee	5.16	25	10	65	15
6	2	River Don	0.53	15	N/A	85	3
7	3	River Don	611	25	25	50	—
8	2	River Don	0.30	40	20	40	1
12	5	River Ythan	3.89	10	10	80	20

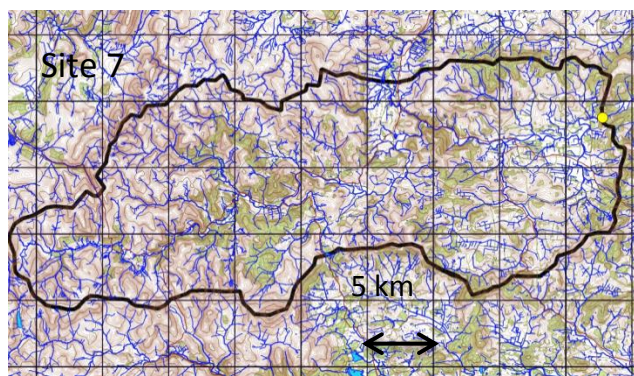
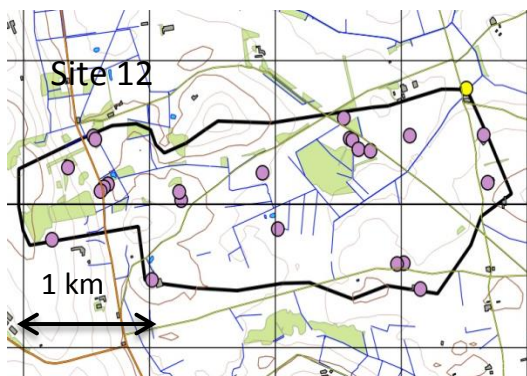
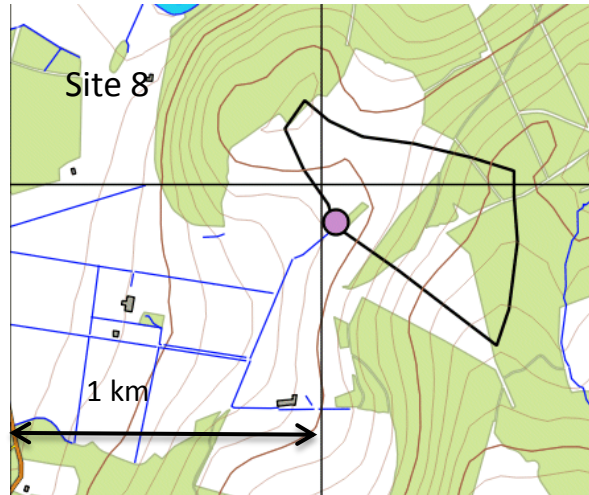
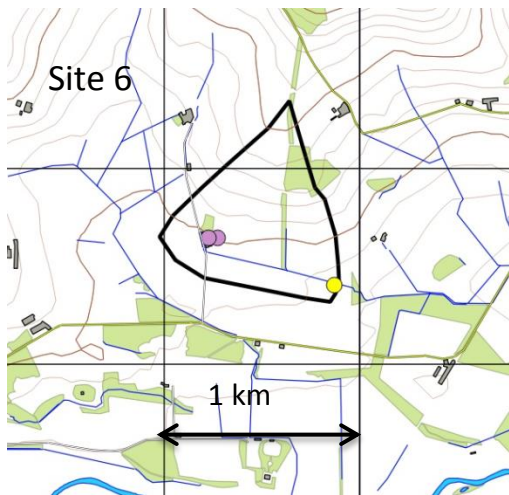
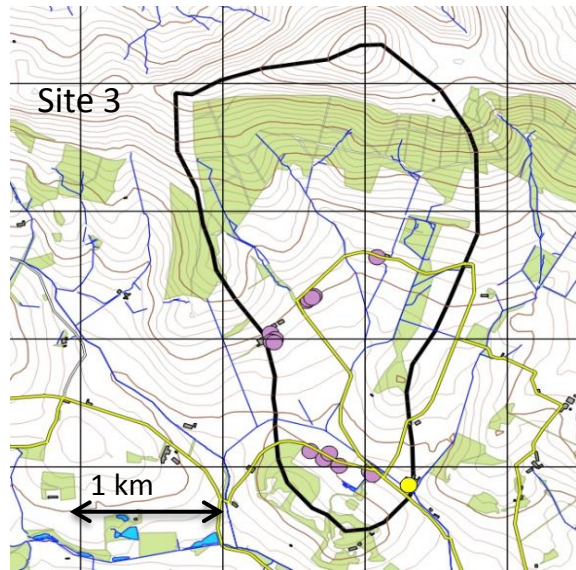
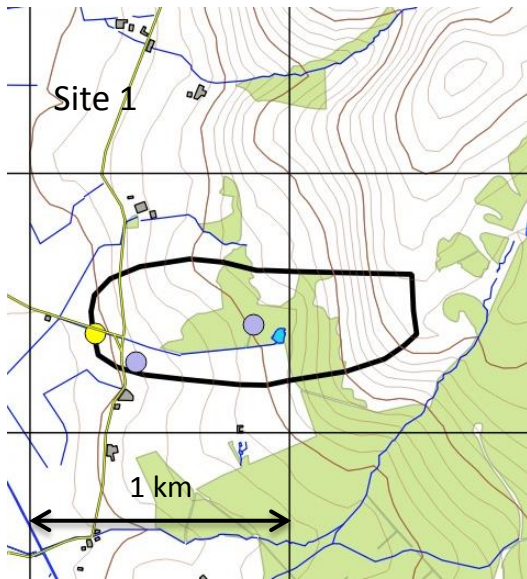


Figure S5.2: The sub-catchments of septic tank sites associated with watercourses in the study.

5.2.2 Effluent sampling

Effluent and stream water samples were collected (40 ml and 1L) into sterile bottles for microbial and physicochemical characterisation, respectively. Additional effluent samples (500 ml) were collected into pre-baked (450°C; 16 h) Duran bottles for caffeine and artificial sweeteners analysis. All samples were kept in a cold box during transportation to the laboratory and then in a cold room at 4°C until processing. Microbial characterisation for both effluent and water samples was performed within 12 h while physicochemical characterisation was performed within 36 h of sample collection.

5.2.3 Effluent and stream waters analyses

A suite of physicochemical analyses was conducted on both STE (n=12) and stream waters (upstream: n= 6 and downstream: n=6). Unfiltered samples were analysed for pH (Hanna pH 210 meter), turbidity (Hach 2100P, Turbidimeter) and electric conductivity (EC; Hanna HI-98312). Filtered samples (0.45 µm) were analysed for alkalinity, ammonium-N (NH₄-N) and soluble reactive P (SRP) by colorimetry using an automated discrete analyser (Konelab Aqua 20, Thermo Scientific, Finland). Chloride (Cl), fluoride (F), nitrate (NO₃) and sulphate (SO₄) were determined by ion chromatography (Dionex DX600, Dionex, California). Total nitrogen and dissolved organic matter were determined by chemical oxidation (Shimadzu, TOC-VCSH analyser, Shimadzu, Japan). The filtrates were also analysed for major and trace element determination by ICP-OES (Agilent 7500ce, Tokyo, Japan) and ICP-MS mass spectrometry (Agilent 7500i, Shield-Torch System), respectively. Ultra violet (UV) absorbance was measured using a Shimadzu UV Probe UV-1800 Spectrophotometer, UV Probe 2.33 software and specific UV absorbance at 254nm (SUVA₂₅₄) was calculated.

For total suspended solids (TSS), a known volume of each sample was filtered using previously washed, dried and weighed GF/F filter papers. The GF/F filters with residue suspended solids were dried at 105°C and TSS was determined gravimetrically. Total particulate P (TPP) and N (TPN) retained on the GF/F filter papers were determined by persulphate digestion followed by colorimetric analyses (U.S. EPA, 1983) using automated colorimetry (San++ analyser, Skalar, Breda, Netherlands).

Five day biochemical oxygen demand (BOD₅) and chemical oxygen demand (COD) were determined on non-filtered STE and stream water using Hach Lange cuvette tests. BOD₅ cuvette tests were incubated for 5 days at 20°C and quantified with colour detection at 620 nm wavelength (Hach Lange, DR2800

spectrophotometer). For COD detection, the samples were oxidized with sulphuric acid and potassium dichromate solution for 2 h at 150°C, and then quantified at 605 nm wavelength (Hach Lange, DR2800 spectrophotometer).

Microbiological analysis such as total viable counts (TVC) was performed on unfiltered samples using a spread plating technique, with serial dilutions made onto nutrient agar plates (Standard Methods for Examination of Water and Wastewater, 1999). Plates were incubated at 37°C for 24 h then bacterial colonies were detected as colony forming units (CFU) in 100 ml. For total coliforms (T coliforms) and *E. coli* detection, samples were diluted appropriately and screened using IDEXX Colilert-18 kit and Quanti-Tray/2000 (IDEXX Laboratories, Westbrook, ME, USA). Samples were incubated for 18-22 h at 37°C and the number of positive yellow wells was counted for coliforms enumeration and ultra violet blue fluorescence for *E. coli* and reported as most probable numbers (MPN) according to applied dilutions.

STE caffeine and artificial sweeteners concentrations were analysed by liquid chromatography-tandem mass spectrometry (LC-MSMS) using a Phenomenex Luna 5 C18 column in Agri-Food Biochemical Institute (Northern Ireland). The presence of the artificial sweeteners: saccharin, sodium cyclamate, sucralose and Acesulfame K were detected in the negative mode and caffeine in the positive mode (Agilent 1100 series LC system, Agilent Technologies, Waldbronn, Germany).

5.2.4 Statistical analysis

Data were subjected to descriptive statistical analysis after Anderson-Darling normality tests were conducted with data log 10 transformed as required. One-way analysis of variance (ANOVA) was performed using GenStat (17 Edition) to examine STE variation between various seasons. Pairwise comparisons (Tukey Tests) were used to evaluate which seasons were significantly different from one another for STE and stream waters. Two-way analysis was conducted to examine the interaction between effluent seasonality and site specifications such as number of tank users (2 people and >2), tank type (concrete and polyethylene) and tank age (≤ 20 years and >20 years). Also, performing two-way analysis on stream water data to test the interaction between the two factors: seasonality and up/downstream. Multivariate principal component analysis (PCA) was performed and a biplot for the scores and loading in the first two PCs were used to evaluate effluent and stream water quality indicators during different seasons. To identify and measure the association among STE variables factored as season, canonical variates analysis (CVA): equivalent to a one-way multivariate analysis of

variance (MANOVA) was performed and canonical factor loading plots of CV1 and CV2 for samples population were generated with 95% confidence for all data. The strong positive and strong negative CV1 and CV2 were tabulated to evaluate vectors whose values are directly related to variate weights.

5.3 Results

The results of this study revealed that STE contained elevated concentrations of $\text{NH}_4\text{-N}$, TP, SRP, DOC and TSS relative to stream waters, while effluent pH was predominantly near neutral (pH 6.4-7.8). Parameters such as EC, BOD, COD, alkalinity, turbidity and microbial indicators were also elevated (Table 5.1). Concentrations for potential components that may serve as future STE tracers such as caffeine and artificial sweeteners were found to have concentrations that ranged from <2-391 $\mu\text{g/l}$, while concentrations of trace metals such as boron (B), barium (Ba), copper (Cu), manganese (Mn), strontium (Sr), tungsten (W) and zinc (Zn) ranged from 2-875 $\mu\text{g/l}$. A septic tank effluent PCA 1 and 2 loading scatter plot which explained 47.25% of total variance (Figure S5.3a) was used to evaluate the relation among effluent indicators variables where parameters with arrows in the same direction and are close together, correlate with each other. The plot showed a strong positive correlation between TN, $\text{NH}_4\text{-N}$, saccharin, SRP, Cl, caffeine, alkalinity, TDP, TP, DOC and COD and collectively a negative correlation with NO_3 and TPN. A loading plot of major and trace elements of STE indicated that sodium (Na), potassium (K), P, B, Cu and magnesium (Mg) were positively correlated with each other, and arsenic (As), zirconium (Zr), lithium (Li) and lead (Pb) were also correlated with each other. Sodium, K and P had the highest weighting values, while Zn, Ca and Cu had the lowest weighting values (Figure S5.3b). Site specification factors such as number of tank users and tank type had significantly ($P < 0.05$) influenced effluent quality in SRP, Na, NH_4 and TDN, while tank age had significantly ($P < 0.05$) influenced effluent quality in alkalinity, TP, Fe, K, Na and TN.

Table 5.1: Concentration ranges for septic tank effluent (STE) parameters throughout the year. It also lists seasonal means of rainfall, temperature and flow rate. ANOVA significant difference (P-value) is listed where seasons are the grouping factor. Tukey test results (capital superscript) where seasons that do not share a letter are significantly different.

Parameter	Unit	STE Range	Spring ± 1SE	Summer ± 1SE	Autumn ± 1SE	Winter ± 1SE	P-value
pH		6.42-7.84	6.96	6.84	6.90	6.82	
EC	µS/cm	300-2560	994 ±113	989 ±167	885 ±123	767 ±127	
Turbidity	NTU	23-386	168 ±27	127 ±24	153 ±30	86 ±18	
Alkalinity	mg/l	101-1027	362 ±45	356 ±68	332 ±52	264 ±52	
TSS	mg/l	18-3895	436 ±268	127 ±19	147 ±24	122 ±41	
BOD	mg/l	57-395	231 ^A ±29	234 ^A ±26	144 ^B ±19	124 ^B ±15	0.002
TP	mg/l	4.47-39.43	15.72 ±2.09	15.00 ±2.79	12.94 ±1.88	10.29 ±1.97	
SRP	mg/l	1.59-30.33	9.36 ±1.55	9.39 ±2.04	8.39 ±1.43	6.29 ±1.40	
TDP	mg/l	2.40-34.26	11.12 ±1.79	11.02 ±2.38	8.76 ±1.45	7.99 ±1.71	
TPP	mg/l	<0.01-9.10	4.38 ±0.68	3.98 ±0.63	4.18 ±0.59	2.30 ±0.42	0.07
NH ₄ -N	mg/l	22-197	66 ±10	65 ±14	63 ±10	49 ±12	
NO ₃ -N	mg/l	0.01-0.26	0.09 ±0.05	0.07 ±0.01	0.08 ±0.03	0.16 ±0.05	
DOC	mg/l	10-179	62 ±12	39 ±9	43 ±7	34 ±6	
SUVA ₂₅₄	l/mg/m	0.39-10.67	1.50 ±0.26	2.69 ±0.68	1.83 ±0.29	1.93 ±0.27	
Cl	mg/l	16-147	57 ±6	51 ±8	56 ±10	47 ±5	
Saccharin	µg/l	<2-115	37 ±8.5	28 ±7.1	38 ±8.9	31 ±8.1	
Sucralose	µg/l	<2-164	20 ±7.4	14 ±5.8	28 ±7.9	18 ±13.3	
Acesulfame K	µg/l	<2-192	51 ±16.6	38 ±12.3	24 ±5.9	29 ±10.8	
Caffeine	µg/l	<5-391	110 ±34.6	61 ±18.0	87 ±33.7	56 ±21.1	
T Coliforms	MPN/100 ml ^a	4.9x10 ⁵ -2.4x10 ⁷	5.2x10 ⁶	5.7x10 ⁶	9.1x10 ⁶	4.3x10 ⁶	
<i>E. coli</i>	MPN/100 ml ^a	2.0x10 ³ -1.4x10 ⁷	3.6x10 ⁵	7.3x10 ⁵	1.0x10 ⁶	1.3x10 ⁶	
TVC	CFU/100 ml ^b	1.6x10 ⁷ -6.0x10 ⁸	2.4x10 ⁸	2.4x10 ⁸	2.5x10 ⁸	3.1x10 ⁸	
Ca	mg/l	4-67	21 ±4	17 ±3	16 ±2	16 ±2	
K	mg/l	7-61	28 ±4	26 ±5	23 ±3	20 ±4	
Na	mg/l	18-157	63 ±7	61 ±11	63 ±9	46 ±7	

As	µg/l	0.50-5.00	1.05 ^B ±0.32	0.74 ^B ±0.14	5.00 ^A ±0.00	5.19 ^A ±0.19	<0.001
B	µg/l	35-318	119 ±18	126 ±19	112 ±14	96 ±23	
Ba	µg/l	71-875	390 ^A ±57	308 ^A ±34	155 ^B ±24	188 ^B ±22	<0.001
Co	µg/l	0.05-11.45	0.39 ^{BC} ±0.14	0.24 ^C ±0.07	0.54 ^{AB} ±0.04	1.51 ^A ±0.91	<0.001
Cr	µg/l	0.25-10.38	1.23 ^B ±0.26	0.90 ^B ±0.25	2.50 ^A ±0.00	3.27 ^A ±0.66	<0.001
Cu	µg/l	2-478	88 ±35	69 ±27	45 ±22	101 ±49	
Mn	µg/l	2-329	80 ^A ±20	78 ^A ±17	31 ^B ±12	101 ^A ±30	0.003
Sr	µg/l	10-236	90 ^A ±15	76 ^A ±11	32 ^B ±5	74 ^A ±11	<0.001
Ti	µg/l	3-30	10 ^B ±2	7 ^B ±2	25 ^A ±0.00	25 ^A ±0.00	<0.001
W	µg/l	5-189	45 ^{BC} ±15	14 ^C ±4	97 ^A ±27	46 ^{AB} ±4	<0.001
Zn	µg/l	14-353	116 ^{AB} ±15	134 ^{AB} ±15	82 ^B ±15	156 ^A ±22	0.029
Atm. Temp. ^c	°C		7.7	14.4	9.7	2.7	
Rainfall ^d	mm		154	335	327	168	
Discharge ^e	m ³ /s		20.79	17.44	23.11	16.64	

a Most probable number in 100 ml.

b Colony formed unit in 100 ml.

c Seasonal average of daily atmospheric temperature (Glensaugh weather station, NO66473; altitude 120-450m above sea level).

d Sum seasonal rainfall across 5 locations (NJ9468430370, NJ88771419, NJ5681817072, NJ3298510480 and NO7973998317).

e Mean discharge across 5 locations (NJ9468430370, NJ88771419, NJ5681817072, NJ3298510480 and NO7973998317).

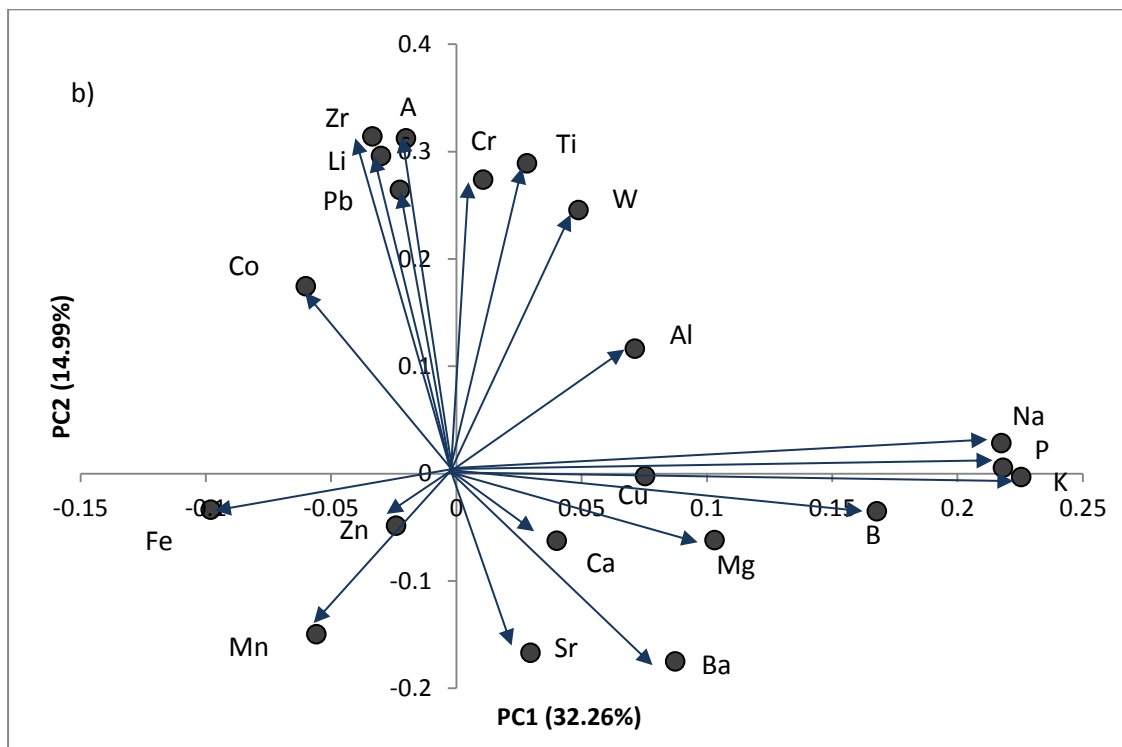
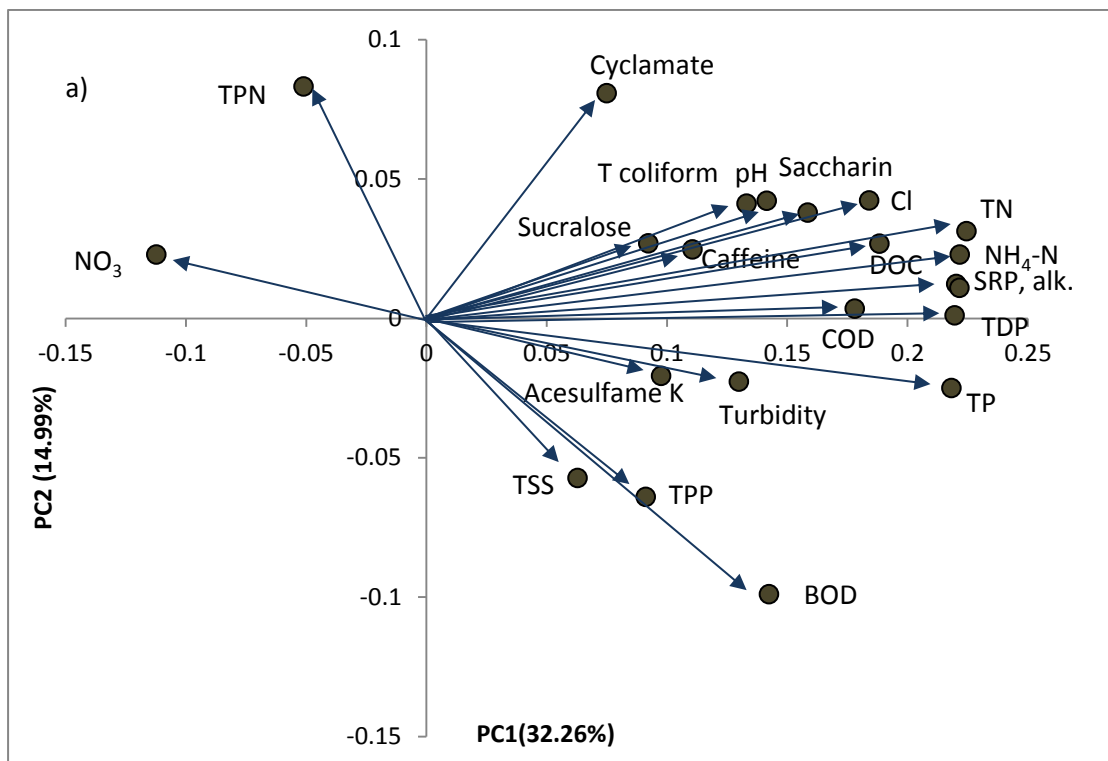


Figure S5.3: Loading plots of weights assigned to a) STE indicator variables including artificial sweeteners and caffeine, b) major and trace metal variables which explain 47.25% of total variance. Arrows represent the weight and the direction of each parameter in relation to others.

5.3.1 Seasonality in STE composition

The seasons were defined as spring (March-May), summer (June-August), autumn (September-November) and winter (December-February). Independently from site specification influences, properties of STE exhibited some seasonal variation which can be categorised into four groups with significant ($P < 0.05$) differences. Group 1 where for BOD and Ba, spring and summer concentrations were greater than autumn and winter; group 2 where conversely spring and summer concentrations of As, chromium (Cr) and titanium (Ti) were less than autumn and winter. Group 3 where winter concentrations of cobalt (Co), Mn and Zn were greater than spring, summer and autumn; and group 4 where for W, autumn concentrations were greater than winter, spring and summer while Sr reached the highest concentrations in spring (Table 5.1). Other physicochemical and microbial characteristics showed no significant seasonal differences ($P > 0.05$). However, nutrient concentrations in STE: NH_4 , TP and TDP were increased in spring and summer and decreased in autumn and winter periods (Table 5.1).

Changes in STE compositions in different seasons were further evaluated using a Canonical Variates factor loading plot (Figure 5.1a), in which seasons were used as a grouping factor. The plot indicated the association/similarities in compositions between spring/summer, and also between autumn/winter samples where the 95% confidence intervals (c.i.) areas were almost exactly superimposed. The plot also showed a clear dissociation between (spring/summer) and (autumn/winter) samples (clear separation of the 95% c.i. areas). The association and the dissociation between seasons was directly related to the variate weights of strongly positive factors within canonical variate 1 (CV1), (S, TN, SRP, Li and turbidity) and the strongly negative factors in CV1 (K, Cl, TP and NH_4) which explained 98.78% of the variation (Table 5.2). The increased use of detergents and household chemicals during warmer periods, the intake of health supplements in colder months and runoff input may have attributed to the grouping of these elements in STE and stream waters. The interaction analysis between season and site specifications revealed that both factors significantly ($P < 0.05$) influence effluent quality in TP, As, Li, Cr and Mn.

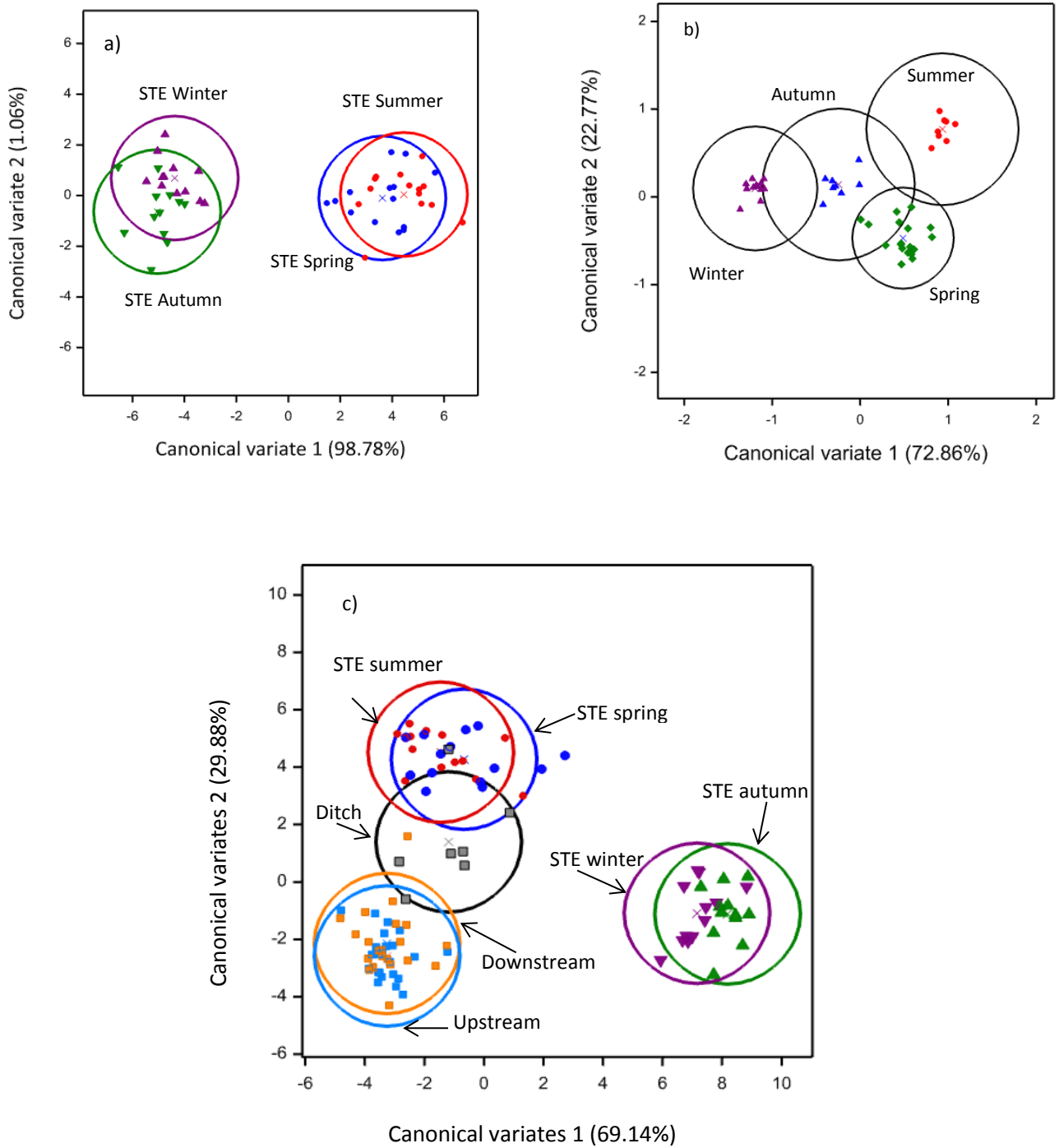


Figure 5.1: Canonical variates plots with 95% confidence; a) septic tank effluent (STE) population with seasons as grouping factor, b) stream water means with seasons as grouping factor, c) relationship between STE, stream and ditch waters.

Table 5.2: Canonical variates 1 and 2 explaining strong negative (-ve) and strong positive (+ve) variates that influenced STE and stream water seasonality as well as combined STE and up/down stream waters.

	Canonical variate 1 (CV1)		Canonical variate 2 (CV2)	
	Strong -ve loading	Strong +ve loading	Strong -ve loading	Strong +ve loading
a) ST season	K (-8.13), Cl (-7.62), TP (-6.51), COD (-5.82), NH ₄ (-4.65), BOD (-4.04), SO ₄ (-3.78), B (-3.02)	S (8.94), TN (8.49), SRP (6.49), Li (6.13), Turb. (4.18), Nb (4.13), Na (4.08), Ca (4.02), Zn (3.59), Mg (3.04)	TDP (-31.93), K (-10.87), TDN (-10.62), TP (-10.23), Cl (-9.61), Sr (-6.28), B (-5.96), BOD (-3.59), Zr (-3.48), Alk. (-3.30), Al (-3.08)	P (31.39), NH ₄ (11.50), Na (9.35), DOC (7.03), Ba (6.88), EC (6.10), SUVA (5.05), Si (4.93), Mg (3.87)
b) Stream season	K (-0.137), Cl (-0.079), Cu (-0.059), TN (-0.058), Nb (-0.048), SUVA (-0.039), Cr (-0.034)	Na (0.132), Si (0.081), DOC (0.072), Pb (0.071)	TDN (-0.125), Pb (-0.107), Na (-0.092), SO ₄ (-0.050), Li (-0.040), TPP (-0.037), NH ₄ (-0.031), TP (-0.029)	SUVA (0.260), K (0.197), Mg (0.106), Si (0.064), Co (0.060), DOC (0.049), Cl (0.048), Nb (0.041), Cr (0.040)
c) STE season and Up/down stream	W (-1.88), Mg (-1.61), SO ₄ (-1.59), TDN (-0.88), TP (-0.76)	Sn (9.60), Nb (4.66), Zr (3.92), SUVA (2.21), Ti (1.58), S (1.53), Sr (1.20), TN (1.14)	S (-2.88), TN (-2.72), P (-2.08), NH ₄ (-0.64), TVC (-0.57)	Si (3.54), Zr (3.41), Sn (3.32), Na (2.71), TDN (2.07), Zn (1.38)

5.3.2 Seasonality of impacts of STE on receiving stream waters

Analysis of stream data (up and downstream combined) revealed that stream waters adjacent to the ST contained varied nutrient concentrations of SRP, TDP, TPP, NH₄-N, TPN, DOC and TSS ranging from <0.01-178 mg/l (Table 5.3 and Figure 5.3), while stream pH values were within a neutral range (6.4-7.5). Stream alkalinity, BOD and COD concentrations also varied from <1-248 mg/l, while total coliforms and *E. coli* counts were 10-10⁴ MPN/100 ml. Major elements such as Na, Ca and K ranged from <1-67 mg/l while trace elements such as B, Ba, Cu, Mn and Zn ranged from <1-196 µg/l (Table 5.3). Rainfall and river discharge data during the period of the study (Figure 5.2) highlighted the high rainfall during summer and low rainfall levels during winter periods (mean 335 and 168 mm, respectively). The uncharacteristically high level of rainfall in the summer period may influence the dilution of STE in stream waters during summer time.

Despite the high level of rainfall and stream discharge, stream waters exhibited seasonal variation that can be categorised into two groups with significant differences ($P < 0.05$). Group 1, where for BOD, alkalinity, DOC, SO₄, *E. coli*, S and Li, summer concentrations were greater than spring, autumn and winter; group 2 where for W, winter concentrations were greater than spring, summer and autumn. Other stream physicochemical characteristics showed no significant seasonal differences ($P > 0.05$). Canonical Variates analysis for stream waters (Figure 5.1b) was used to explore the composition and differences of stream waters when seasons were used as the grouping factor. The plot indicated clear separation (in terms of the 95% c.i.) between summer and winter and also between spring and winter samples while the 95% c.i. area for autumn samples overlapped with that for winter, summer and spring. These separations were attributed to variate positive weightings in CV1 (Na, Si, DOC and Pb) and negative weightings in CV1 (K, Cl, Cu and TN), which explained 72.86% of total variation; also the positive weightings in CV2 (SUVA, K, Mg, Si, Co and DOC) and negative weightings in CV2 (TDN, Pb, Na and SO₄), which explained 22.77% of the variation (Table 5.2).

Table 5.3: Ranges, means and standard of errors for upstream and downstream water parameters that exhibited increase in concentration downstream from the source. ANOVA significant difference, (P-value) is also listed where up and downstream was the grouping factor.

Parameter	Unit	Upstream waters n=24		Downstream waters n=24		Up/down P-value
		Range	Mean±1SE	Range	Mean±1SE	
Turbidity	NTU	<1-17	4±1	1-88	11±5	
Alkalinity	mg/l	5-99	36±8	8-195	45±12	
EC	µS/cm	70-360	220±37	70-360	230±40	
TSS	mg/l	2-37	7±2	3-178	26±11	0.018
COD	mg/l	<1-73	24±6	<1-248	45±14	
BOD	mg/l	<1-17	4±1	<1-71	9±4	
SRP	mg/l	<0.01-0.03	0.02±0.01	<0.01-2.98	0.20±0.17	
TDP	mg/l	0.01-0.04	0.031±0.01	0.01-4.00	0.27±0.23	
TPP	mg/l	<0.01-0.49	0.07±0.03	<0.01-2.20	0.30±0.16	0.035
TP	mg/l	0.02-0.53	0.10±0.03	0.03-6.20	0.57±0.37	0.060
TN	mg/l	1.15-10.54	4.20±0.80	1.06-27.29	6.04±1.56	
NH ₄ -N	mg/l	<0.01-0.05	0.02±0.00	<0.01-1.07	0.17±0.07	0.029
TPN	mg/l	0.06-0.55	0.24±0.04	0.12-8.76	0.96±0.51	0.041
T. Coliform	MPN/100 ml ^a	10-1.9x10 ⁴	2.7x10 ³	20-2.4x10 ⁵	8.4x10 ⁴	0.044
<i>E. coli</i>	MPN/100 ml ^a	10-1.2x10 ³	2.6x10 ²	10-2.4x10 ⁴	2.0x10 ³	0.037
TVC	CFU/100 ml ^b	3.3x10 ⁴ -3.9x10 ⁶	8.6x10 ⁵	4.8x10 ⁴ -4.4x10 ⁷	4.3x10 ⁶	
Na	mg/l	7.21-27.44	15.05±1.84	7.34-27.75	15.84±2.05	
Ca	mg/l	4.16-67.21	16.13±3.61	4.12-46.24	15.01±2.58	
K	mg/l	0.62-16.91	2.93±0.90	1.1-34.19	4.01±1.90	
B	µg/l	6.85-46.68	26.61±2.57	8.13-79.33	33.07±4.97	
Ba	µg/l	45-423	114±23	31-376	118±23	
Cu	µg/l	0.15-11.82	2.30±0.85	0.15-8.17	2.12±0.63	
Mn	µg/l	2-196	32±13	<1-152	34±12	
Zn	µg/l	1-53	23±3	4-121	31±7	

a Most probable number in 100 ml

b Colony formed unit in 100 ml

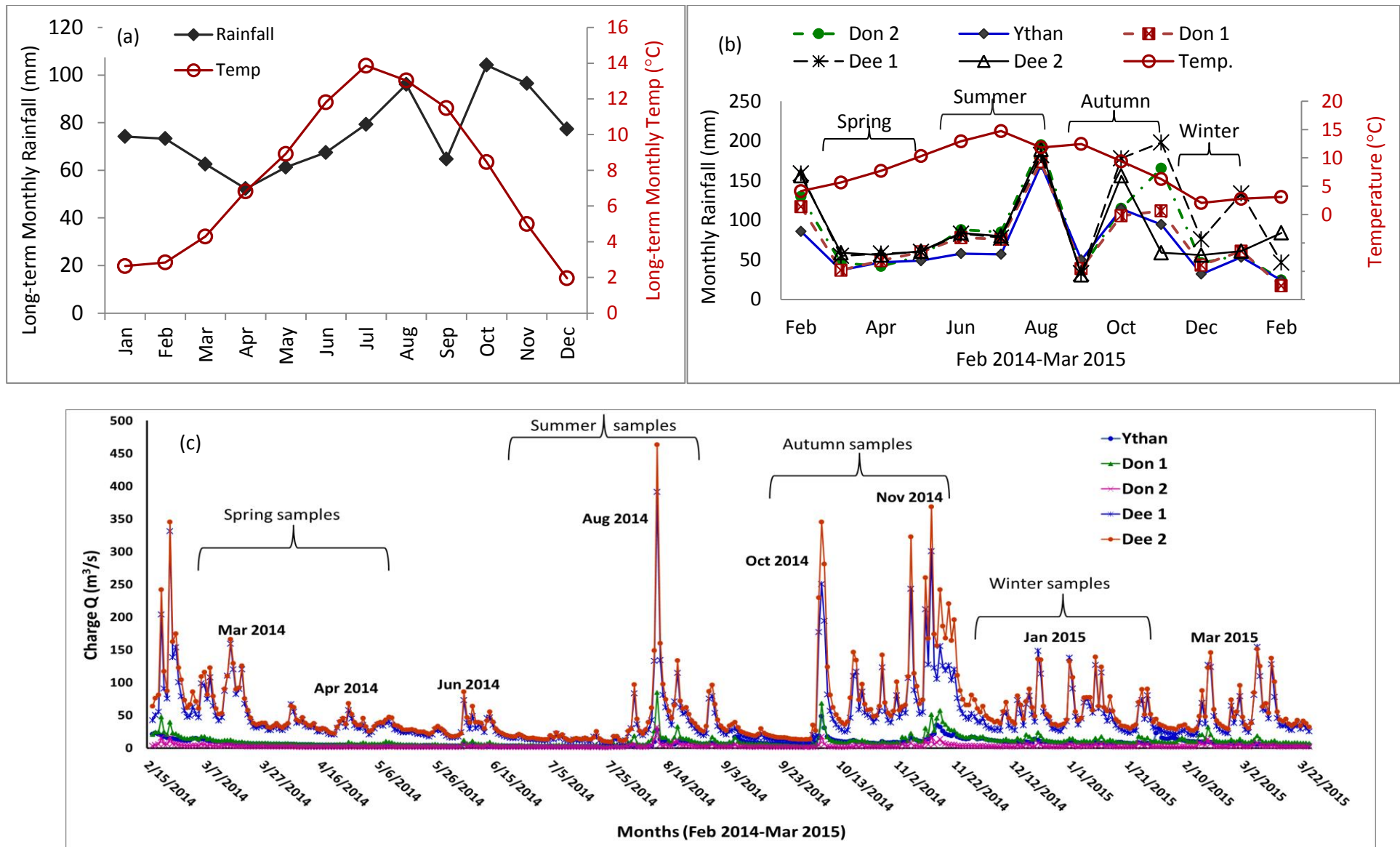


Figure 5.2: (a) The long-term monthly rainfall (mm) and temperature (°C), (b) The monthly rainfall and air temperature during 2014-2015 and (c) The daily river discharge (Q) within the three river catchments (Ythan, Don and Dee) during 2014-2015.

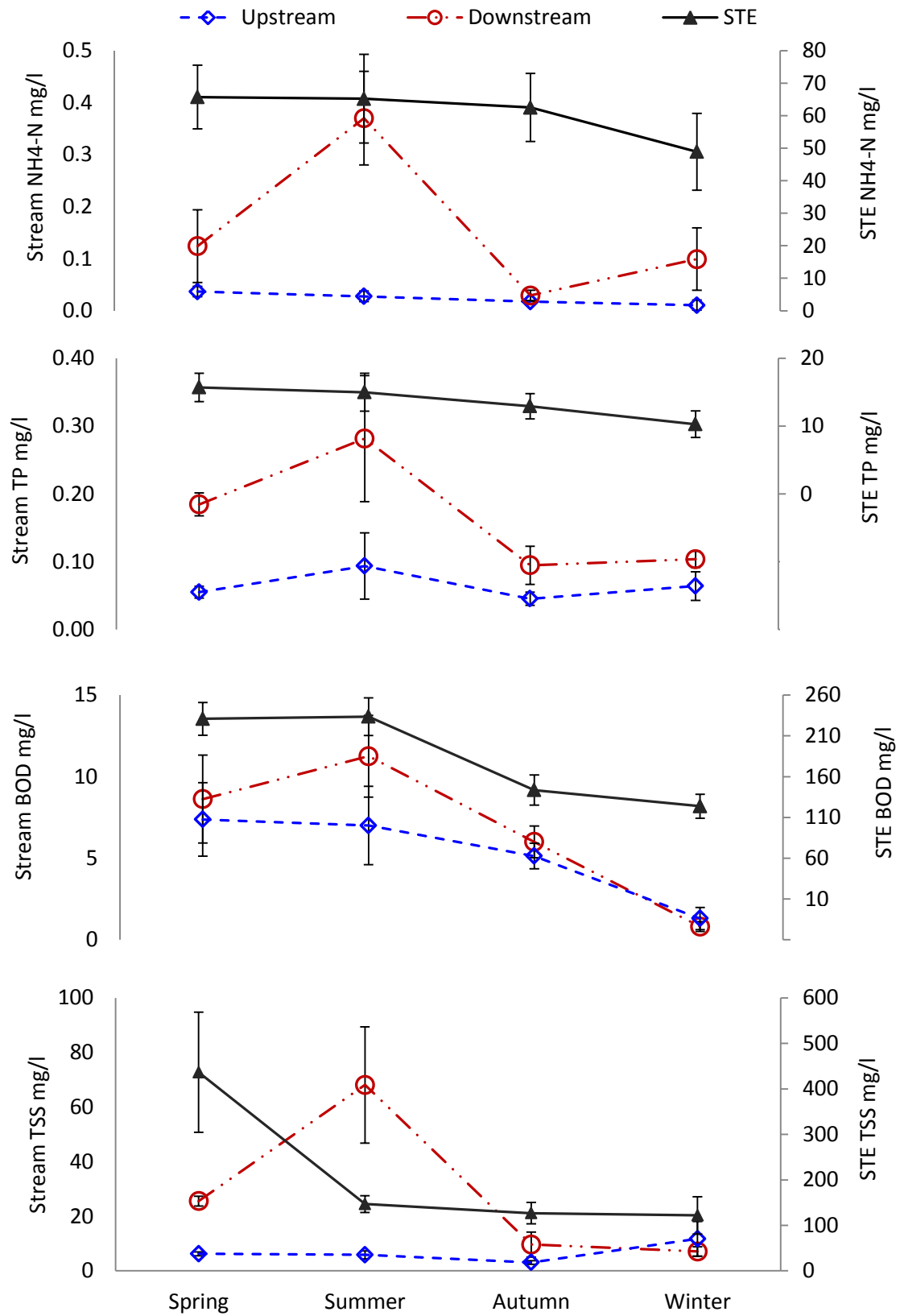


Figure 5.3a: Seasonal variation in upstream, downstream and septic tank effluent (STE) indicators (mean concentration of all sites with watercourses).

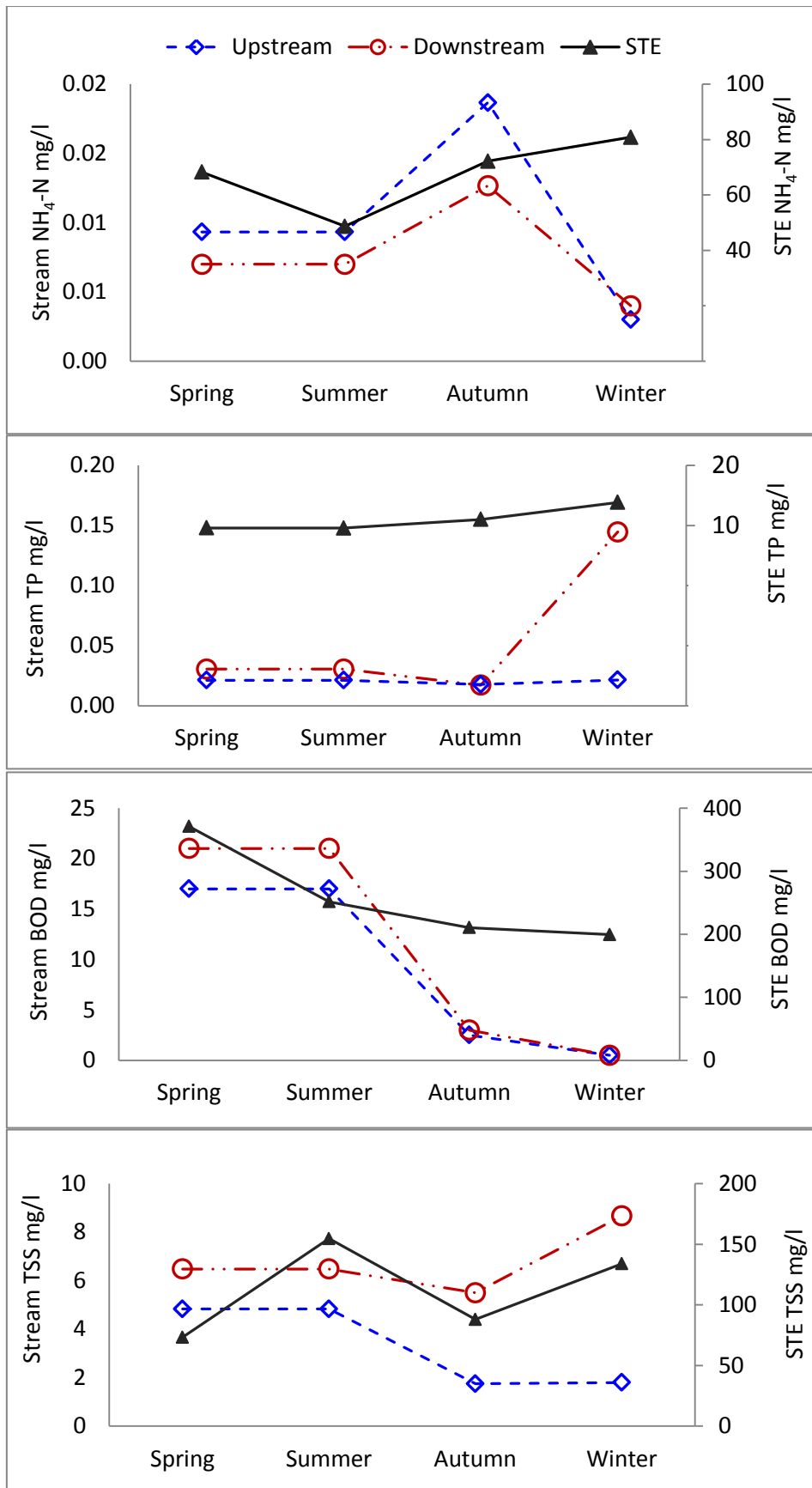


Figure 5.3b: Seasonal variation in upstream, downstream and septic tank effluent (STE) indicators for Site 1.

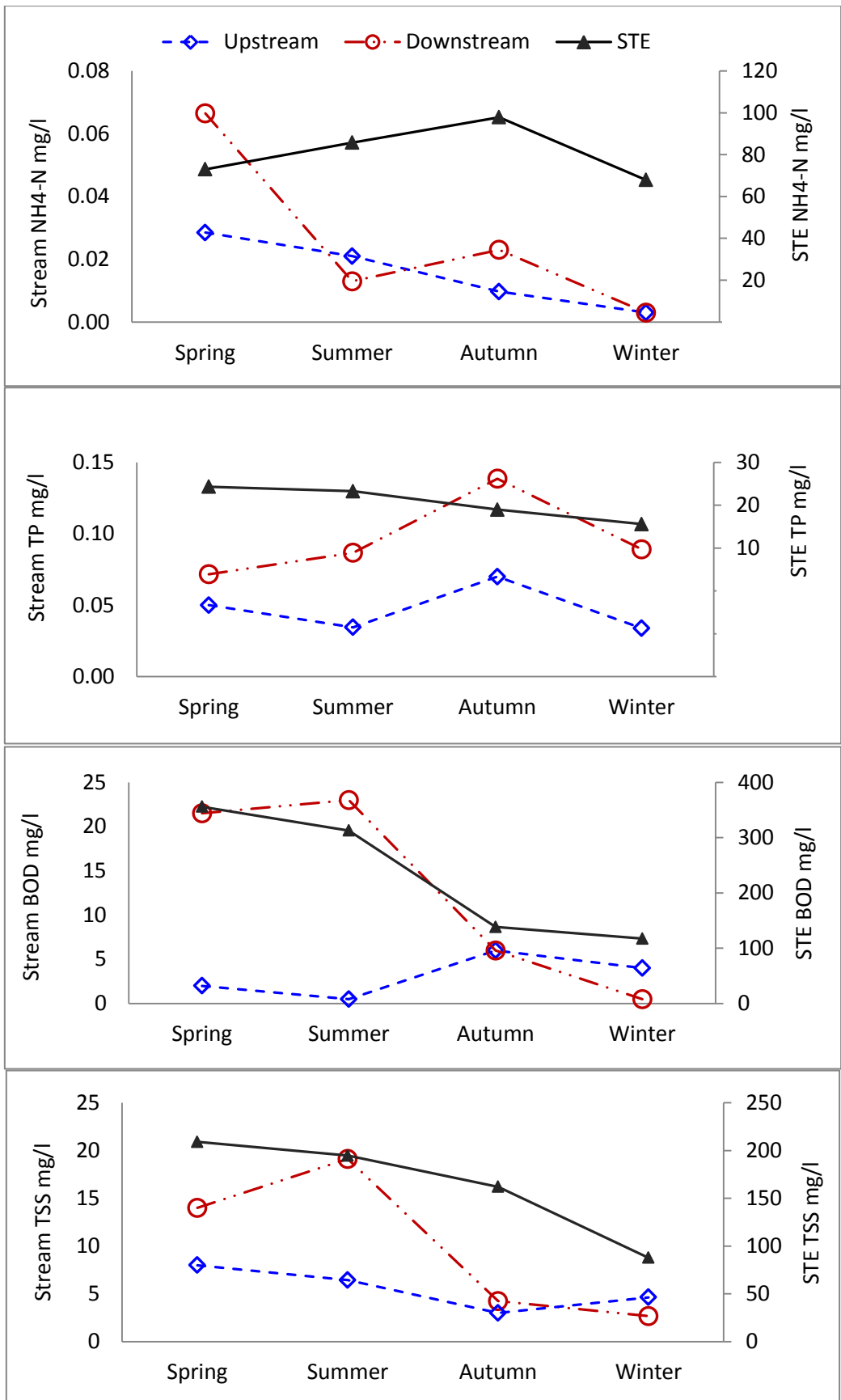


Figure 5.3c: Seasonal variation in upstream, downstream and septic tank effluent (STE) indicators for Site 6.

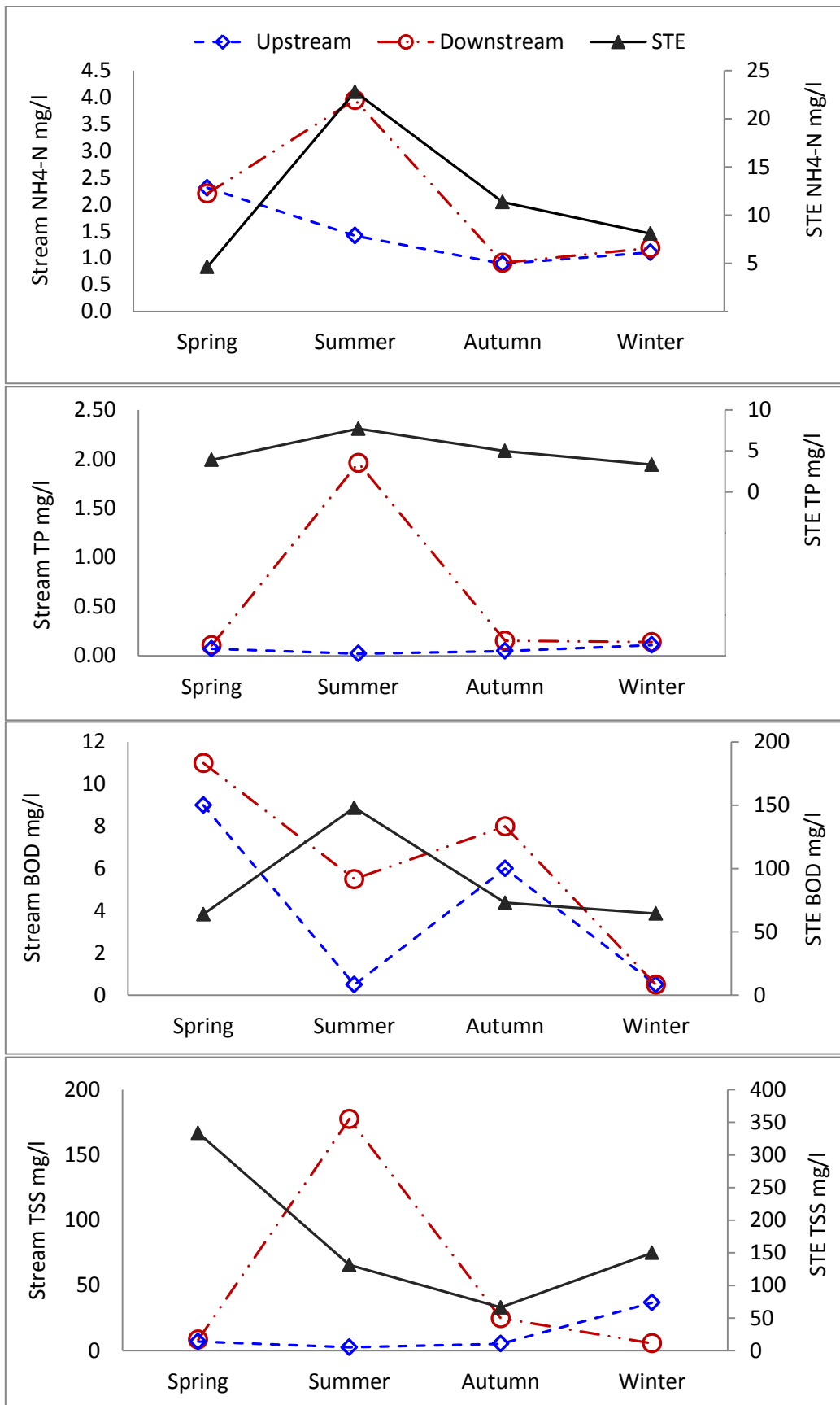


Figure 5.3d: Seasonal variation in upstream, downstream and septic tank effluent (STE) indicators for Site 8.

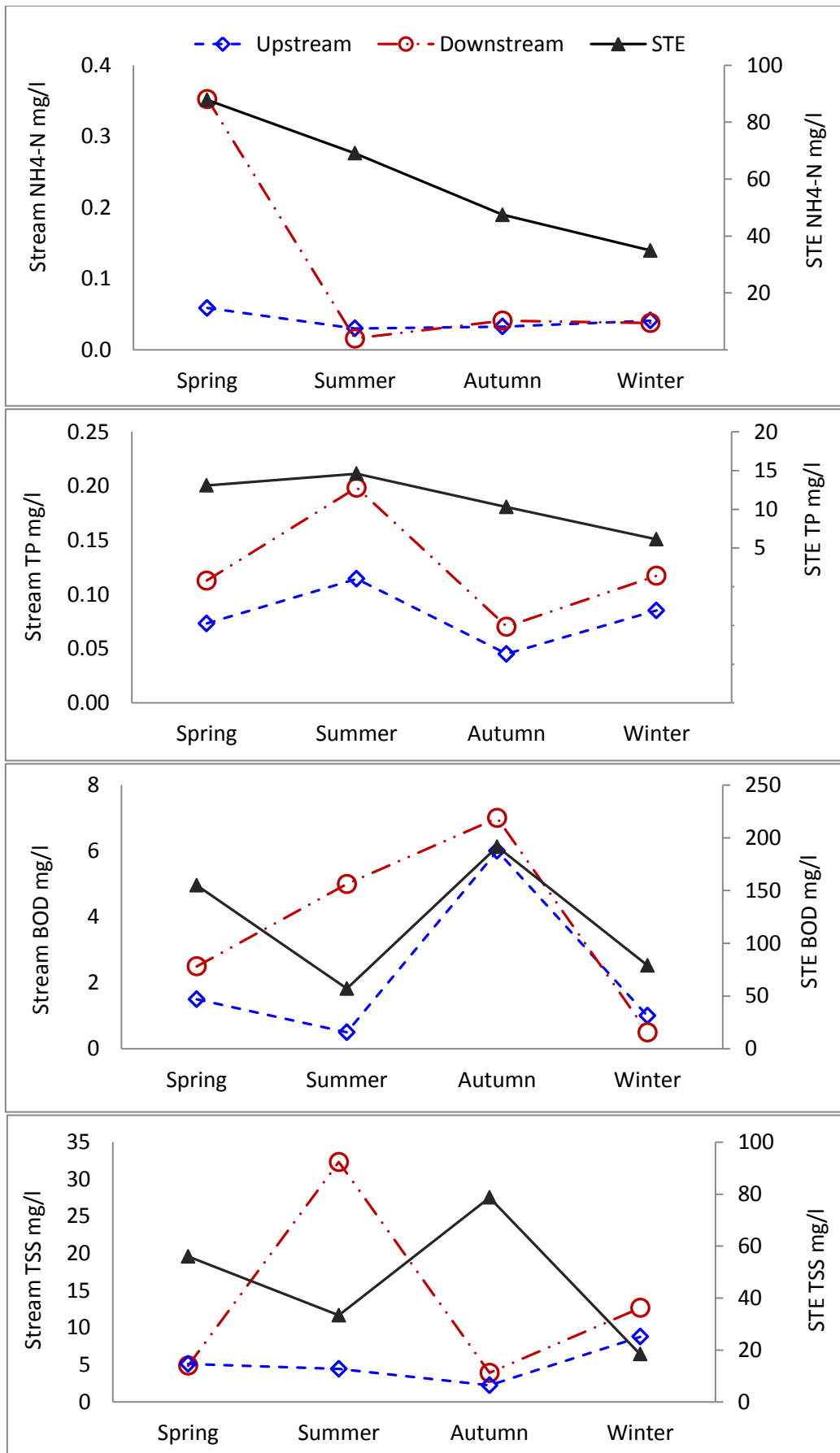


Figure 5.3e: Seasonal variation in upstream, downstream and septic tank effluent (STE) indicators for Site 12.

The combined stream water data throughout the four seasons, and when upstream and downstream were used as the grouping factor in ANOVA one-way analysis, showed that contaminant concentrations in downstream waters were greater and significantly different ($P < 0.05$) than those upstream for TSS, TPP, NH_4 , TPN, coliforms and *E. coli* (Table 5.3). Turbidity of downstream waters was >2.5 times greater than upstream waters, and nutrients such as SRP, TDP, TP and TN concentrations were also greater in downstream samples: mean TP downstream (0.57 mg/l) was 5 times greater in concentration than mean TP upstream (0.10 mg/l) from the source. Ditch waters where the dilution of received effluent was less than streams, showed composition and concentration more similar to STE (Figure 5.1). The Canonical Variates Analysis plot (Figure 5.1c) for all data combined (STE, ditch, up and downstream waters) with 95% c.i., showed similarities (overlapping) between up and downstream waters and that ditch samples were intermediate to STE (summer/spring) and stream waters. The plot also showed the separation of STE (winter/autumn) from stream waters, ditch and STE (spring/summer) samples. The data positions in this CVA were attributed to strongly positive weighting in CV1 (Sn, Nb, Zr, SUVA, Ti, S, Sr and TN) and the strongly negative weightings in CV1 (W, Mg, SO_4 , TDN and TP), which explained 69.14% of total variation, also by strongly positive weightings in CV2 (Si, Zr, Sn, Na, TDN and Zn) and the strongly negative weightings in CV2 (S, TN, P, NH_4 and TVC), which explained 29.88% of the variation (Table 5.2). However, interaction testing within two-way ANOVA of stream water data did not support that upstream vs downstream concentration differences were enhanced in any particular season over another (Table S5.2).

Table S5.2: ANOVA one-way analyses and the significant difference (P-value) of stream water where seasons was the grouping factor, and where upstream and downstream from the septic tank source was the grouping factor.

Parameters	Seasons P-value	Up/down stream P-value
Alkalinity	0.036	
TSS		0.018
BOD	0.003	
TDP	0.076	
TPP		0.035
TP		0.06
NH ₄ -N	0.087	0.029
TPN		0.041
DOC	0.050	
SO ₄	0.030	
T. Coliforms	0.08	0.044
<i>E. coli</i>	0.053	0.037
S	0.028	
Li	0.050	
W	0.019	
Zn	<0.001	

5.4 Discussion

The primary aim of this study was to present the first comprehensive data on the seasonal variation in STE composition for 12 typical ST systems during 2014/2015, which was on average a wet summer (rainfall of 335 mm compared to 13 years average of 233 mm; CEH, UK, 2016). The study aimed to help identify STE potential impact on the water quality of receiving streams, for example during ecologically sensitive periods of low flow and elevated temperature. In most literature, the temporal variation in concentrations of STE throughout the year is not taken into account, assuming constant composition and concentration throughout the year. Although, it is generally recognised that effluent quality is related to the household behaviour, number of ST users, water use, tank size and management (Lowe et al., 2009; Richards et al., 2016a), the population of effluents sampled did show some seasonal significant ($P < 0.05$) differences (Table 5.1 and Figure 5.1a) in some parameters, notably BOD, As, Ba, Co, Cr, Li, Mn, Sr, Ti, TPP, W, and Zn.

STE compositions were comparable between spring and summer, with similar concentrations in most parameters (Table 5.1) including P species, BOD, Ba, As, Cr and Ti. Effluent BOD concentrations were particularly greater in spring and summer (Figure 5.3) and can be a clear indication of increased effluent OM in warmer months. The effect of increased OM in STE on stream water composition may have influenced stream water quality as stream BOD concentrations were significantly increased ($P = 0.003$) in the summer, and conversely were lowest during winter. During periods of low flow, limited dilution coupled with increased OM in STE discharges can impact stream water quality (Withers et al., 2011). Additionally, at this time elevated water temperature and microbial activities causes depletion of dissolved oxygen during OM metabolism which further impact on stream ecology (Shanahan et al., 1998; Talke et al., 2009). The elevated atmospheric temperature in the summer (mean 14.4 °C), (Table 5.1) seemed to have had no influence on microbial population inside the tank as the scum layer in the tank (accumulated, hardened fat and grease) may have acted as an insulator against outside temperature changes. During this work, it was observed that effluent temperature was only increased when ST users used large quantities of hot water as in hot baths, which may have contributed to a similar level of microbial activity during winter periods to the rest of the seasons.

The association between autumn and winter STE compositions were due to having similar concentrations of BOD, TDP, TDN, Ca, Mg, S, As, Ba, Cr and Ti. The increased concentration of Ti, Cr

and As in STE during autumn and winter relative to summer and spring may be explained by the increase human consumption of vitamin supplements over winter, or from diets as these elements are present in many fruits, vegetables, grains, mushrooms and seafood (Weeks et al., 2006). However, the high concentrations of these trace elements does not seem to have affected seasonal stream water concentrations due to dilution by the high rainfall caused by storm events during summer and the increased stream discharge in August of 32.68 m³/s compared to August's long-term average of 15.07 m³/s (Figure 5.2). Moreover, stream discharge during sampling time in autumn was greater than in winter periods (23.11 and 16.64 m³/s), which may have contributed to stream dilution during sampling time. The alkalinity of STE and stream waters during winter months was the lowest, while STE discharges in summer probably contributed to the greater stream alkalinity (P=0.036), with levels of up to 80 mg/l. Although it is recognised that stream alkalinity can also be influenced by background lithology, Palmer and Roy (2001) associated high alkalinity level in fresh water with eutrophication and considered a stream with alkalinity concentration >30 mg/l to have exceeded the eutrophic state regardless of the source.

Point source discharges are known to be a source of elevated nutrients (P, N) and toxic substances such as pathogens, heavy metals and detergents that can impact natural stream waters (Klein, 1979; Macintosh et al., 2011). Phosphorus forms in STE showed an increase in TP, TDP and SRP concentrations in spring/summer months and a decrease in winter. This may be due to household habits of increase frequency of washing cycles during warmer months using phosphate based laundry and dishwasher detergents (Richards et al., 2015). This trend of increased P concentration was mirrored in stream waters during sampling time in the summer period despite high summer rainfall of 335 mm compared to long term average of 233 mm (CEH, 2016). The increased P concentration in stream waters may indicate agriculture runoff and the inputs from land use (Table S5.1); however, the recorded increase of P species downstream from ST sources is a direct link between STE discharges and the increased level of steam nutrients. Withers et al. (2014) stated that P concentration in STE discharge as low as 2 mg/l may be high enough to cause eutrophication of receiving waters under low flows. The positive correlation between SRP and sewage markers such as caffeine and saccharin in STE (Figure S5.3) is an indication of the potential of these compounds to be used as effluent tracer for the more environmentally targeted element such as P. Although microbial populations (*E. coli* and total coliforms) in STE exhibited no significant variation (P>0.05) over seasons, stream waters showed increased *E. coli* and total coliforms concentrations in warmer summer periods, possibly due to elevated atmospheric temperature of 14°C at summer sampling time.

In this study, sampling, upstream and downstream from the source revealed clear influence of STE on several parameters. Downstream BOD and COD levels were >double the concentration of upstream, while *E. coli* and total coliforms populations were one factor greater than upstream from ST sources. Elevated metal concentrations of stream water can be attributed to both anthropogenic (STE discharge or agriculture runoff) and/or natural (stream parent rock weathering) inputs (Martin and Meybeck, 1979; Ahlgren et al., 2012). Ahlgren et al. (2012) considered Ba concentration (>22 µg/l) as a potential indicator of agricultural P; however, the increased concentration of P, B and Zn directly downstream from ST source indicated by this work, and in the absence of other sources, is a clear evidence of STE enrichment to local watercourses. Increased metal concentration in aquatic environment can be growth limiting or toxic particularly during fish spawning times, while persistent exposure to low dosage of heavy metals can also be detrimental to aquatic organisms and may pose a health risk to humans and the environment (Jarup, 2003).

Concentrations of P and N downstream from ST source (mean 0.57 and 6.04 mg/l, respectively) indicated by this study, had exceeded upstream samples with >50% in the soluble form. This indicates that stream waters were enriched by STE and may have exceeded oligotrophic and eutrophic conditions for rivers TP ≤0.01 and 0.035-0.1 mg/l, respectively, (Palmer and Roy, 2001). Downstream waters had also exceeded eutrophic condition for TN ≥0.5 mg/l (Maddock, 2008) while the eutrophic levels for NO₃-N concentration were exceeded in both up and downstream under the effect of STE discharges. Although nutrient transfer (P and N) from agricultural soils to watercourses is frequently recognised to be a major contributor to eutrophication, diffuse nutrient loads are predominantly delivered during storms events and is often depending on the hydrological proximity to watercourses (Haygarth et al., 2005; Jordan et al., 2007). However, nutrient loads from point sources are more constant throughout the year (Ahlgren et al., 2012). Despite being a relatively wet summer (rainfall 335 mm), signs of stream impairment (increased concentrations P, N, BOD, alkalinity, DOC, SO₄, *E. coli*, Li and Zn) was observed during summer compared to winter (rainfall 168 mm) and thus in a more typical year, the input of STE in summer would be greater. However, the high summer rainfall caused by storm events will have increased the dilution factor of STE discharges, and likely contributed to the lack of significant interactions between season and sample location (up and downstream) on stream water parameters. However, Figure 5.1c clearly indicates that ditch waters are related to STE discharges in spring and summer while downstream waters are related to ditch waters; demonstrating a pathway of STE influence on downstream waters.

It is evident that point source discharges from STs can lead to high contaminant loadings to stream waters with the potential consequence of a decline in stream health, biodiversity, increase of algal growth, decrease in dissolved oxygen; conditions that may alter aquatic ecosystem structure and function. This study has shown there may be additional impact from elevated BOD in STE on stream waters despite the dilution received during high precipitation in summer period. To date, many old STS that are clustered adjacent to rivers in many countries all over the world are still in use, posing risks to watercourses. Many of these systems are in need of upgrading, relocating or replacing (Day, 2004; May et al., 2010; Withers et al., 2014). Legislation does not often consider all factors related to ST direct discharge. For instance, septic effluent direct discharge to watercourses in Northern Ireland may be allowed if 95% of BOD was removed (Withers et al., 2014). However, this does not take P and N concentrations in the effluent and their seasonal variation into consideration. A new rule came into force in January 2015 by the UK government concerning direct effluent discharge indicating the need to replace or upgrade STS by 1st January 2020 (Gov. UK, 2015), which is a welcome starting point for the remediation of stream waters throughout the UK. However, a stream monitoring programme may also be required to assess small point risks during different seasons and implement a robust stream remediation plan to improve and safeguard water quality. Applying and implementing measures such as ensuring the presence of properly functioning soakaway; installing additional treatment units to ST discharges during low flow warmer months to reduce their impact; re-directing effluent away from watercourses or increase connection to main sewerage network system may be necessary to improve and maintain water quality.

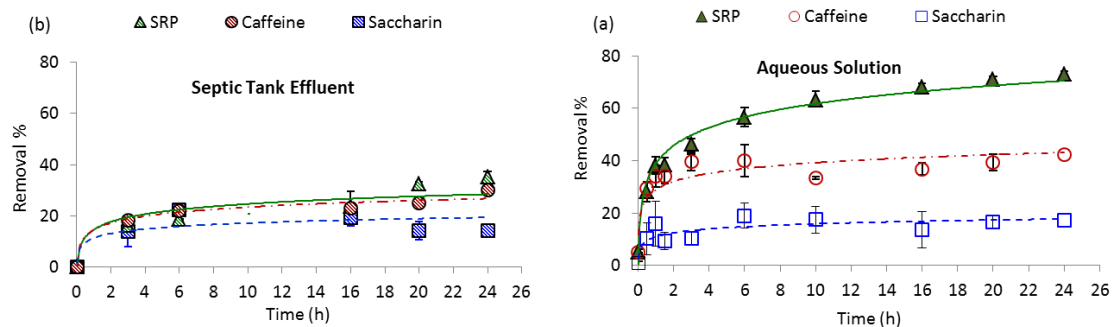
5.5 Conclusion

This study has provided comprehensive and fundamental information on seasonal variation in STE composition from household sources and their associated stream waters, and their influence on downstream water quality. STE exhibited a distinct seasonal variation in BOD, As, Ba, Co, Cr, Mn, Sr, Ti, W and Zn ($P < 0.05$) which were not related to site specifications. Stream waters also exhibited seasonal variations ($P \leq 0.05$) in alkalinity, BOD, DOC, SO_4 , *E. coli*, S, Li and Zn despite the dilution received by storm events in warmer months. The results of this study revealed that stream waters adjacent to ST discharges were influenced by ST discharge and may have exceeded eutrophic conditions in alkalinity, P and N. The effect of STE discharges on stream waters was apparent in most indicator contaminants including *E. coli* and total coliforms, BOD, TSS, TPP, NH_4 -N and TPN which exhibited higher concentrations downstream from the ST source ($P < 0.05$). The correlation between caffeine/saccharin and SRP suggested their potential use to trace effluent discharge and effluent P. This work has highlighted that STE discharges are a key factor influencing adjacent downstream water quality and call for a long term monitoring programme of STE and stream waters especially during low flow periods and implementing appropriate measures to reduce STE discharges sufficiently to improve water quality.

Chapter 6

Removal and attenuation of sewage effluent combined tracer signals of phosphorus, caffeine and saccharin in soil

Graphical Abstract



Adsorption % of soluble reactive phosphorus (SRP), caffeine and saccharin from septic tank effluent (STE) and aqueous solution in soil

Less Phosphorus was removed from STE than from aqueous solution as the complex composition of STE may have competed for soil adsorption sites

This work is submitted to Environmental Pollution, 2017.

Richards, S., Withers, P.J.A., Paterson, E., McRoberts, C.W., Stutter, M., 2017.
Environmental Pollution 223, 277-285.

Author Contributions:

SR designed and performed the experiment. McR performed instrument analysis for caffeine and saccharin. SR also analysed the data, wrote the paper and all co-authors reviewed and commented.

Abstract

Contaminants in septic tank effluent (STE) are expected to be removed by the soil system before discharging to the wider environment. However, potential contaminants such as phosphorus (P), caffeine and artificial sweeteners do find their way to watercourses impacting aquatic eco-systems. In this study, the attenuation of STE P, caffeine and saccharin were investigated in untreated soil and in soil with reduced microbial activity, in aqueous solutions and in the complex matrix of STE. Time series sorption and desorption experiments using batch equilibrium and a column experiment of STE P attenuation were conducted. The results revealed that the soil distribution coefficients (K_d) were: P 81.57 > caffeine 22.16 > saccharin 5.98 cm³/g, suggesting greater soil affinity to P adsorption. The data revealed that 80% of saccharin attenuation was associated with microbial activities rather than adsorption processes. However, a complete removal of saccharin and caffeine did not occur during the equilibration period, suggesting their leaching potential. The dominant mechanism of P attenuation was adsorption (chemical and physical), yielding P retention of >73% and 35% for P in aqueous solution and in STE matrix, respectively, for batch equilibrium. The soil in the column acted as an effluent P sink retaining 125 µgP/g soil of effluent P. The attenuation of P, caffeine and saccharin in the aqueous solution was greater than in STE, suggesting that the complex composition of STE reduced soil adsorption ability, and that other substances present in STE may be competing for soil binding sites. The data revealed that caffeine and P had similarities in the interaction with soils and thus caffeine may be considered as a STE tracer of anthropogenic source of P in receiving waters.

Keywords: Phosphorus removal, Saccharin, Caffeine, Sorption and desorption, Sewage effluent

6.1 Introduction

Small point sources such as septic tanks (ST) contribute to stream microbial and nutrient enrichment of receiving waters through the persistent direct discharge of effluents or diffusely through soil soakaway discharges (Dudley and May, 2007; Withers et al., 2014; Ockenden et al., 2014). The release of contaminants and their metabolites from ST to surface waters poses potentially serious localised risks to human health and stream ecology. Streams are increasingly contaminated with pharmaceutical products, caffeine, artificial sweeteners, detergents and other man-made compounds (Haggard et al., 2006, Richards et al., 2015) most of which are not or only partially degradable by STS, nor by the more advanced wastewater treatment plants (WWTP) (Andreozzi et al., 2003; Ying et al., 2009). The transport and the reduction of these compounds may occur through dilution, hydrolysis, sorption, bacterial assimilation and biodegradation which may reduce their toxicity to the environment (Gill et al., 2009a; Lin et al., 2006; 2010). For septic tank effluent (STE), these processes are expected to attenuate potentially harmful substances from the effluent within soil soakaway systems that constitute the final stage of household waste treatment. However, the ability of many soil systems to remove pollutants becomes increasingly exhausted with time (Jordan et al., 2005), or where soil conditions are not suitable (Gill et al., 2009a; 2009b; Withers et al., 2011). For many contaminants, the adsorption capacity diminishes as soil particles become saturated with contaminants causing the pollutants to spread further away from the soakaway and eventually reaching ground and surface waters (Guigard et al., 1996; Robertson et al., 1998; 2008).

Little is known about the occurrence, extent, transport, and fate of many synthetic organic chemicals after their release. Only a few analytical methods have been developed that are capable of detecting these contaminants at the low concentrations that might be present in soil and aquatic environments (Barnes et al., 2004; Gros et al., 2006; Fatta et al., 2007). Their presence in the environment is of concern as their potential to cause harm to the environment is poorly understood. However, the presence of such contaminants in soil solutions and surface waters can also show the presence and migration of other potential key pollutants associated with wastewater including ST discharge sources. Provided environmental behaviours of certain contaminants are known (e.g. degradation, sorption and desorption) they may be used as tracers for the presence of other chemicals that are more difficult to detect, or come from multiple environmental sources.

Phosphorus and trace organic molecules of human origin (caffeine and saccharin) found normally in STE discharges were selected to investigate their leaching versus attenuation behaviour in soil. Phosphorus was selected as it is a major pollutant constituent of STE discharges, which is present in high concentrations from 1-32 mg/l (Lowe et al., 2009; Withers et al., 2011; Richards et al., 2016a) and is of concern due to its role in surface water eutrophication. Saturation of adsorption sites of soakaway soils will also lead to plume migration, progressively toward ground and surface waters (Robertson et al., 1998; 2008). In addition to P, the environmental behaviour in soil of two potential effluent tracer compounds was investigated. Caffeine was investigated due to the worldwide anthropogenic source, found in coffee, tea, soft drinks, medications and toothpastes. Caffeine is a moderately water soluble alkaloid (N-containing substance) of formula $C_8H_{10}N_4O_2$, extracted from plants (e.g. cacao, tea and coffee), and has the effects of temporarily preventing/reducing drowsiness and restoring alertness (Gürü and İçen, 2004). Caffeine is often excreted un-degraded from the human body and is present in domestic STE at concentrations from 3-391 $\mu\text{g/l}$ (Conn, 2008; Gill et al, 2009a; Richards et al., 2016b) due to its constant wide consumption in large quantities. The presence of caffeine in surface waters is directly indicative of human source and should indicate the source of pollutants (Buerge et al., 2003). Sotelo et al. (2012) studied the adsorption of caffeine solution to activated carbon and found its adsorption capacity was 270 mg/g, but its sorption by soil is not fully understood.

The globally abundant artificial sweetener saccharin was also investigated. Artificial sweeteners are often substitutes for sugars in processed food products to reduce calorie intake for dietary controls. Saccharin ($C_7H_5NO_3S$) is 300 times as sweet as table sugar (Scheurer et al., 2009) and, as with all artificial sweeteners compounds, saccharin does not hydrolyse as do carbohydrates and is excreted without degradation by humans. Artificial sweeteners constitute an integral part of STE discharges with various concentrations from 15-51 $\mu\text{g/l}$ (Robertson et al., 2013; Richards et al., 2016b) and have been detected in surface and groundwaters (Buerge et al., 2009; Scheurer et al., 2009; Robertson et al., 2013).

Very few studies have been conducted on the attenuation of these compounds through soil using sewage effluent. Thus the factors controlling the migration of combined signals of tracer chemicals (e.g. caffeine, saccharin) alongside that of major environmental pollutants such as P, are not well understood. This knowledge is required to facilitate source tracing and apportionment from multiple sources in catchments. In this work the behaviour and the attenuation of P, caffeine and saccharin in

soil was investigated through soil-solution batch equilibration comparing between simple aqueous solutions and the actual STE matrix. The STE was also used in a column experiment to further evaluate P attenuation in soil. The objectives were: 1) to determine the natural attenuation and the sorption of these compounds by a test soil; 2) to investigate biogeochemical processes of the attenuation (biotic or abiotic); 3) to determine real STE P behaviour in soil compared to aqueous solutions; 4) to investigate the potential of caffeine and saccharin to behave as tracers for STE discharges.

6.2 Materials and Methods

6.2.1 Soil treatment and characterisation

Soil (10-30 cm depth) was collected from near Dundee, UK (NO307327) and used in sorption and column experiments. The soil was sieved (2 mm) then stored at 4°C. A subsample of the soil was air-dried and characterised for pH (Hanna pH 210 meter), moisture content, carbon and nitrogen content (Thermo-Finnigan, Flash EA 1112 CN analyser, Naples, Italy), particle size (Mastersizer 2000, Malvern, UK) and soil phosphorus (Olsen, Morgan, total and oxalate extractable phosphorus tests). A fraction of the fresh soil was subjected to a constant stream of ozone flow for 4 h to reduce microorganism populations (Pawlat et al., 2010; Ebihara et al., 2012) with minimum change to soil structure and chemistry with the intention to compare abiotic and biotic attenuation in untreated soil to behaviour in a soil where microbial activity was reduced. We chose this method recognising that no soil sterilisation process is perfect for sorption and leaching studies, particularly for nutrients. Bacterial total viable counts (TVC) for ozone treated and untreated soil's solutions were performed using a spread plating technique onto nutrient agar plates (Standard Methods for Examination of water and Wastewater, 1999). Plates were incubated at 37°C for 24 h then bacterial colonies were detected and counted as colony forming units (CFU) in 100 ml.

6.2.2 Septic tank effluent and reagents for batch equilibrium experiments

Septic tank effluent was collected from an 11 year old concrete tank serving 3 people that discharged onto a soil bed. Effluent was collected at the tank exit before the soil soakaway. The effluent was filtered through a pre-washed GF/F (0.7 µm) filter stacked onto a 0.45 µm filter paper. The filtered effluent was used for batch equilibrium and column experiments. Phosphate (KH₂PO₄), caffeine and saccharin (purity >98%) compounds were obtained from Sigma Aldrich (Dorset, UK). A stock solution was made for each compound by dissolving the appropriate amount in calcium chloride electrolyte solution (0.01M) to give concentrations that equal mean concentrations found in STE discharges (Richards et al., 2016a) of approximately 10.0 mg/l for soluble reactive P (SRP) and 0.6 mg/l for caffeine and saccharin.

Sorption and desorption batch equilibrium experiments for effluent and aqueous solutions were conducted separately according to OECD guidelines for the testing of chemicals (2000), in triplicates at room temperature using sterilised glassware (450°C for 18 h). For each compound, time series attenuation and sorption experiments were conducted in aqueous solution using untreated soil to investigate biotic plus abiotic processes (both sorption and biodegradation) and ozone treated soil to compare dominantly abiotic processes (principally sorption). An additional batch equilibrium experiment (Figure S6.1) was conducted on untreated soil using the effluent matrix composition. Soil and effluent mixtures (1:30 dry matter to solution ratio) were shaken on an orbital shaker (120 rpm) at room temperature and equilibrated for multiple time points up to 24 h in the dark. Soil leaching in CaCl₂ electrolyte (0.01M, pH 5.5) and blanks (no soil) for controls were also included in the experiments. The aqueous solution samples were taken off the orbital shaker at 0.5, 1, 1.5, 3, 6, 10, 16, 20 and 24 h time points during the equilibration period and filtered using pre-heated (450°C) GF/F filter papers. Effluent samples were taken off the orbital shaker at 3, 6, 16, 20 and 24 h time points before filtering.



Figure S6.1: Preparation of batch equilibrium experiment (left) and filtration after equilibration (right).

Subsequently desorption experiments were conducted on the soils that had 24 h contact with either aqueous solution or effluents. Soil was recovered by centrifuging and removing effluent and aqueous phase as recommended by OECD, 2000. The volume of the removed effluent and aqueous phase from the vessels was replaced by adding an equivalent volume of CaCl₂ (0.01M) without the test substances to the soil. Following equilibration at 120 rpm for 24 h, the aqueous solution was recovered and analysed for desorption of the test substances.

The effluent and solutions of the sorption and desorption tests were analysed for pH (Hanna pH 210 meter) and SRP by automated colorimetry (San++ analyser, Skalar, Breda, Netherlands). Caffeine and saccharin concentrations were determined by liquid chromatography tandem mass spectrometry

(LC-MS/MS) after the addition of a stable labelled internal standard of each compound using a Phenomenex Luna 5 C18 column. The presence of saccharin was detected in the negative and caffeine in the positive electrospray mode (Agilent 1100 series LC system interfaced to a Waters Quattro Ultima Platinum triple quadrupole mass spectrometer, Agilent Technologies, UK). Detailed method is provided in the supplementary material.

6.2.3 Column sorption and desorption using effluent

The column experiment was conducted using STE to examine P attenuation and behaviour in the test soil. Approximately, 31.5 g of dry untreated soil was packed into a glass column (2.5 cm diameter and 5 cm length) fitted with PTFE filters (20 μm). The column was filled with Millipore water with upwards flow using a peristaltic pump. The soil pore volume (PV) was calculated as the difference between saturated and dry soil in the column: (PV = mass saturated column and soil – mass column and soil). Three phases of flow were initiated: 1) Electrolyte (NaCl 1mM) was pumped to the column at a flow rate of 0.3 ml/min to collect a volume of 6 ml every 20 min for 3.3 h; 2) this was immediately switched to STE pumped into the column for 24.3 h until approximately expected breakthrough; 3) the column was then leached with 1mM NaCl electrolyte for a further 23 h. Collected column fractions were analysed for SRP and DOC colorimetry (San++ Skalar analyser Skalar, Netherland); and pH (Hanna pH 210 meter). Column hydraulic parameters were attained using a subsequent pulse breakthrough experiment with an inert tracer chloride (Cl^-). The column was first flushed with Millipore water for 3.3 h then switching to a pulse of 4.91 cm^3 of 500 mgCl/l for the duration of 15.5 min, before switching back to Millipore water. Chloride concentrations in the collected fractions were determined (Dionex DX600, Dionex, California, USA).

6.2.3.1 Calculations for batch equilibrations

Sorption data were collected and the difference between the initial and final P, caffeine and saccharin concentrations were considered to be due to degradation and sorption to soil. Concentration means and standard errors were calculated and the absorbed amount of P, caffeine and saccharin along with the percentage of Removal (R %) for biotic and abiotic uptake were calculated from the decrease in their concentration after equilibrating time using equation (1):-

$$R\% = \left(\frac{C_0 - C_t}{C_0} \right) \times 100 \quad (1)$$

where: R is the adsorbed percentage of P, caffeine and saccharin and C_0 is their initial concentration (mg/l) and C_t is equilibrium final concentrations (mg/l). The adsorption capacity of the soil was calculated by concentration difference, and the uptake (mg/g) was calculated as per equation (2):-

$$R = (C_0 - C_t) \times \left(\frac{V}{M_{soil}} \right) \quad (2)$$

where: R is the mass of P, caffeine or saccharin removed (mg/g soil); V is volume of equilibrium solution (l) and M is dry soil mass (g). The distribution coefficient K_d is the most common measure used to describe the extent to which contaminants are adsorbed to soils. The distribution coefficient, K_d , is also defined as the ratio of the quantity of the adsorbate (P, caffeine and saccharin) adsorbed, to the amount of the adsorbate remaining in solution at equilibrium, and was obtained from theoretical calculation as per equation 3 (OECD,2000):

$$K_d = \left(\frac{m_s}{m_{aq}} \right) \times \left(\frac{V}{M_{soil}} \right) \quad (3)$$

where: K_d = the partition coefficient of the substance of interest (cm^3/g), m_s = mass of adsorbed substance on the soil at adsorption equilibrium (μg), m_{aq} = mass of substance remaining in the solution at equilibrium (μg), M_{soil} = mass of dry soil (g) and V = initial aqueous volume in contact with the soil (ml or cm^3). The organic carbon normalised adsorption coefficient (K_{oc}) connects the distribution coefficient K_d to organic carbon content in the soil and allows comparison between the present study and others reporting K_d and K_{oc} values across soils varying in C contents. Therefore, K_{oc} values depended on the characteristics of the soil's humic substances and were calculated as per equation 4:

$$K_{oc} = \left(\frac{K_d}{\%OC} \right) \times 100 \quad (4)$$

where: K_{oc} is the organic carbon normalised adsorption coefficient (ml/g) and % oc is the percentage of organic carbon in the soil (g/g).

During the desorption phase, the mass of test substance desorbed was calculated using equation (5):

$$m_{des} = \left(\frac{(C_0(V/1000)) - (C_{des}(V/1000))}{M_{soil}} \right) \times 1000 \quad (5)$$

where: $m_{(des)}$ is the mass of test substance desorbed (μg), C_0 is the initial desorption concentration (mg/l), V is solution volume (ml), C_{des} is desorption concentration (mg/l) and $M_{(soil)}$ is dry soil mass (g).

6.2.3.2 Calculations for the column experiments

The convective-dispersive transport characteristic of the solution by the soil was determined using equation 6 (Stutter et al., 2007):

$$C_{(L,t)}^f = \frac{(M_R / (\frac{Q}{1000}))L}{2\sqrt{\pi Dt^3}} \exp\left(-\frac{(L-vt)^2}{4Dt}\right) \quad (6)$$

where: $C_{(L,t)}^f$ is average Cl concentration (mg/l); Q is column flow rate (ml/min), L is the length of the column (cm), t is the time of the observation and M_R is mass recovered of Cl tracer (mg). The convective-dispersive nature for Cl⁻ tracer transport in the soil was determined from the Péclet number (Pe), equation 7:

$$Pe = \frac{vL}{D} \quad (7)$$

where: v is the velocity of the flow and D is the dispersion values obtained from fitting transport model to the breakthrough curve. A Péclet number >40 indicates convective transport. Sorption isotherms for effluent P, effluent batch equilibrium and aqueous solution were obtained using equilibrium mass concentration (C_t/C_0) vs P concentration (mmol/l).

6.3 Results

Soil characteristics are summarised in supplementary material (Table S6.1). The soil can be described as a well-drained silty-loam (7% clay, 55% silt and 38% sand), with organic matter content of 5% of which carbon content was 3% and soil pH in water and CaCl₂ was 5.98 and 5.56, respectively. The silty loam soil covers >58% of Scottish soils in the N. E. of Scotland. Treating soil with ozone exposure reduced microbial abundance by 65% compared to untreated soil (TVC 1.9 x10⁴ and 5.7 x 10⁴ CFU/100 ml for treated and untreated soil, respectively).

Table S6.1: Test soil characteristics.

Soil parameters	Unit	value
pH in water		5.98
pH in CaCl ₂		5.56
Moisture content	%	16.28
Clay particle size	%	7.35
C content	%	2.62
N content	%	0.23
Oxalate P	mg/kg	889
Oxalate Al	mg/kg	7824
Oxalate Fe	mg/kg	5923
Morgan P	mg/kg	6.79
Olsen P	mg/kg	28.27
TP	mg/kg	1377

6.3.1 Attenuation of test substances from aqueous solution (batch equilibrium)

Concentrations as (C_t/C_0) of P, caffeine and saccharin during batch equilibrations with the soil are presented in Figure 6.1 and sorption partition coefficients K_d and $\log K_{oc}$ are presented in Table 6.1. The order of solute in the aqueous matrix by the test soil (both treated and untreated form) was: P>caffeine>saccharin. For P a maximum C_t/C_0 of 0.27 was attained in 24 h in aqueous matrix. The high affinity for P adsorption was shown by the high K_d of 81.57 and 90.98 cm³/g for untreated and treated soils, respectively. However, the adsorption curves for P in the untreated and treated soils were nearly identical (Figure 6.1a and 6.2a), which suggested P adsorption was dominated by chemical and physical processes rather than microbial assimilation. In the aqueous P matrix pH did not vary greatly during the equilibration period (5.8-6.0) and P adsorption reached its maximum at 20-24 h point (pH 6.0).

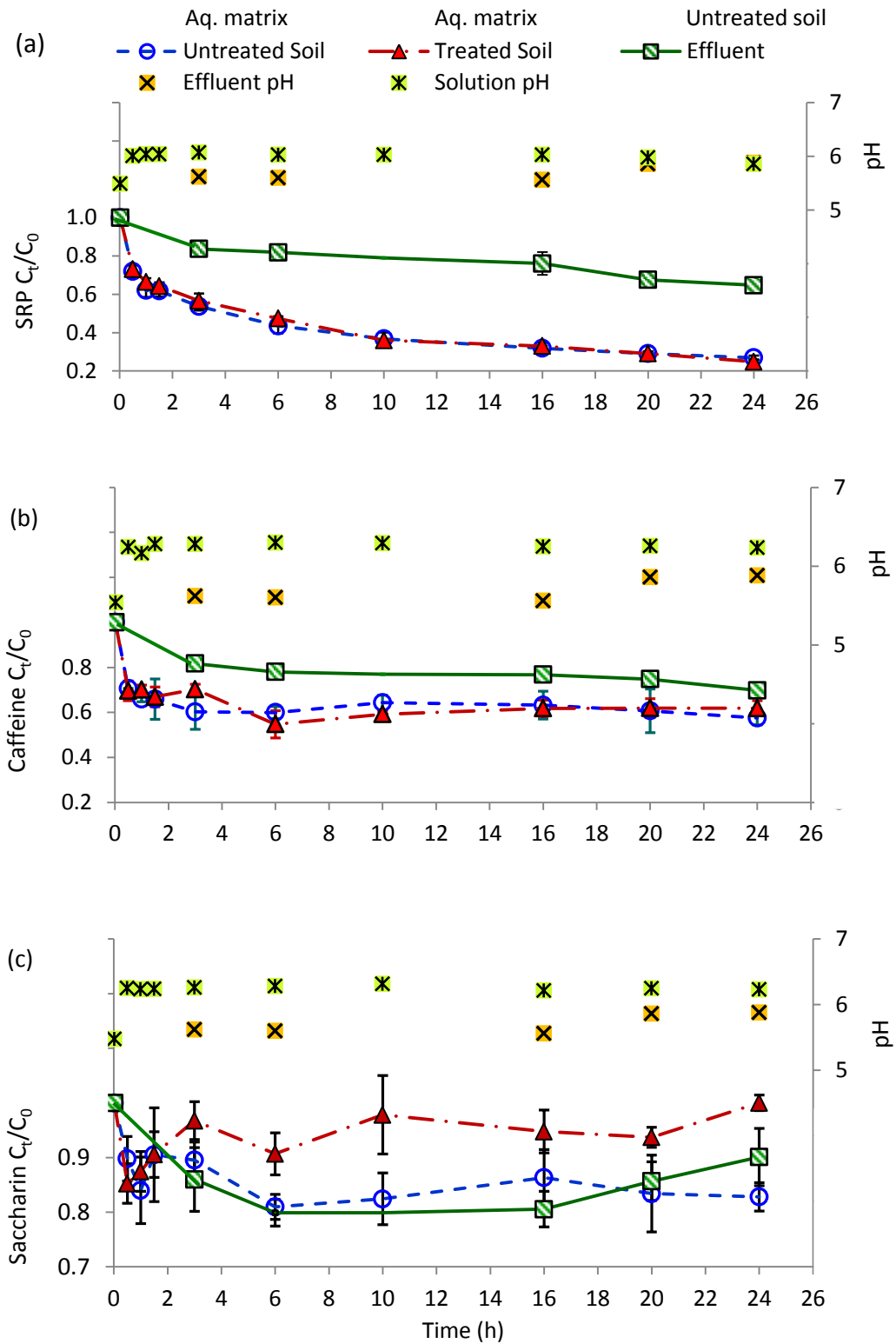


Figure 6.1: Mass concentration and pH against time in artificial aqueous solutions (untreated and treated soil with ozone flow) and in septic tank effluent (untreated soil), including 2xS.E. for (a) Soluble reactive phosphorus (SRP), (b) Caffeine and (c) Saccharin (note different axis scale).

Table 6.1: Soil distribution coefficient K_d and organic carbon normalised adsorption coefficient K_{oc} and mass reduction and desorption of tested substance for untreated and treated (microbial reduced) soil in artificial aqueous solution and in septic tank effluent (batch and column systems), \pm standard of errors (1S.E.) and percentage recovery.

Parameter	Matrix	Unit	SRP	Caffeine	Saccharin
K_d for Untreated soil	Aq.	cm ³ /g	81.57	22.16	5.98
K_d for Treated soil	Aq.	cm ³ /g	90.98	19.72	2.58
K_d for Untreated soil	STE	cm ³ /g	16.34	12.86	5.02
Log K_{oc} for Untreated soil	Aq.		3.49	2.96	2.36
Log K_{oc} for Treated soil	Aq.		3.54	2.88	1.99
Log K_{oc} for Untreated soil	STE		2.80	2.75	2.35
Mass reduced (batch)	Aq.	µg/g	212.29±1.67 (73%)	7.20±0.28 (42%)	3.21±0.25 (17%)
Mass reduced (batch)	STE	µg/g	91.30±2.02 (35%)	6.30±0.17 (30%)	2.84±0.35 (14%)
Mass desorption (batch)	Aq.	µg/g	15.67±0.15 (7%)	3.59±0.16 (49%)	0.58±0.03 (18%)
Mass desorption (batch)	STE	µg/g	18.27±0.45 (20%)	4.72±0.09 (74%)	0.58±0.03 (20%)
Mass reduced (column)	STE	µg/g	125.58 (14%)	—	—
Mass desorbed (column)	STE	µg/g	30.71 (25%)	—	—

The adsorption behaviour of caffeine is illustrated in Figure 6.1b, 6.2b and Supplementary material Figure S6.2, and indicates that caffeine adsorption capacity increased in the first 1.5 h (from 0.0 to 5.8 µg/g). The aqueous solution pH for caffeine did not vary greatly during equilibration period (6.2-6.4), however, the K_d values (19.72 and 22.16 for treated and untreated soils, respectively) for caffeine demonstrated its potential for sorption onto the soil. A maximum C_t/C_0 of 0.57 for caffeine was attenuated in 24 h. As with P, caffeine exhibited similar attenuation behaviour in contact with treated and untreated soil during the 24 h equilibration time.

Conversely, saccharin showed more limited sorption in aqueous solution than P and caffeine with K_d of 5.98 and maximum C_t/C_0 of 0.83 occurred at 24 h for untreated soil. During the equilibration period, saccharin pH did not vary (6.2-6.3), apart from the initial rise in the pH from 5.5 to 6.2 in the first 0.5 h. Saccharin exhibited an early high affinity for the attenuation process, from 0.0 to 3.5 µg/g at 1.5 h for untreated soil and from 0.0 to 3.0 µg/g at 0.5 h for treated soil (Figures 6.1c and 6.2c). Attenuation curves of saccharin exhibited great separation between untreated and treated soils (Figure 6.2c), suggesting that saccharin attenuation by soil included microbial degradation.

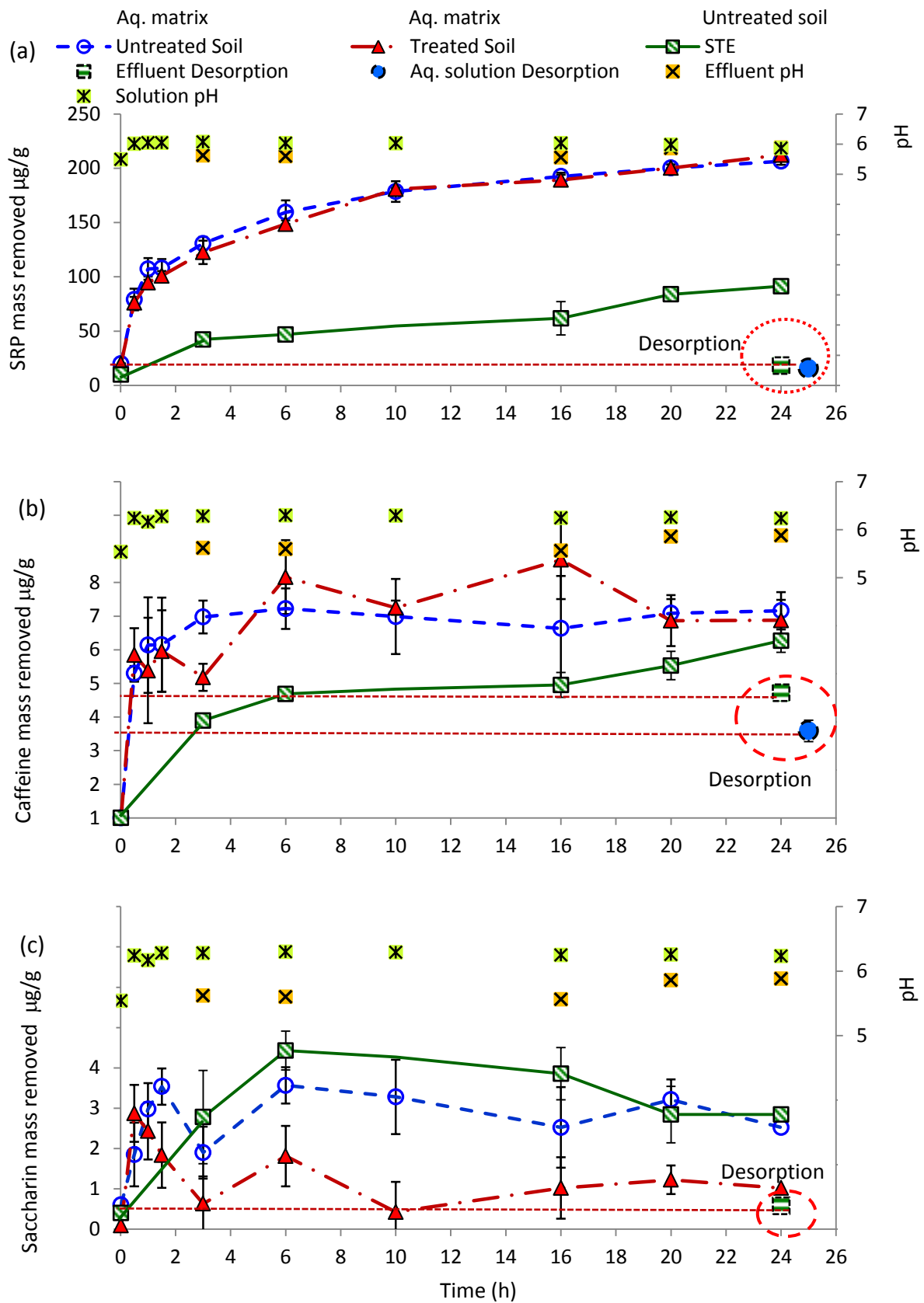


Figure 6.2: pH and substances mass removed $\mu\text{g/g}$ including 2xS.E. for (a) SRP, (b) caffeine and (c) saccharin. Desorption mass of effluent and aqueous solution are in dotted circles.

6.3.2 The attenuation of test substances present in STE by untreated soil (batch equilibrium)

Sorption behaviours of P, caffeine and saccharin with the untreated soil in the effluent matrix are presented in Figures 6.1, 6.2 and S6.2. Effluent pH did not vary greatly (5.6-5.9) during the 24 h equilibration period. The soil had a strong affinity to sorb effluent P and a lesser affinity for caffeine and very weak affinity for saccharin. The K_d value in the effluent matrices were 20% and 50% of that in aqueous solution for P and caffeine, respectively, while the saccharin K_d remained more similar in both matrices (Table 6.1). Phosphorus mass reduced (batch equilibrium) from the effluent was 91 $\mu\text{gP/g}$, which was much less compared to 212 $\mu\text{gP/g}$ in aqueous solution despite similar pH ranges (5.6-5.9 and 5.8-6.0 in effluent and aqueous solution, respectively; Figure 6.2a). Caffeine mass reduced from the effluent by the soil was 6.3 compared to 7.2 $\mu\text{g/g}$ soil in the aqueous solution and saccharin mass reduced was 2.8 and 3.2 $\mu\text{g/g}$ in the effluent and the aqueous solution, respectively. While attenuation of P was greatest in aqueous solution compared to STE, caffeine and saccharin attenuation was more similar in both media.

6.3.3 Desorption of test substances (untreated soil)

The desorption tests aimed to investigate whether a substance was reversibly or irreversibly adsorbed by the untreated test soil and thus inform on the leaching potential. Desorption tests showed that the mass of P and caffeine desorbed from STE was greater than the mass desorbed from the aqueous solution matrix (Table 6.1). Approximately 20% of the adsorbed P was desorbed from the effluent compared to 7% from aqueous solution, while for caffeine 74% and 49% were desorbed from the effluent and the aqueous solution, respectively. Saccharin desorption from the effluent and aqueous solution matrices were comparable 20% and 18%, respectively (Table 6.1). Saccharin had the lowest desorption value (0.58 $\mu\text{g/g}$ soil), consistent to both effluent and aqueous solution.

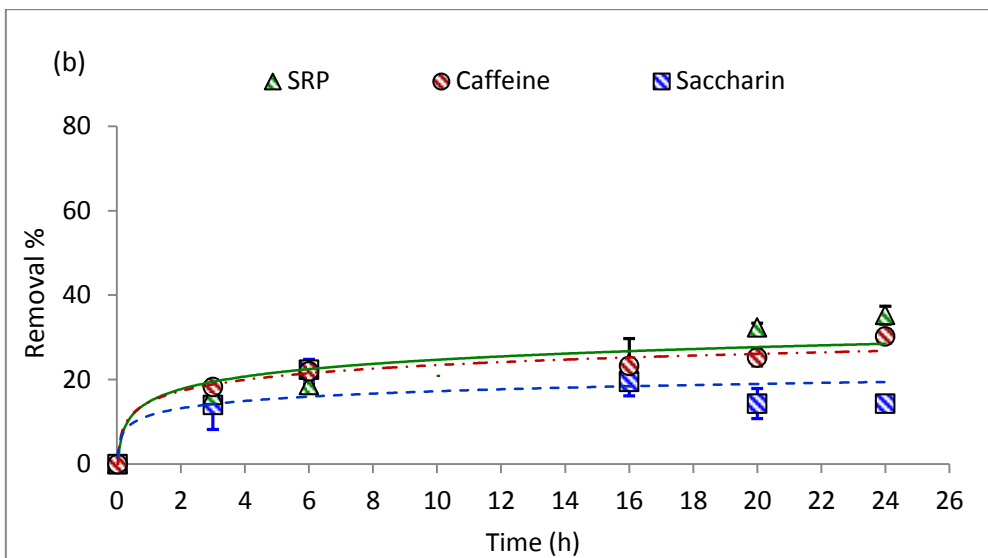
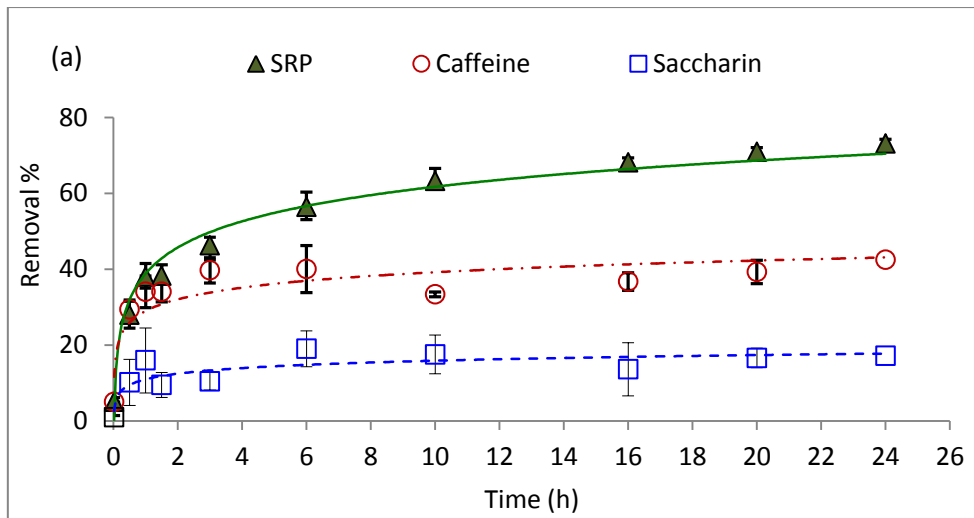


Figure S6.2: Removal % (abiotic and biotic) of untreated soil for SRP, caffeine and saccharin including 2xS.E. in (a) artificial aqueous solution, (b) Septic tank effluent.

6.3.4 Septic tank effluent P sorption to soil (column experiment)

Figure 6.3 shows the sorption and desorption of P in STE and the break-through curve for P at initial concentration of 19.2 mg/l, soil mass 31.5 g, flow rate of 0.3 ml/min and pH for the leachate leaving the column (7.06-8.20). The cumulative P removed from the column was 3.96 mgP = 125.58 $\mu\text{gP/g}$ soil at 31 PVs (28.7 h) from the effluent. Figure 6.3 showed that after the switch from effluent to background electrolyte (zero P concentration) at 31 PVs (29 h), the collected eluent P concentration continued to increase to its maximum of 10.1 mg/l at 35 PVs (32 h) after which, P concentration declined to reach its minimum of 3.5 mg/l at 55 PVs (51.7 h). Approximately 25% of the adsorbed P mass was desorbed from the column 0.97 mgP = 30.71 $\mu\text{gP/g}$ soil was leached. The subsequent Cl pulse breakthrough experiment gave a calculated Péclet number of 538 suggesting that solution transport inside the column was of a convective nature.

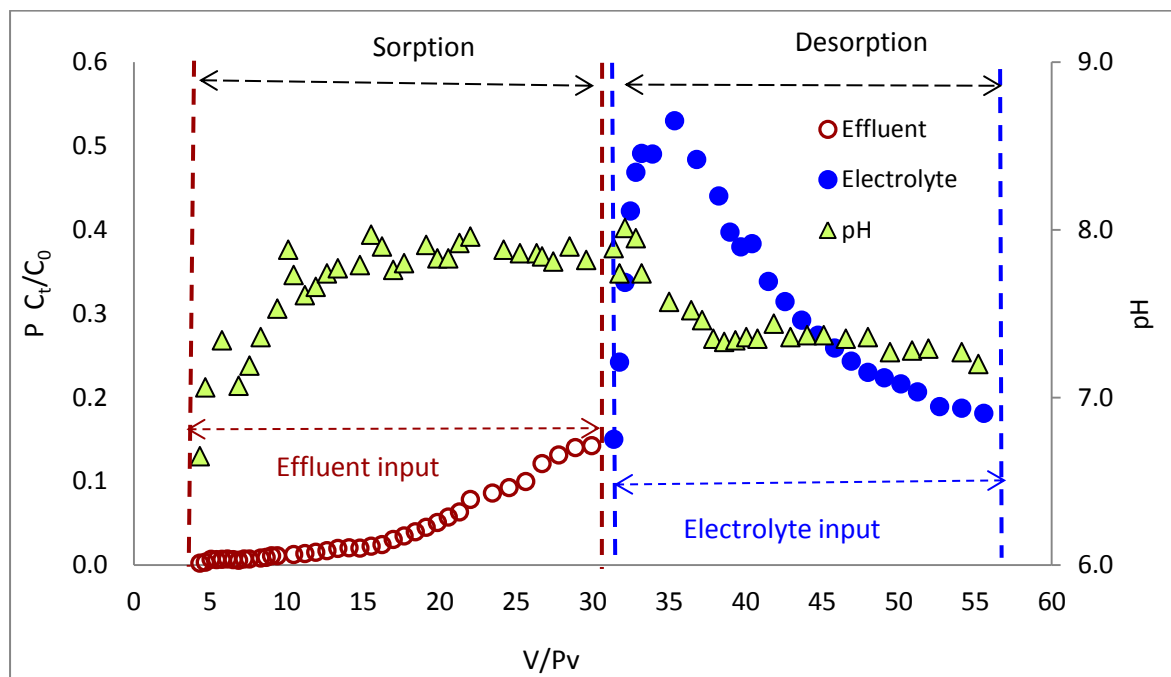


Figure 6.3: Adsorption/desorption kinetics of septic tank effluent phosphorus (P) in column reactor and the corresponding pH.

6.4 Discussion

This study aimed to evaluate the solid: solution partitioning of three solutes often found in wastewaters using batch and column sorption and desorption methods comparing interactions of aqueous and real STE matrices with one test soil.

6.4.1 Substance behaviour in aqueous solution (batch equilibrium)

Sorption results indicate that P, caffeine and saccharin had a strong, moderate and low tendency to partition from the aqueous to the solid phase, respectively. In the aqueous matrix, there were similarities in caffeine and saccharin's sorption behaviours as both reached their maximum adsorption within 3 and 1.5 h of equilibration, respectively in untreated soil (Figure 6.2). There was also a distinct difference in their attenuation behaviour between different soil treatments (as defined by mass removed from solution). Caffeine's attenuation curves over time for untreated and treated soils had little separation (Figure 6.2b) suggesting that only a very small proportion of caffeine attenuation was associated with microbial degradation during the 24 h equilibration, and hence was dominated by abiotic sorption. Conversely, large separation between the attenuation curves for saccharin with untreated and treated soils suggested that a substantial proportion of the saccharin was degraded by soil microorganisms, which is in agreement with Buerge et al. (2011). Schleheck and Cook (2003) suggested that saccharin was a source of carbon and energy for microorganisms which was readily converted to cell material, sulphate, ammonium and CO₂. Conversely, caffeine degradation by microorganisms involved a slow rate enzymatic process of the demethylation of caffeine compound (Middelhoven and Bakker, 1982).

The mobilization/migration property of a chemical in soil is related to the chemical's hydrophobic characteristics and its distribution in a media (Swann et al., 1983), and is expressed by the chemical's K_d and $\log K_{oc}$ values, in which low values show high mobility in soil solution phases. Caffeine K_d and $\log K_{oc}$ values produced in this current work for untreated soil (Table 6.1) are in agreement with that produced by Karnjanapiboonwong et al. (2010) of 18.5 cm³/g and 3.89, respectively, for similar sandy loam soil. Our results also showed that caffeine had greater values of K_d and K_{oc} than saccharin (Table 6.1), suggesting caffeine's stronger affinity for soil surfaces relative to weaker for saccharin and that saccharin would readily leach from soil. The low adsorption potential of saccharin can be explained by its small molecular weight of 183.18 g/mol, small surface area, therefore hydrophobic

interaction with soil is not likely to occur (Hofman et al., 2015). Moreover, a saccharin molecule contains 3 oxygen atoms, an amide and sulphide group, all of which may be involved in the formation of hydrogen bonds with soil particles. Therefore, hydrogen bonding would be the more likely process to occur for saccharin adsorption to soil, and thus, saccharine would be in competition with water molecules over hydrogen bond binding sites on soil particles.

The results of treated and untreated soil also suggested that saccharin attenuation may be dominantly due to microbial degradation rather than chemical or physical adsorption, which is in agreement with Robertson et al. (2013). However, a complete degradation did not occur during the experimental period suggesting that saccharin may leach to surface or groundwater. Saccharin leaching was shown by Robertson et al. (2013), who reported saccharin concentrations in groundwaters similar to that found in STE. Saccharin retention curve on soil surfaces (Figure 6.2c) suggests that saccharin is the least retained compound of the tested substances and that the soil under our experimental conditions was not effective in saccharin removal. Thus, the presence of saccharin in surface and groundwaters not only can indicate anthropogenic activity but also may be used as a tracer for sewage effluent.

Conversely, the stronger adsorption of caffeine (moderate values of K_d and $\log K_{oc}$; Table 6.1) can be explained by caffeine being a hydrophilic organic base: pKa 14 at 25°C (Clarke, 1986), moderately soluble in water: 2 g/100 ml (Pavia et al., 2005). The $\log K_{oc}$ values (2.75-3.59) for caffeine obtained in this study are in agreement with those reported by Karnjanapiboonwong, et al. (2010) of 3.89 and 2.87 for sandy loam and silt loam soils, respectively. Caffeine is a small organic molecule and contains 2 oxygen atoms, so its attenuation and sorption mechanisms are not likely to be through hydrophobic interactions, but rather by hydrogen bonding, cation exchange or surface complexation (Nam et al., 2014), as well as microbial degradation.

Phosphorus adsorption to soil particles was explained by Frossard et al. (1995) as an initial rapid reaction comprising ligand exchange between P and the reactive soil surface groups followed by slow cation exchange reactions involving soil clay crystal lattices. In this current work, adsorption of P was the greatest of all three substances tested with K_d of 81 and 90 cm³/g for untreated and treated soils, respectively. The high affinity of soil to adsorb P was due to soil iron (Fe) and aluminium (Al) contents, 5923 and 7824 mg/kg, respectively (Table S6.1), which resulted in 73-75% of P removed from aqueous solution. Other studies reported that P adsorption was closely related to

the soil extractable Al and Fe and that soil acidity increased P adsorption as P was retained with Fe^{2+} , Fe^{3+} and Al^{3+} minerals on the soil particles (Roy and De Datta, 1985; Sakadevan and Bavor, 1998; Gichangi et al., 2008; Gill et al., 2009b).

6.4.2 Substance behaviour in septic tank effluent

Saccharin had similar K_d values and similar mass adsorbed for effluent and aqueous solution alike in untreated soil (Table 6.1 and Figure 6.2) suggesting that the limited sorption that occurred was not greatly affected by the matrix. Conversely, caffeine sorption behaviour differed between effluent ($K_d = 12.86$) and aqueous solution ($K_d = 22.16$; Table 6.1 and Figure 6.2). The low soil affinity for caffeine in the effluent resulted in 12.5% less caffeine mass removed from the effluent compared to aqueous solution (Figure 6.2b). Phosphorus in the effluent also had lower K_d value than in aqueous solution (Table 6.1) resulted in a 56%, less effluent P was adsorbed, suggesting that components of the complex matrix composition of the effluent such as metals, bacteria and DOC were in competition with P and caffeine for soil adsorption sites, which is in agreement with Grolimund et al. (1995).

6.4.3 Substances desorption behaviour

In aqueous solution, the adsorption and desorption of caffeine of 7.20 and 3.59 $\mu\text{g/g}$, respectively, suggests that caffeine may have the potential for great mobility through soil. However, phosphorus sorption seemed to be a dominantly irreversible processes as 73% of P was adsorbed (aqueous matrix) and only 7% of that P sorbed was subsequently desorbed over 24 h. Desorption in the aqueous matrix followed the order: caffeine 49% > saccharin 18% > P 7%, suggesting that caffeine and saccharin were more weakly and reversibly sorbed than P. However, the high P accumulation on the soil resulted in a proportionally higher concentration of P to desorb than caffeine and saccharin, which was confirmed by the mass desorbed from effluent ($\mu\text{g/g}$ soil): P (18.3) > caffeine (4.7) > saccharin (0.6) $\mu\text{g/g}$ soil, which may be attributed to their different initial concentrations and mass loading. Thus, soil condition may favour P desorption implying the likelihood of P to leave the soil and contaminate groundwaters in higher concentrations.

6.4.4 Effluent phosphorus adsorption and behaviour (column and batch techniques)

The aim of the column method was to utilise conditions more realistic of soil to solution dynamics for soil soakaway systems compared to the batch equilibrations. The highest level of saturation reached in the column for P ($C_t/C_0 = 0.53$; Figure 6.3) was considered to be low compared to batch method, and can be attributed to the high SRP concentration and the high soil-effluent solution pH (7-8). The low C_t/C_0 adsorption ratio may also be due to low soil clay content of 7% which may limit the presence of active adsorption sites (Olsen and Watanabe, 1956). A combination of elevated P concentration and low soil clay contents can cause soil adsorption sites to become rapidly saturated with the consequence that untreated effluent travelling further for new active sites (Robertson et al, 1998). Thus, pollutants of faecal and black water origin in the effluent may reach and contaminate surface and groundwaters.

In this study, soil affinity to adsorb P from STE was apparent when comparing batch and column adsorption methods. In the column method, a constant flow of effluent was supplied to the system and the displaced eluent was ejected. This contrasts the batch method, where the lack of removal of eluent imposes an equilibrium that can influence, and potentially limit the amount of P adsorbed. Thus, supplying an effluent with a constant composition as in the column, may suggest that adsorption should be higher than in the batch equilibrium (Limousin et al., 2007). Conversely, in the batch equilibrium, P remains in the effluent and may compete with other effluent constituents for soil binding sites, which can suggest lower P adsorption level (Grolimund et al., 1995). The shaking of soil-effluent mixture in the batch method may have increased the collision and the contact of effluent-soil particles leading to greater P adsorption (Limousin et al., 2007). However, in the column experiment, a constant supply of STE with high P concentration may have contributed towards a fast saturation of adsorption sites, which led to a lower adsorption % in the column system than the in batch method (14% compared to 35%, respectively). The convective nature of the flow inside the column suggested that the slow sorption reaction was not due to the fast flow but was a result of effluent and soil interaction.

When considering effluent P reduction, it was found that 35% of effluent P was removed by batch method, while 73% of P removal was from aqueous solution (batch method). The high % of P removal from aqueous solution can be attributed to the lack of competition with other compounds

over soil adsorption (Limousin et al., 2007). In the column method, 25% of adsorbed P (3.96 mgP = 125.58 $\mu\text{gP/g}$ soil) was desorbed from the soil (Table 6.1). In all three techniques, the ability of soil to immobilise P from solutions was great until P concentration exceeded the ability of the soil to retain it, which suggests that a significant proportion of P if not retained or taken up by plants, may end up in surface and groundwaters. Thus, soil P sorption capacity should be considered when designing new septic tank systems, and in old systems, it may be necessary to treat STE chemically or biologically to reduce P impact when soil P sorption capacity is relatively low. The installation of additional treatment such as mechanical aeration or filter systems may be necessary to reduced STE pollutants and accelerate microbial degradation of organic matter.

6.5 Conclusion

Sorption and desorption data for phosphorus, caffeine and saccharin present in STE on soil particles by batch equilibrium and the column experiment, revealed that soil affinity to P sorption was greatest. Caffeine had greater value of distribution coefficient K_d than saccharin, suggesting that caffeine's adsorption ability to soil particles was greater than saccharin. However, a complete attenuation did not occur during a 24 h equilibration period, suggesting that saccharin and caffeine leaching potential to surface and groundwaters. The experimental data also suggested that the adsorption of saccharin on soil particles was particularly weak, and the soil under the experimental conditions was not effective in the removal of saccharin from both STE and aqueous solution. Conversely, phosphorus attenuation was dominated by adsorption processes and its K_d value was the greatest of all 3 substances. The fraction removed of all 3 substances in the aqueous matrices was greater than in STE, suggesting that the complex composition of STE reduced the adsorption of these substances and that other substances present in STE may be competing over soil binding sites. Thus, soakaway soil may not provide a complete removal of pollutants during STE secondary treatment in the soil, increasing the risk of a proportion of effluent contaminants and pollutants reaching groundwater untreated. This was confirmed by the desorption data, which revealed that for STE P had the greatest leaching potential followed by caffeine. Thus, soil condition may favour P and caffeine desorption suggesting the likelihood that P and caffeine would reach surface and groundwaters. Moreover, the presence of saccharin and caffeine in surface and groundwaters can indicate anthropogenic source and may be considered as tracers for sewage effluent in watercourses.

Supplementary material: Detailed method for saccharin and caffeine detection:

This analytical procedure describes the sample preparation for liquid chromatography tandem mass spectrometry (LC-MS/MS) method for the determination of the artificial sweetener: saccharin and Caffeine.

450µl of sample was transferred to an LC vial and 50µl of a 1µg/ml mixed internal standard solution containing Saccharin-¹³C₆ and Caffeine-d₉, which was added.

Analysis was carried out using an Agilent 1100 series LC system interfaced to a Waters Quattro Ultima Platinum triple quadrupole mass spectrometer operating in both positive and negative electrospray ionisation (ESI) modes. The HPLC-MS/MS system was controlled by MassLynx™ software and data processing was carried out using MassLynx™ 4.1 software.

The HPLC column was a Waters XSELECT CSH C18 3.5µm x 2.1mm x 150mm. The mobile phase consisted of 95% methanol/5% water/10 mM ammonium acetate in channel A and 95% water/5% methanol/10 mM ammonium acetate in channel B at a constant flow rate of 0.2 ml/min. The HPLC was programmed to hold 95% channel B for 2 minutes followed by a linear decrease to 50% channel B over 5 minutes, then held at 50% for 8minutes before returning to 95% with a runtime of 22minutes. The injection volume was 5µl.

The electrospray voltage was set at 3.0 and 1.0 kV for positive and negative modes respectively. The desolvation and source temperatures were set at 350 °C and 120 °C in positive mode and 400 °C and 120 °C respectively in negative mode. Nitrogen was employed as the desolvation and cone gas with a flow rate set to 500 L h⁻¹ and 70L h⁻¹ respectively. The collision gas was argon at a pressure of 2.7 x 10⁻³ mBar.

Ions monitored in –ve mode

Ions monitored	Cone voltage	Collision energy	Compound
181.90 > 62.00	40	13.0	Saccharin
181.90>105.80	55	14.0	Saccharin
187.80>105.60	55	14.0	Saccharin- ¹³ C ₆ (1,2-(Benisothiazol-13C6)-3(2H)-one 1,1-Dioxide)

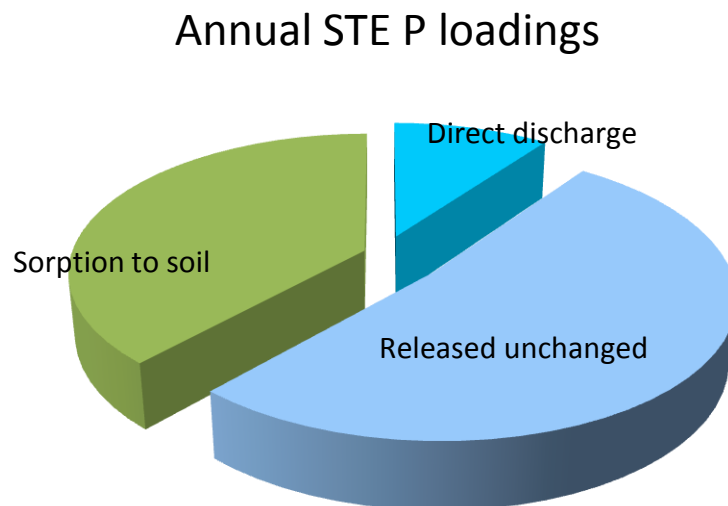
Ions monitored in +ve mode

Ions monitored	Cone voltage	Collision energy	Compound
194.90 >110.10	40	19.0	Caffeine
195.10 > 138.10	60	15.0	Caffiene
203.80 > 143.80	60	15.0	Caffeine-d ₉ (1,3,7-Trimethyl-d ₉)

Chapter 7

Phosphorus annual *per capita* loads from septic tank effluent and the associated impact on soakaway soil and receiving waters

Graphical Abstract



Estimated distribution of septic tank effluent annual P loadings

Abstract

Nutrient transfer to fresh waters from septic tanks (ST) has the potential to cause detrimental impacts on stream eco-systems, particularly during ecologically sensitive periods of low flow. The impact of septic tanks on streams is magnified when they act as cumulative, multiple points of pollutants in catchments; giving a potential to transform adjacent stream water from oligotrophic to eutrophic states. Here, we provide a synthesis of this study existing and new data on the potential of septic tank effluent (STE) to impact stream waters. Soil and stream sediments from ST sites were also investigated for bioavailable phosphorus (BAP) concentrations. Bioavailable P in stream sediments and soakaway soils receiving effluent discharges indicated elevated P concentration levels (ranged 26-99 mgP/kg and 26-320 mgP/kg, respectively). The cumulative effect of STE was apparent in reduced soil pH and increased soil BAP concentrations, with concentrations in older ST systems >12 times of those in newly installed systems (320 mgP/kg and 26 mgP/kg, respectively). More than 45% of stream water total P was present in the dissolved form of P, of which >58% was in the soluble reactive form. Phosphorus annual loadings from STE to soakaways were calculated based on mean effluent data to be 0.797 and 0.956 kgP/person/year for water use of 150 and 180 L/person/day, respectively. The annual P loadings were also modelled on the spatial and temporal effluent data (median, top 5 percentile and 95 percentile), which revealed that effluent P loads were influenced by water use and that a large proportion of P may reach watercourses even with fully functioning ST systems. The findings of this work suggest and implicate ST discharges in causing continuous accumulation of P in the soakaway soil, increasing the risk of P leaching to watercourses and influencing stream water quality. It is necessary to implement appropriate measures to reduce ST P transfer to freshwaters to achieve the good chemical and ecological status in freshwaters.

Key words: Phosphorus annual loading, Detergents P loading, P leaching, Septic tank effluent, Bioavailable phosphorus

7.1 Introduction

Eutrophication of fresh water bodies caused by algal growth is a major health and ecological problem around the world. It is a result of the increased levels of nutrients in fresh water systems caused by diffuse pollution from the intensifying use of fertilizers in agricultural practices (Smith et al., 1999; Kurz et al., 2001; Haygarth et al., 2005) and from point source of pollution including septic tank (ST) discharges (Withers et al., 2011). Although nutrients like nitrogen (N) and phosphorus (P) are important for algal growth, P is considered the most limiting factor in this process. A small increase in P concentration in a water body can promote undesirable algal growth causing deterioration in water quality (Dodds et al., 2002). Small point sources such as STs also play their role in increasing stream nutrient levels through the persistent direct discharge of untreated effluents, or from the discharge of the partially treated effluents via soakaway discharges (Macintosh et al., 2011). O’Keeffe et al. (2014) suggested that 76% of ST in Scotland discharged to soakaway or land, while 21% of ST discharged to inland water. Septic tanks often fail due to their limited capability for removing nutrients and pathogens. They also fail due to aging, users’ neglect, poor management and lack of maintenance. Failure of septic tank systems increases the risk of contaminants entering stream waters which pose risks to human health and impact on water quality (Jarvie et al., 2006; Withers et al., 2012 and 2013).

The high abundance of microorganisms and high concentrations of metals and nutrients normally present in STE are expected to be attenuated by filtration, absorption and adsorption to soil within soakaway systems. However, many old ST systems are sited on unsuitable soils and the ability of soakaway soils to remove pollutants from the effluent becomes increasingly exhausted over time (Day, 2004; Jordan et al., 2005) causing effluent contaminants to move further from the soakaway and eventually may reach ground and surface waters (Robertson et al., 2013). It is important to estimate P loads from STE inputs to watercourses to assess effluent impacts, then prioritise and target the effective mitigation measures. Evaluation of ST pollution is often conducted in terms of the annual load of an environmentally targeted element such as phosphorus (P) for its contribution to eutrophication of surface waters.

A better understanding of ST P loads to stream waters and the contribution of effluent direct discharge is required to influence policies and decision making to control stream nutrient enrichment. Most literature uses export coefficients for estimating P losses from ST, which rely on

data from the literature. In this work soil and effluents from ST sites were investigated with the aims to: 1) Examine the effect of prolonged domestic sewage effluent exposure on soil quality; 2) Investigate P loads from STE to soakaway using synthesised effluent data.

7.2 Materials and Methods

7.2.1 Study sites

Septic tank effluents were sampled and tested for their elemental composition from conventional residential septic tank systems serving permanently occupied houses in the N.E. Scotland during 2014 and 2015 from 32 sites (Chapter 4) to provide spatial variation. Sampling regime varied from one visit to 5 visits for some of the sites for temporal variation (Chapter 5). Twenty five percent of ST sites were located within 0-10 m from watercourses of which 10% of the tanks discharged their effluent directly to watercourses without soakaway secondary soil treatment.

7.2.2 Soil sample collection and analysis

Soil and stream sediment samples were collected from 8 ST sites where soakaway locations were known through consultation with householders and visual observation of effluent discharge. Site 1, 2 and 3 discharged their effluent to soil bed above the surface, while site 4, 5 and 6 discharged their effluent to soakaway soil systems underneath the surface (Table 7.1). Site 7 and 8 discharged their effluent directly to stream waters without soil treatment systems, thus stream sediments were collected from location before and after the tank discharge. Soil samples were also obtained at the locations before and after the tank from a depth of 30 cm and were kept in a cold box during transportation to the laboratory and kept at 4 °C till processing.

The soil and stream sediment samples were air dried, passed through a 2 mm sieve, and stored in air-tight containers until analysis. Soil pH in water was determined using Hanna pH 210 meter (Standard Test Method for pH of Soils, 1995). Bioavailable phosphorus (BAP) was determined using iron-oxide impregnated filter papers by allowing BAP of the soil to be attached to iron-oxide paper (area =19.6 cm²) (Lin et al., 1991; Robinson et al., 1994; Chardon 2008). One g of soil or sediment and iron oxide paper was shaken in 80 ml of 0.01M of CaCl₂ on an orbital shaker in the dark for 16 hours at room temperature at 200 rpm. The iron oxide papers were then gently rinsed with Millipore waters and the sorbed P on the filter paper was extracted in 50 ml of 0.1M H₂SO₄ by shaking for 1 h. The resulting P in the solution was quantified as soluble reactive P (SRP) by colorimetric analyses using automated colorimetry (San++ analyser, Skalar, Breda, Netherlands) and termed BAP as mgP/kg dry matter.

Table 7.1: Septic tank sites, discharge information, effluent P concentration, bioavailable phosphorus (BAP) concentration and P accumulation in each site soakaway soil.

Site no	Tank age	Discharge nature	Effluent [P] mg/l	soakaway soil BAP (mg/kg)	P accumulation in soil (mg/kg)
1	78	Above soil surface	19.11	320	166
2	12	Above soil surface	23.13	202	188
3	60	Above soil surface	16.07	165	155
4	15	Beneath soil surface	22.68	126	68
5	75	Beneath soil surface	8.07	100	77
6	2	Beneath soil surface	11.39	26	5
7	35	Direct to stream water ^a	4.92	99	85
8	20	Direct to stream water ^b	13.08	26	15

a Stream with low level of dilution

b Stream with high level of dilution

7.2.3 Phosphorus annual per capita loading estimation

The phosphorus loads to soakaway from STE were estimated by multiplying mean TP concentration (Chapter 4) with STE flow rate (Gross et al., 2005), using standard scenario of effluent discharge volumes 150-180 l/person/day (US EPA 2002; Gilmour et al., 2008). It was not possible to determine effluent flow rate accurately due to the different nature of effluent discharges at different sites and at different times. Therefore, in estimating effluent P load for an average household occupancy of 2.7 persons (obtained from catchment survey; Appendix 1) and minimum effluent retention time of 24 h (Seabloom et al., 2005; The Environment Agency, UK, 2012) for two water use scenarios were considered (water use of 150 l/person/day: scenario 1 and water use of 180 l/person/day: scenario 2). For scenario 1, effluent flow rate was calculated to be 405 L/tank/day and TP load = TP mg/l x 405 L/tank/day, giving a TP load of 0.797 kgP/person/year produced from the effluent alone (sludge was not included). Phosphorus annual loading scenarios were also determined using STE spatial and temporal P concentrations combined (Chapter 4 and 5) and P loadings were modelled on the median, the top 5 percentile and the bottom 5 percentile of effluent P concentration data. The different scenarios of annual P loadings were produced and the proportion of the direct effluent discharge (10% ST in this sample) and soil P removal (35% batch system: 24h, and 14% column experiments system: 51h for silty loam test soil; Chapter 6) were considered and calculated.

7.3 Results

7.3.1 Bioavailable P (BAP) in soakaway soils

The concentration of BAP in soakaway soil and stream sediments situated after receiving STE seemed to have been enriched (elevated BAP) relative to soils and sediment situated before the tank (Figure 7.1). The elevated P was particularly profound in open bed soakaway systems such as in site 1, 2 and 3. Soil enrichment after the sewage loading ranged from 2-14 times that of soil located before the tank. It appeared that the level of BAP in soakaway soil may have been affected by the age of the soakaway as the smallest level of BAP concentration of 26 mgP/kg was associated with a relatively newly built house served by a 2 year old tank (site 6), while the greatest BAP concentration of 320 mgP/kg was associated with an older soakaway receiving effluent from a 78 year old tank (site 1).

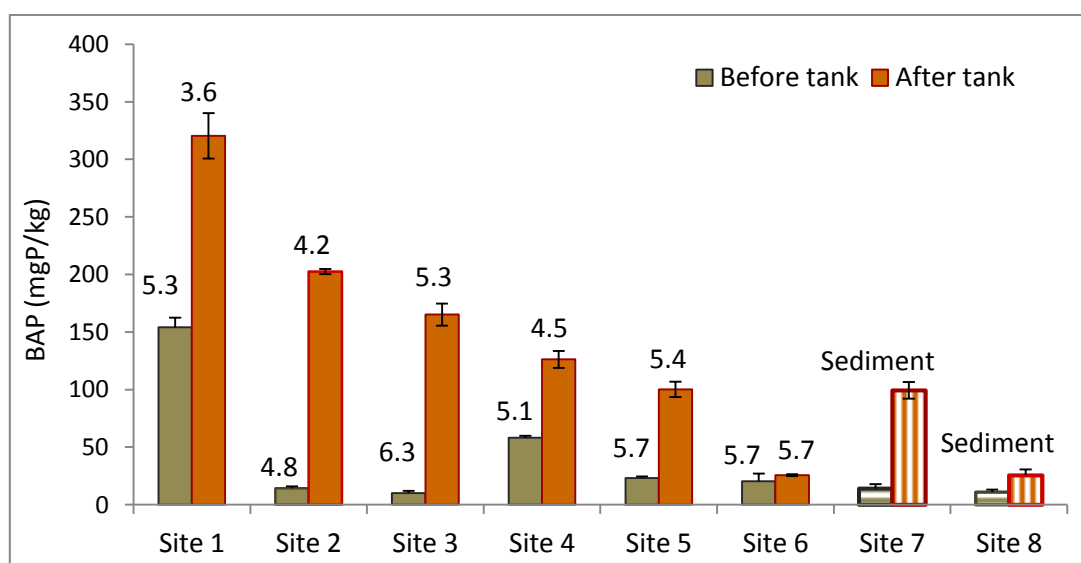


Figure 7.1: Bioavailable phosphorus concentration in soil located before the source and in soil after receiving STE including 2xS.E. Site 6 is a new dwelling with a newly installed tank and site 7 and 8 are stream sediments before and after STE direct discharge. The values above the columns are soils pH before and after the tank.

Stream sediments also exhibited elevated concentration of BAP downstream from the source relative to upstream sediment with P enrichment of 2-7 times in downstream sediments (Figure 7.1). Soil pH ranged 4-6 and 3-6 before and after receiving STE, respectively, and the most acidic soil observed after receiving STE was associated with older soakaways of site 1 (Figure 7.1). Conversely,

soil pH before and after the tank did not vary for the more recently installed ST at site 6, suggesting that the increase in soil acidity was associated with the prolonged sewage loading.

7.3.2 Phosphorus loadings (spatial and temporal STE P concentrations)

Figure 7.2 shows the spatial (as percentiles) and the temporal (as standard errors) variation of STE samples population for TP concentrations (Chapter 4 and 5) with the bold curve is the mean TP and the dotted lines are the mean \pm standard of errors. The median value for TP was 10.8 mgP/l, the top 5 percentile was 30.5 mgP/l and the 95 percentile (bottom 5 percentile) was 5.3 mgP/l, while the mean TP value was 14.55 mgP/l.

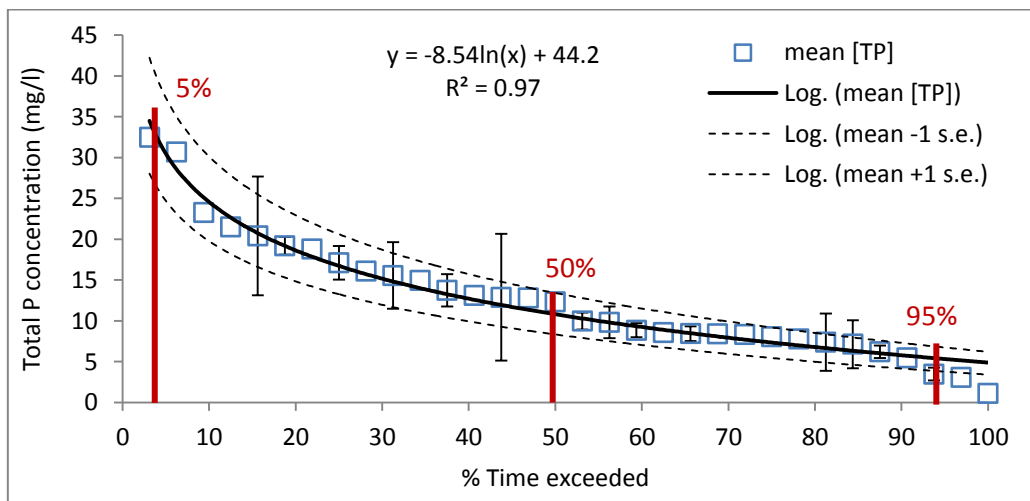


Figure 7.2: Septic tank effluent spatial and temporal variability for TP concentration against time exceeded with 1S.E. standard of errors. The top 5 percentile, median and 95 percentiles are highlighted in red.

Phosphorus loadings scenarios calculated from the mean and the median concentration values are listed in Table 7.2, and P loadings were increased when water use was increased from 150 to 180 l/person/day.

Table 7.2: Estimated total phosphorus loadings (kgP/person/year) from STE to the soakaways based on: mean TP concentration of 14.55 mg/l, median TP concentration of 10.08 mg/l and daily water use of 150 and 180 l/person/day, average household of 2.7 people and direct effluent discharge of 10%.

Daily water use	Mean [P] = 14.55 mg/L		Median [P] = 10.8 mg/L	
	150 l/person	180 l/person	150 l/person	180 l/person
	Scenario 1	Scenario 2	Scenario 1	Scenario 2
Effluent annual P loadings	0.80±0.05	0.96±0.06	0.60±0.13	0.71±0.16
P direct discharge (10%)	0.08±0.01	0.09±0.01	0.06±0.01	0.07±0.01
Detergents P loading%	19%	16%	25%	21%

The annual P loadings scenarios based on the spatial and the temporal P data (Figure 7.3) illustrates P loads to the soakaways from STE alone without including P fraction from the sludge, modelled on the median P, the top 5 percentile and the bottom 5 percentile P concentrations, and for water use of 150 and 180 l/person/day. The estimated annual P loadings to the soakaways were 0.60-0.71, 1.67-2.00 and 0.29-0.35 kg/person/year for median P, top 5 percentile and 95 percentile, respectively. However, when considering the spatial data mean TP concentration, annual P loadings to the soakaways were increased relative to the median P concentration (Table 7.2). Detergents P loading in STE was estimated (Chapter 3) and reported by Richards et al. (2015) as 0.154 kg P/person/year of which the dishwasher contribution was 0.147 kg P/person/year (based on survey results: 78% of dwellings use dishwasher detergents; Chapter 3). The estimated detergents %P loading in STE was 16-25% of the total P (Table 7.2). Phosphorus loading scenarios were explored further to consider the proportion of the effluent that directly discharged to stream waters (10%, Chapter 3) and the amount of P that may be expected to be removed by the silty loam test soil (Chapter 6), (Figure 7.3).

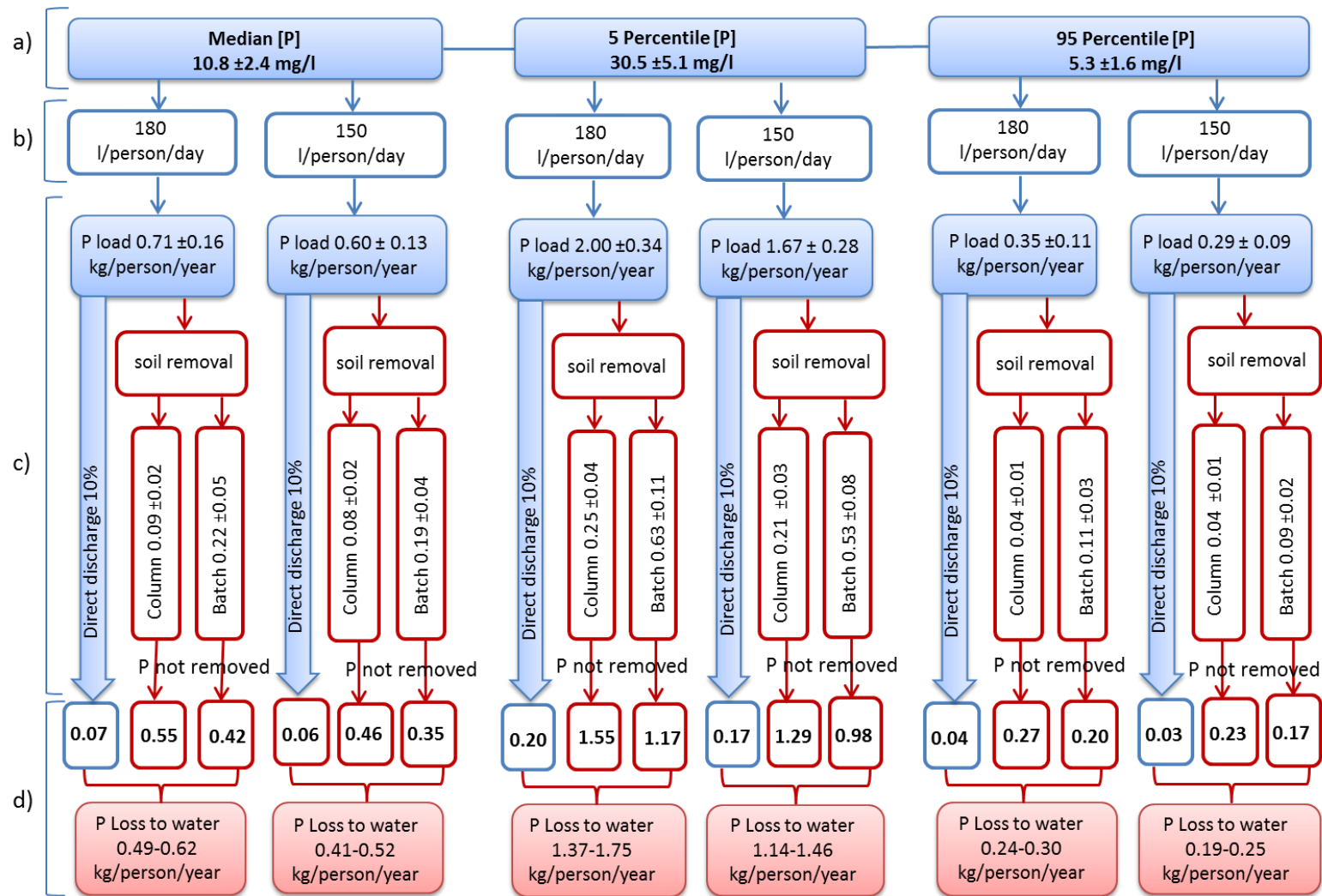


Figure 7.3: A flowchart of annual P loadings scenarios from septic tank effluents, where a): spatial and temporal concentration of effluent P; b): different daily water use/person; c): P loadings to soakaway soil and possible effluent pathways (10% direct discharge and 90% directed to soil removal: column 14% and batch equilibrium 35% for silty loam test soil) and d): predicted scenarios for potential P loads losses to watercourses.

7.4 Discussion

The primary aims of this study were to investigate the influence of STE irrigation on soil chemical properties in soakaway system and to calculate P loads from STE to soakaways using synthesised effluent P data, and considering the proportion of direct discharge. Septic tank data (Chapter 4, Table 4.1) shows that domestic sewage effluents were highly enriched in nutrients relative to their immediate stream waters. A large percentage of nutrients in STE were present in the soluble form (mean TN concentration of 68 mgN/l was dominated by ammonium-N ($\text{NH}_4\text{-N}$) 80%, while 58% of mean TP concentration of 14.55 mgP/l was present in the form of SRP of 8.4 mg/l). The mean values of TP and SRP (Chapter 4, Table 4.1) were greater than the mean values of 4.6 and 3.2 mg/l, respectively, reported by Withers et al. (2011).

The long term loading of STE to the same soakaway soil system can affect soil's ability to remove pollutants, as it becomes increasingly saturated with pollutants causing soil adsorption capacity to diminish with time (Jordan et al., 2005). As a result, many contaminants spread further away from the soakaway towards ground and surface waters (Guigard et al., 1996; Robertson et al., 1998 and 2008). In this study, the long term effect of STE irrigation on soakaway systems was apparent in soakaway soil acidity, which was increased in soakaway soil relative to soil not receiving effluent. As the soakaway soil aged, soil pH became more acidic compared to no change in pH in the newly constructed soakaway soil as was observed in site 1 and 6, respectively (Figure 7.1). The reduction in soil pH of this current work is in agreement with studies by Rattan et al. (2005), Al Omron et al. (2012) and Withers et al. (2016), in which the authors observed a pH drop in soils affected by sewage irrigation or biosolids application. The decrease in soakaway soil pH can be attributed to the increase in the soil organic matter (OM) and heavy metals from the persistent release of enriched STE to soakaway soil. The increase in soil OM, which holds an overall negative charge, allows the attachment of the positively charged heavy metals to soil particles, increasing soil cation exchange mechanism and releasing hydrogen ion causing increase in soil acidity (McCauley et al., 2009).

The soakaway soil capacity for holding phosphorus also diminishes with time (Robertson et al., 1998) as adsorption active sites on the soil particles become saturated and effluent P migrates further away from the soakaway (Katz et al., 2010; Katz et al., 2011). O'Keefe et al. (2014) suggested that P discharges from ST are likely to be high in the soluble bioavailable P relative to agricultural runoff. In this work, soakaway soil receiving domestic sewage wastes had elevated concentration of BAP

relative to soil not receiving sewage wastes. The concentration of BAP was also elevated in the more aged soakaway soil (Site 1, tank and soakaway age 78 years) compared to a newly constructed soakaway soil (Site 6, tank and soakaway age 2 years; Figure 7.1), suggesting that the soil may have become a P sink over the years with greater potential of leaching to surface and groundwater (Sharpley et al., 1993). Many research studies observed that even with ST systems that are functioning properly, P migration in soil system is <0.3m/year for clay-silt soil and 1m/year for sandy gravel soil (Robertson et al., 1998; Zurawsky et al., 2004) and for old ST systems P plumes may gradually develop, reaching groundwater or surface water with time. In this research, STE discharges influenced immediate downstream waters, which reached a critical TP concentration of 0.57 mg/l adjacent to the ST discharge (Chapter 5, Table 5.2).

Giving that P from STE may migrate through the soil at rates ranging from 0.3-1.0 m/year (Robertson et al., 1998), and the expected ST age can exceed 75 years or more, the minimum setback distance from watercourses ought to be increased to >100 m (depending on soil type) to increase the possibilities for effluent P attenuation in the soil. In the UK, this setback distance is currently 10 m from watercourses and 50 m from water abstraction (UK Building Regulation, 2014), which can be, for older soakaway systems (with highly permeable soil) insufficient distance for pollution prevention. In a study by Day (2004), it was revealed that many ST systems require a horizontal distance to streams of 130 m to provide adequate treatment. In many countries, planning regulations require a minimum of 1.2 m of vertical undisturbed soil between the base of the percolation trenches and either the bedrock below, or the highest level of the water table (EPA, 2000; Gill et al., 2004; PPG4, 2010). In Scotland, this vertical distance is 1m (PPG4, 2010; Scottish Government, 2012), which in the light of this research, may be considered insufficient distance. Many old ST systems do not meet current regulation of setback distance separation requirement and may contaminate groundwater directly (ESB international, 2008). A re-evaluation of ST setback distances may be required to safeguard water quality.

The temporal and spatial data for TP (Figure 7.2) showed the variability for P concentration in STE (e.g. mean TP concentration [14.55 mg/l], median [10.8 mgP/l], the top 5 percentile [30.5 mg/l] and the bottom 5 percentile [5.3 mg/l]). There is no regulation on the concentration of P in STE and the technology to remove P from the domestic effluent is currently limited and often expensive. Phosphorus removal inside the tank is only achieved by precipitation of organic matter and particulate P in the form of sludge (20-30% of TP) in the base of the tank (Canter and Knox, 1985;

Wood, 1993). It is expected that soakaway soil removes/reduces effluent P as well as other pollutants during effluent secondary treatment in the soil. In Chapter 6, it was revealed that 35 and 14% of effluent P was removed by silty loam soil test particles in the batch equilibrium and the column experiment, respectively as other substances present in the effluent may compete with P over soil adsorption sites. These percentages of effluent P removal may become even more reduced if the soakaway was used persistently for a number of years. Figure 7.3 suggests that even with ST systems that are maintained and functioning properly, a large proportion of P may still pass through soil system untreated. To validate and enhance P sorption data, P adsorption experiments (batch equilibrium or column method) by different soil types in newly constructed and other older soakaway soils are required, to investigate the soil ability for P adsorption when the soil becomes saturated by the persistent release of effluent.

The estimated annual P loadings to soakaway soils from this work (Table 7.2 and Figure 7.3), which was based on analytical result of P concentration and the stated effluent flow rate in literature 150-180 l/person/day (EPA, 2000; US EPA, 2002; Gill et al., 2004; PPG4, 2010). The annual per capita P loads from STE to soakaway soils modelled on the mean P concentration of this work (0.80 and 0.96 kgP/person/year) are in agreement with the values of 1.0-1.13 and 0.63-0.72 kg/person/year reported by Gold and Sims (2000) and Pieterse et al. (2003), respectively. It should be noted that the annual P loadings are highly influenced by water use scenarios (Table 7.2 and Figure 7.3), and annual P loadings values would increase if water use was increased causing reduction in effluent retention time inside the tank as water use would exceed 180 l/person/day or if the ST was failing.

Detergents P loading fraction of 0.154 kg/person/year that was quoted in Chapter 3, and reported by Richards et al. (2015) can be controlled and regulated by ST users, if they were to use reduced-P detergents. This work estimated the reduction of >90% of detergent P loading by switching to P-reduced detergents (Chapter 3). However, consumers criticized the P-reduced detergents products as being ineffective and costly (Chapter 3 and Appendix 1). So to entice consumers to use these P-reduced detergents, they should be affordable, the quality and their cleaning ability should be improved.

At present, many incorrectly installed, old and aging or poorly maintained ST systems are in operation presenting a source of an unknown quantity of pollution to watercourses in the UK. If a septic system does not function properly, there is a risk of discharging a significant volume of

untreated wastewater directly to the environment posing risks to surface and groundwater contamination. Therefore, a call for an appropriate stream monitoring programme may be required to assess ST risks and implement robust stream remediation measures.

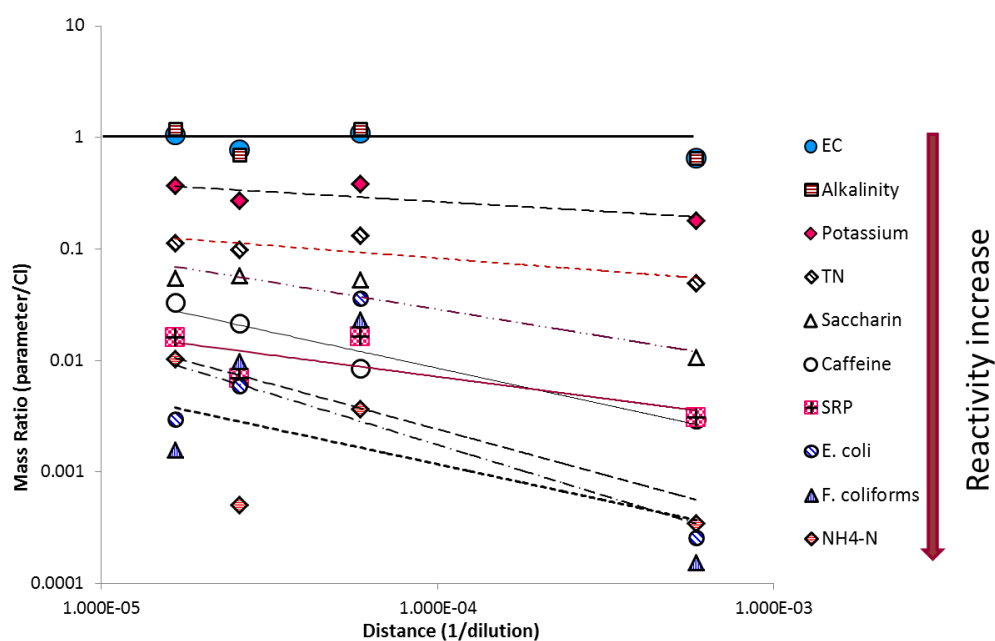
7.5 Conclusion

This study provides information on domestic sewage irrigation to soakaway soils, and on the annual phosphorus loadings from STE inputs. The results revealed that long term sewage loading to soakaway soil can affect soil properties and the ability for pollutants removal, as the soil becomes increasingly saturated with pollutants. The long term effect of STE irrigation to soakaway system was apparent in the increased soil acidity in soakaway soil relative to soil not receiving effluent. The bioavailable phosphorus (BAP) in soil situated after receiving STE was enriched (elevated) relative to soil situated before the tank. The annual P loadings per person from STE to soakaway soil were calculated based on mean analytical P results to be 0.79 and 0.95 kgP/person/year for water use of 150 and 180 l/person/day, respectively, of which detergents loading constitute 16-25%. The study also revealed that P annual loadings would increase with increased water use or with decrease in water retention time inside the tank. The annual P loadings were modelled on the spatial and temporal effluent data, which revealed that a large proportion of P may reach watercourses even with fully functioning ST systems. This work highlighted that persistent ST discharge can impact soil quality increasing the risk of P leaching to surface and groundwater.

Chapter 8

Potential tracers for tracking sewage effluent discharges in watercourses

Graphical Abstract



Reactivity and dilution of septic tank parameters
downstream from septic tank source

Richards, S., Withers, P.J.A., Paterson, E., McRoberts, C. W., Stutter, M., 2017.

Environmental Pollution

Author Contributions:

SR designed and performed the experiment and the extraction. McR performed instrument analysis for caffeine and artificial sweeteners. SR also analysed the data, wrote the paper and all co-authors reviewed and commented.

Abstract

Septic tank effluent (STE) contributes to catchment nutrient and pollutant loads. To assess the role of STE discharges in impairment of surface water, it is essential to identify the sources of pollution by tracing contaminants in watercourses. We examined tracers that were present in STE to establish their potential for identifying STE contamination in two stream systems (low and high dilution levels) against the background of upstream sources. The studied tracers were microbial, organic matter fluorescence, caffeine, artificial sweeteners and effluent chemical concentrations. The results revealed that tracer concentration ratios Cl/EC, Cl/NH₄-N, Cl/TN, Cl/TSS, Cl/turbidity, Cl/total coliforms, Cl/sucralose, Cl/saccharin and Cl/Zn had potential as tracers in the stream with low dilution level ($P < 0.05$). Fluorescence spectroscopy could detect STE inputs through the presence of the tryptophan-like peak, but was limited to water courses with low level of dilution and was positively correlated with stream *Escherichia coli* (*E. coli*) and soluble reactive phosphorus (SRP). The results also suggested that caffeine and artificial sweeteners can be suitable tracers for effluent discharge in streams with low and high level of dilution. Caffeine and saccharin were positively correlated with faecal coliforms, *E. coli*, total P and SRP, indicating their potential to trace discharge of a faecal origin and to be a marker for effluent P. Caffeine and SRP had similar attenuation behaviour in the receiving stream waters suggesting caffeine's potential role as a surrogate indicator for the behaviour of P downstream of effluent inputs. Taken together, results suggest that a single tracer alone was not sufficient to evaluate STE contamination of watercourses, but rather a combination of multiple chemical and physical tracing approaches should be employed. A multiple tracing approach would help to identify individual and cumulative STE inputs that pose risks to stream waters in order to prioritise and target effective mitigation measures.

Keywords: Water quality, Tracers, Sewage contaminants, Phosphorus, Saccharin, Caffeine

8.1. Introduction

Septic tank discharges increase the risk of contaminants entering ground, surface and drinking waters and may pose serious risks to human health and the environment. Septic tank (ST) systems comprise small scattered point sources at a range of densities across rural landscapes and their pollution impact is therefore difficult to quantify. Hence, it is essential to locate and trace septic tank effluent (STE) pollution sources to water courses to evaluate effluent discharge impact and to target problem areas for mitigation. US EPA (2002a) stated that septic tanks process 4 billion gallons of wastewater per day in the USA and the resulting effluent is released to the environment, and that 10-20% of these STs fail at some point (US EPA, 2016). Okeeffe et al. (2015) reported that in Scotland, there are 161000 ST that are registered by Scottish Environmental Protection Agency and 21% of these tanks discharged directly to watercourses (without soakaway). It is often very difficult to distinguish between pollution sources (e.g. agriculture vs ST) for pollutants such as phosphorus (P), ammonium-N ($\text{NH}_4\text{-N}$) or faecal indicator organisms (FIOs). The effect of ST discharges can be severe to adjacent receiving waters and can be responsible for elevated background concentrations of nutrient, pathogen and emerging contaminant pollution across catchments (Jarvie et al., 2006; Withers et al., 2014). In order to safeguard surface waters it is important to identify sources of pollution to remediate persistent sources and manage their impacts.

Tracing effluent contaminants can provide a powerful tool for evaluating pollutant sources and loadings to water courses. To determine the source of pollution and detect STE discharges that can impact water quality, a constituent tracer or a set of tracers in the effluent (in situ), or added external tracers can be used. Generally, added tracers should be conservative, stable, non-toxic to humans or to the environment, easy to detect and should be transported in a similar way to the target pollutants. Studies have used in vitro tracers, such as the non-carcinogenic, low toxic fluorescent dye Rhodamine WT (YSI, 2001) or chemical tracers such as sulphur hexafluoride (Wanninkhof et al., 2005) and dichlorobenzene to investigate STE attenuation and contamination in wells and ground waters (Robertson, 1994; Dillon et al., 1999).

Naturally present pollutants in STE such as total coliforms, faecal coliforms and *Escherichia coli* (*E. coli*) are often used as microbial tracers for groundwater contamination (Fong et al., 2007). Coliforms are excreted in human faecal wastes, and therefore can be used to monitor the movement of STE in

ground and surface waters. However, faecal coliform concentrations alone are not considered a powerful tracer for effluent contamination as it is difficult to differentiate between humans and alternate sources from a variety of farmed and wild animals or migratory birds (Carson et al., 2001).

Many studies have investigated the use of boron (B) as a component of modern detergents and chloride (Cl) to detect sewage and point source impacts including ST on river waters (Neal et al., 1998; Schreiber and Mitch, 2006; Jarvie et al., 2006 and 2012). Neal et al. (2010) considered B to be a good indicator of sewage pollution along with sodium (Na) concentration combined with discharge behaviours (concentration – flow relationship) in river waters to evaluate point source impacts of phosphorus (P) associated with effluent sources. While, Bundschuh et al. (1993) stated that elevated B concentrations are indicative of anthropogenic inputs, Verstraeten et al. (2005) called for caution when relying on B alone as a sewage tracer as the B source can be natural (rain water, parent rock and soil erosion), agricultural runoff (fertilizers) as well as from anthropogenic source (detergents). The authors suggested a combination of B and additional indicators should be more informative in tracing sources of catchment pollution. Alhajjar et al. (1990) utilised elevated Cl concentrations and electric conductivity (EC) in STE to infer P transport to ground water from domestic ST, with a focus on P-based detergents. Moreover, Vengosh and Pankratov (1998) used Cl/Br ratios to distinguish between water impacted by sewage from urban runoff (high ratios) and from agriculture runoff (low ratios). Williams et al. (2013) investigated 4 tracers for effluent discharge to surface waters and concluded that the pharmaceutical carbamazepine and anthropogenic metal gadolinium were more sensitive indicators of human influence, when compared to EC and organic matter (OM) fluorescence. Fluorescence spectroscopy can be used to identify organic compounds in wastewaters that fluoresce in both ultraviolet (UV) and visible light ranges and to characterise them by their specific excitation emission spectra and their intensities (So and Dong, 2002; Baker et al., 2003; Hudson et al., 2008).

It is crucial to provide a composite, cost-effective tracer approach to evaluate current environmental impacts and aid future policy to safeguard water quality and human health. Due to the potential limitations of individual tracers, a combination of STE indicators may result in an improved effluent tracing method. In this study, we explored the potential of effluent in situ properties (alkalinity, EC, turbidity, fluorescence, nutrient concentrations and microbial abundances) to be combined into a suite of tracers to identify effluent sources. Also, fluorescence of STE and stream waters was

explored in tracking STE discharge to watercourses as well as the application of liquid chromatography – tandem mass spectrometry (LC-MS/MS) to identify and quantify trace organic compounds of STE. In this study, solid phase extraction (SPE)-LC-MS/MS was used to isolate trace organic compounds caffeine and artificial sweeteners (acesulfame K, saccharin, sodium cyclamate and sucralose) from stream waters that are adjacent to ST discharge.

The hypothesis is that STE have characteristically high concentration of microbial, chemical, OM and fluorescence compared to background levels of upstream catchment waters and therefore, these properties may be used in tracing effluent discharge. The current study examined STE and adjacent upstream and downstream water compositions at low flow periods in two different streams. The aims were: 1) investigate the presence and concentrations of appropriate in situ tracer indicators in two STE discharge sites, 2) investigate the viability of selected tracer signatures for determining STE presence in the stream waters relative to background levels in two contrasting receiving waterbodies.

8.2 Materials and Methods

8.2.1 Field sites and sampling

Septic tank effluent and receiving stream waters were sampled during a low flow period in August on four occasions from two sites within the major catchments of Rivers Ythan and Don in N.E. Scotland, during 2015. Two streams were selected that directly received STE without soakaway or any secondary treatment; typical of 21% of ST discharge in Scotland (Okeeffe et al., 2015). The first site had a 60 year old concrete septic tank serving 2 people and discharged to a small stream with a low flow rate and a low level of dilution of STE (hereafter termed Site 1). The sub-catchment area of this site was 0.3 km², with 40% forestry, 20% moorland and 40% arable/intensive grassland, land cover, therefore, stream water (up and downstream) is expected to be relatively influenced by some agricultural input such as Na, K and nutrients. Upstream of this site was considered free from discharge from other STs and receive no other wastewater or industrial discharges. The tank outlet was submerged under stream water level and tank effluent was diffused with stream water directly, thus the effluent discharge rate for this site could not be measured. The second site had a 20 year old polyethylene tank serving 5 people, where the effluent outlet pipe discharged above water level to a larger stream with a higher flow rate and a higher level of dilution (hereafter termed Site 2). A diagram of septic tank system for Site 1 and Site 2 is illustrated in the supplementary material (Figure S8.1). The sub-catchment area of this second site was 3.9 km², with 10% forestry, 10% moorland and 80% arable/intensive grassland, land cover. The upstream sub-catchment of this site had 19 other ST, based on the number of dwellings and assuming each had a ST. As with Site 1, the upstream of Site 2 receive no other wastewater or industrial discharges and expected to be relatively influenced by some agricultural input. Stream flow rates were measured (Table S8.1) at each sampling visit as flow velocity multiplied by the measured cross section of each stream according to the method described by Michaud and Wierenga (2005) and USGS (2015). Three duplicate samples of each: tank effluent, upstream and downstream waters (50 m both ways) were sampled from each site on four occasions (4 sampling times) during low flow periods. The distances of sampling up and downstream from the tanks were considered sufficient for effluent mixing despite being constrained by the presence of a safe access to the watercourses and the presence of a secondary nearby source or neighbouring tank.

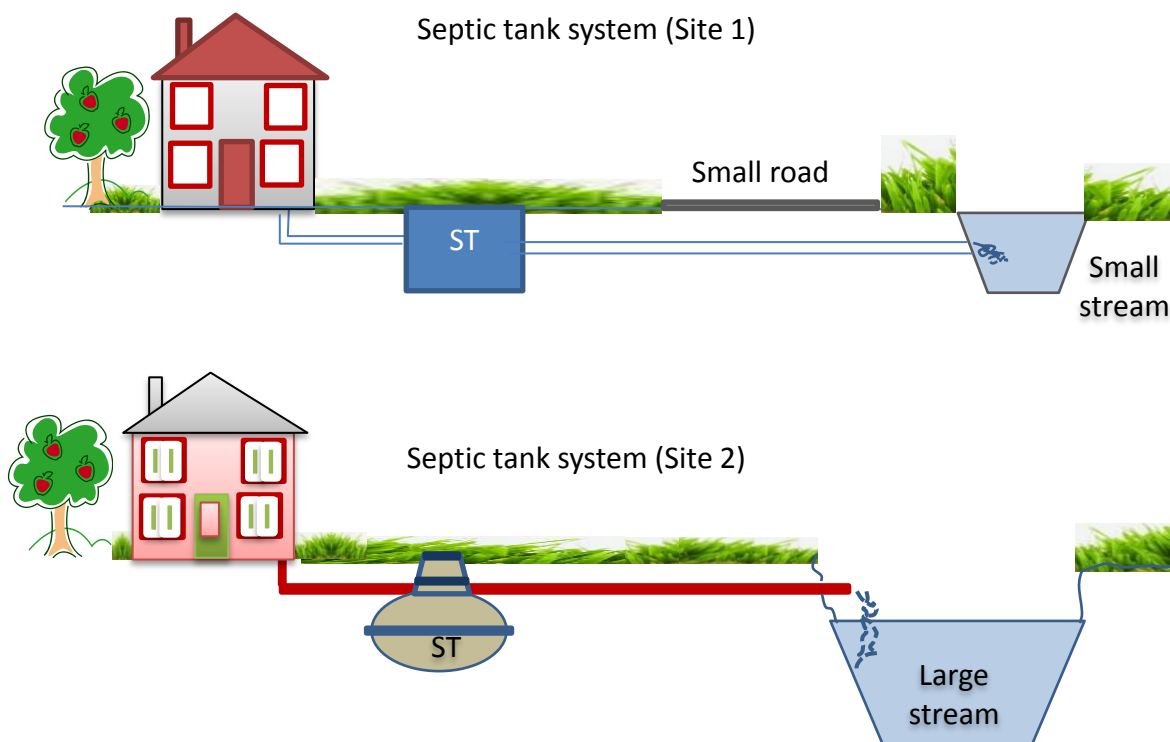


Figure S8.1: Diagram of septic tank systems: Site 1 and Site 2.

Table S8.1: Stream discharge and effluent flow rate for Site 1 and Site 2 during sampling times. Effluent flow rate at Site 1 was not measured due to discharging under stream water level.

	Stream discharge m ³ /s		Effluent flow rate ml/s	
	Site 1	Site 2	Site 1	Site 2
Sampling 1	0.0016	0.023	-	13.78
Sampling 2	0.0015	0.026	-	0.44
Sampling 3	0.0047	0.078	-	2.00
Sampling 4	0.0022	0.034	-	2.00
Mean at site	0.0025	0.040	-	4.55

Microbial samples were placed into sterile vials, samples for physical, chemical and fluorescence were collected into polyethylene bottles, and for caffeine and artificial sweeteners into pre-baked glassware (450°C for 16 h). Samples were kept in a cold box during transportation and at 4°C in the dark until processing. Microbial analyses were performed within 5 h while physical, chemical and fluorescence analyses were performed within 16 h of collection.

8.2.2 Sample analysis

8.2.2.1 Microbial analyses

For microbial analyses of total coliforms, faecal coliforms and *E. coli* detection, samples were diluted appropriately using sterilised saline phosphate buffer (pH 7.3) and the diluted effluents and water samples screened using IDEXX Colilert-18 kits and Quanti-Tray/2000 (IDEXX Laboratories, Westbrook, ME, USA). Samples were incubated for 18-22 h at 37 °C for total coliforms and *E. coli* and at 44 °C for faecal coliforms. The number of positive yellow wells was counted for coliforms enumeration and UV blue fluorescence for *E. coli* and reported as most probable number (MPN) according to manufacturer's instructions and applied dilutions.

8.2.2.2 Dissolved substances

Analyses for pH, turbidity and EC were carried out on unfiltered sub-samples using a Hanna pH 210 meter, Hach 2100P (Turbidimeter, Camlab) and Hanna HI-98312 conductivity tester, respectively. Samples were filtered through a pre-washed GF/F (0.7 µm) filter stacked onto a 0.45 µm filter paper for solute analyses. Alkalinity, ammonium-N (NH₄-N) and soluble reactive P (SRP) were determined using an automated discrete analyser (Konelab Aqua 20, Thermo Scientific, Vantaa, Finland). Chloride, nitrate (NO₃) and sulphate (SO₄) were determined by ion chromatography (Dionex DX600, Dionex, California, USA). Total dissolved nitrogen (TDN) and dissolved organic carbon (DOC) were determined using automated total organic carbon analyser (TOC-V_{CSH} analyser, Shimadzu, Japan). The filtrates were also analysed for major and trace element concentrations by ICP-OES (Agilent 7500ce, Tokyo, Japan) and ICP-MS (Agilent 7500i, Shield-Torch System, Tokyo, Japan), respectively. Total suspended solids (TSS) were determined gravimetrically by filtering a known volume of sample onto prewashed GF/F (0.7 µm) filters, which were dried at 105 °C.

8.2.2.3 Organic matter spectroscopy

Sample filtrates were scanned between 200-700 nm wavelengths using a Shimadzu UV Probe, UV-1800 Spectrophotometer, Shimadzu, Japan and UV Probe 2.33 software. Specific UV absorbance at 254 nm (SUVA₂₅₄) as a measure of the aromaticity of DOC was calculated as UV absorbance at 254 nm divided by DOC concentration expressed as L mg⁻¹m⁻¹ (Wieshaar et al., 2003). Filtrates were also analysed for fluorescence spectral areas associated with tyrosine, tryptophan, fulvic and humic

substances (Gilden Photonics Fluorimeter, fluoroSENS1.88.7, Glasgow, UK). Excitation emission matrices (EEMs) were obtained at wavelength intervals ranging (Ex 200-450 nm) at 2 nm increments, (Em 270-500 nm) at 5 nm increment with a band pass width of 5 nm and 0.1 s integration time over both UV and visible light fluorescence regions. Sample spectra were Raman normalised against Millipore water at 397 nm. Dissolved OM peaks were picked and determined using a Gilden Photonics Contour Visualizer (V. 1.0) to provide the relative intensity of fluorescence at various wavelengths (Ex 220-420 nm) and (Em 200-500 nm) focussing on regions indicative of tyrosine-like, tryptophan-like fluorophores (amino acids), fulvic-like and humic-like fluorophores, with peaks in fluorescence intensity units (FIU).

8.2.2.4 Analysis of caffeine and artificial sweeteners

Prior to analysis of caffeine and artificial sweeteners (acesulfame K, saccharin, sodium cyclamate and sucralose) by LC-MS/MS, a SPE pre-concentration method was employed for stream water samples. All samples had a stable label internal standard added for each analyte. Analytes were extracted from samples (100 ml) and concentrated using polymeric reversed phase (PRP) Oasis HLB 200 mg cartridges utilising a polar (aqueous) matrix (mobile phase) and a polar-non polar balanced phase. The cartridges were first conditioned using 5 ml of 50:50 methanol:acetonitrile, followed by 5 ml acidified Millipore water (pH 2) using HCl (1M). The acidic condition of the samples was maintained to optimise the trapping of polymeric bonding (Poole, 2003; Fontanals et al., 2005). After passing samples through the cartridges, they were washed with 10 ml of acidified Millipore water, then eluted with 5 ml of a non-polar solvent (50:50 methanol:acetonitrile). The concentrated extracts were analysed for the presence of caffeine and artificial sweeteners (acesulfame K, saccharin, sodium cyclamate and sucralose) by high performance liquid chromatography tandem mass spectrometry (LC-MS/MS) using a Phenomenex Luna 5 C18 column. Analysis was carried out using an Agilent 1100 series LC system (Agilent Technologies, Waldbronn, Germany) interfaced to a Waters Quattro Ultima Platinum triple quadrupole mass spectrometer operating in both positive and negative electrospray ionisation (ESI) modes. The LC-MS/MS system was controlled by MassLynx™ software and data processing was carried out using MassLynx™ 4.1 software (Waters Corporation, Milford, Massachusetts). Artificial sweeteners were monitored in the negative mode while caffeine was monitored in the positive mode (detailed method, detection limits and maximum detectable dilutions are provided in the supplementary material and Table S8.2). Filtered effluent samples were analysed directly by LC-MS/MS without SPE for organic compounds due to being more concentrated relative to stream waters.

Table S8.2: Detection limit and maximum detectable dilution (MDD).

Parameters	Detection Limit	STE Range	MDD
Alkalinity mg/l	2.000	157-334	79-167
Turbidity NTU	0.020	95-210	4753-10504
SRP mg/l	0.002	2.4-8.5	4236-1178
TDP mg/l	0.020	3.5-9.2	175-457
TP mg/l	0.009	3.1-9.5	345-1054
NH ₄ -N mg/l	0.006	19.7-70.6	3276-11774
TN mg/l	0.020	20.9-73.8	1046-3690
Cl mg/l	0.003	32-101	10501-33518
K mg/l	0.020	13-23	627-1170
B µg/l	7.000	33-41	42861.000
Ba µg/l	0.600	522-634	871-1057
Zn µg/l	0.400	90-213	226-533
Total coliforms MPN	1.000	1.5x10 ⁶ -1.9x10 ⁷	1.5x10 ⁶ -1.9x10 ⁷
Faecal coliforms MPN	1.000	6.9x10 ⁵ -2.2x10 ⁶	6.9x10 ⁵ -2.2x10 ⁶
<i>E. Coli</i> MPN	1.000	3.8x10 ⁴ -1.2x10 ⁶	3.8x10 ⁴ -1.2x10 ⁶
Sucralose µg/l	2.000*	44-56	22-28
Saccharin µg/l	2.000*	58-80	29-40
Acesulfame k µg/l	2.000*	67-69	34-35
Caffeine µg/l	5.000*	17-95	3-19

* Detection limit for direct injection for septic tank effluent is in (µg/l) and for stream waters solid phase extraction method is in (ng/l).

8.2.3 Data handling and statistical analysis

Effluent and stream water data were subjected to descriptive statistical analysis using GenStat (17 Edition) and Anderson-Darling normality tests with log 10 transformations applied where necessary. One way analysis of variance (ANOVA) was performed ($P < 0.05$) to examine the significance of ST discharge tracers effect on downstream waters as up and downstream was used as the grouping factor for each site separately. Pearson correlation coefficients between faecal coliforms, *E. coli*, SRP and stream indicators were also evaluated.

To investigate and compare the conservative versus reactive behaviours of the potential tracer signals from the effluent in the downstream receiving waters an approach analogous to looking at the recovered mass of the tracer relative to that of Cl was used. Instead of looking at relative attenuation of the parameter of interest (in mass terms to the conservative Cl reference) against distance downstream (during a single sample time, for example) we instead looked at the attenuation across a range of different dilution levels (effluent to stream volume) from the multiple sample times. The use of Cl as a conservative reference is well justified in the literature since Cl is classically used as a stable hydrological tracer, for example in flow dilution gauging. The first stage of this approach was to determine concentration ratios with Cl concentrations in the STE and downstream waters for a set of eight parameters deemed to cover conservative (EC and alkalinity) to reactive (SRP and NH_4) behaviours with the organic tracers (caffeine and three sweetener compounds) as unknowns to be assessed in terms of reactivity. The second stage was to calculate (divide the x/Cl ratio for the downstream water by that of the effluent) thus:

$$\text{Downstream change in tracer recovery normalised to Cl} = \frac{\left(\frac{x}{\text{Cl}}\right)_{\text{downstream}}}{\left(\frac{x}{\text{Cl}}\right)_{\text{effluent}}} \quad (1)$$

Where x is the parameter of interest.

Thirdly, these values, (for the four sample times) were plotted against 1/dilution, thus:

$$\frac{1}{\text{Dilution}} = \frac{1}{\left(\frac{Q_{\text{effluent}}}{Q_{\text{stream}}}\right)} \quad (2)$$

Where Q is the discharge in l/s. This latter term was conceptualised as representative of residence time for the parameter in the stream that would be a governing factor on comparative stream reach uptake (degradation and sorption). These relationships were plotted for Site 2 to assess comparative reactivity of the tracers in the stream reaches.

8.3. Results

8.3.1 Septic tank effluent characterisation

The septic tank effluent at Site 1 and 2 contained elevated concentrations of P, N, DOC and TSS and smaller $\text{NO}_3\text{-N}$ concentrations relative to stream water throughout sampling times. The effluent also contained bacterial concentrations (total coliforms, faecal coliforms and *E. coli* that ranged $10^6\text{-}10^7$, $10^5\text{-}10^6$ and $10^4\text{-}10^6$ MPN/100 ml, respectively). The range of fluorescence intensity of the tryptophan-like peak found in all STE samples was $6.1\text{-}6.7 \times 10^3$ fluorescence intensity units (FIU), which were elevated relative to downstream waters. However, STE composition was found to vary between the two sites (Table 8.1). Septic tank effluent at Site 2 had elevated concentration of alkalinity, EC, SRP, TP, $\text{NH}_4\text{-N}$, TN, Cl, K, total coliforms and faecal coliforms, *E. coli* and caffeine relative to STE at Site 1. Conversely, effluent at Site 1 had elevated concentration of turbidity, TSS, Zn and saccharin relative to effluent at Site 2 (Table 8.1).

The mean stream discharge over the sampling period for Site 1 and Site 2 were $0.0025 \text{ m}^3/\text{s}$ and $0.040 \text{ m}^3/\text{s}$, respectively highlighting stream low flow at Site 1. Stream discharge was greatest at sampling time 3, particularly for Site 2 ($0.078 \text{ m}^3/\text{s}$) compared to Site 1 ($0.005 \text{ m}^3/\text{s}$) due to rainfall (Supplementary material Figure S8.2). This elevated discharge caused by rainfall at sampling time 3 was linked to the observed reduction in microbial and chemical concentrations of STE at Site 2 relative to other sampling times, which suggested that septic tank at Site 2 may have received roof runoff.

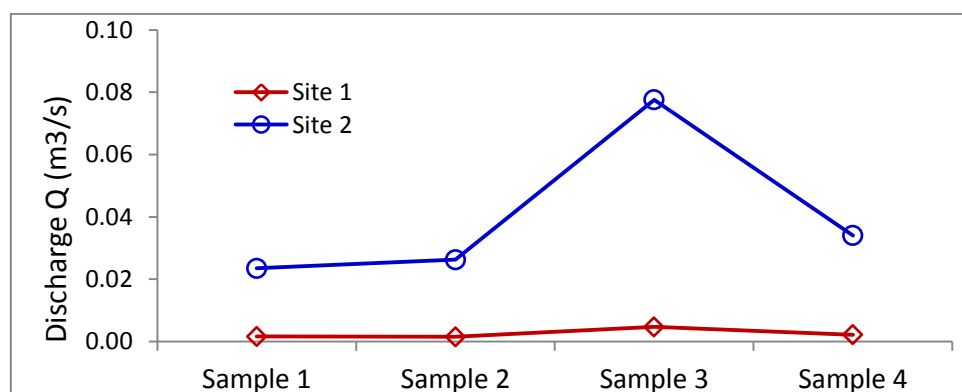


Figure S8.2: Stream discharge Q (m^3/s) during sampling time for the smaller stream at Site 1 and for the larger stream at Site 2.

Table 8.1: Septic tank, upstream and downstream mean parameter concentrations for Site 1 and Site 2. Also listing ANOVA significant value $P < 0.05$ as upstream and downstream was the grouping factor for each site. The term (UDL) indicates under detection limit and (ND) not detected.

Parameters	Site 1							Site 2						
	STE		Upstream		Downstream		<i>P-value</i>	STE		Upstream		Downstream		<i>P-value</i>
	Conc.	±1 S.E.	Conc.	±1 S.E.	Conc.	±1 S.E.		Conc.	±1 S.E.	Conc.	±1 S.E.	Conc.	±1 S.E.	
Alkalinity mg/l	157	±11	23	±2	67	±14	*	334	±32	107	±4	108	±4	
Turbidity NTU	210	±46	3	±1.1	66	±21	*	95	±51	6	±0.7	7	±1.0	
EC µS	485	±33	98	±5	220	±38	*	1140	±151	345	±10	355	±12	
TSS mg/l	116	±30	4	±2	107	±28	*	69	±29	3	±1	5	±1	
SRP mg/l	2.36	±0.34	0.02	±0.01	0.74	±0.25	*	8.47	±0.6	0.02	±0.01	0.03	±0.01	
TDP mg/l	3.5	±0.44	0.03	±0.01	0.95	±0.33	*	9.15	±0.85	0.03	±0.01	0.04	±0.01	
TP mg/l	3.11	±0.45	0.04	±0.01	0.99	±0.30	*	9.49	±0.81	0.05	±0.01	0.06	±0.01	
NH ₄ -N mg/l	19.7	±1.84	0.01	±0.00	5.22	±1.74	*	70.6	±7.1	0.01	±0.00	0.08	±0.04	
TN mg/l	20.9	±2.20	0.49	±0.07	6.72	±2.11	*	73.8	±7.8	2.33	±0.14	2.43	±0.11	
Cl mg/l	31.50	±2.19	13.26	±0.22	19.00	±1.61	*	101	±22	33.52	±0.88	33.78	±0.97	
K mg/l	12.53	±1	0.98	±0.22	4.44	±1.09	*	23	±1.99	2.38	±0.14	2.44	±0.15	
B µg/l	33	±8	13	±1	57	±14	*	41	±7	30	±5	35	±5	
Ba µg/l	634	±50	72	±3	318	±77	*	522	±75	128	±14	201	±9	**
Zn µg/l	213	±15	17	±0.3	72	±31	*	90	±13	13	±2	21	±3	
Total coliforms ^a	1.5x10 ⁶		2.4x10 ³		4.7x10 ⁵			1.9x10 ⁷		5.8x10 ³		1.3x10 ⁵		
Faecal coliforms ^a	6.9x10 ⁵		5.2x10 ²		1.3x10 ⁵			2.2x10 ⁶		8.4x10 ²		4.7x10 ³		
<i>E. Coli</i> ^a	3.8x10 ⁴		2.5x10 ²		6.8x10 ³			1.2x10 ⁶		6.4x10 ²		4.9x10 ³		
Sucralose µg/l	44	±7	UDL		16	±7	*	56	±15	0.17		0.34		
Saccharin µg/l	80	±3	UDL		29	±4	*	58	±9	0.63		0.76		
Acesulfame k µg/l	69	±9	UDL		25	±6	*	67	±16	0.40		0.55		
Caffeine µg/l	17	±1	UDL		7	±2	*	95	±70	UDL		0.48		
Tryptophan FIU ^b	6.7x10 ³		ND		6.3x10 ³		*	6.1x10 ³		ND		ND		

a MPN/100 ml (most probable number in 100 ml)

b FIU (Fluorescence intensity unit)

* *P-value* < 0.05 and ** *P-value* < 0.01

8.3.2 Catchments interaction between up and downstream waters

Stream parameters exhibited greater concentration downstream from STE discharge relative to upstream waters at both sites for $\text{NH}_4\text{-N}$, B, Ba, Zn, total coliforms, faecal coliforms, *E. coli* and artificial sweeteners, while the rest of stream parameters exhibited elevated concentration downstream at Site 1 only (Table 8.1). The upstream of Site 1 was considered free from discharge from other STs and little agricultural input. Thus anthropogenic input of parameters such as artificial sweeteners and caffeine were minimal (under detection limit) upstream of Site 1. Conversely, for Site 2, with an upstream catchment of 80% agricultural and 19 STs, the concentration of alkalinity, EC, TN, Cl, K, B, Ba and saccharin were elevated upstream at Site 2 relative to upstream at Site 1 (Table 8.1).

The influence of STE discharge downstream of Site 1 was observed in the elevated concentrations of TSS, Zn, artificial sweeteners, caffeine and tryptophan relative to downstream of Site 2. However, the effect of the low flow downstream of Site 1 was observed in the elevated concentration of SRP, TP, TN, $\text{NH}_4\text{-N}$, K, B, Ba and Zn relative to downstream of Site 2. Conversely, the influence of STE discharge downstream of Site 2 was noted in the elevated concentration of alkalinity, EC and Cl relative to downstream of Site 1. Moreover, tryptophan was not detected downstream of Site 2 (Table 8.1).

The concentration of all stream water parameters tested downstream of STE discharge were greater relative to upstream water ($P < 0.05$) for Site 1, throughout the sampling period (Table 8.1). Conversely, for Site 2, water parameters concentration downstream relative to upstream were similar for alkalinity, turbidity, TSS, P species, $\text{NO}_3\text{-N}$, TN, Cl and K or only slightly greater for B, Ba, Zn, coliforms, *E. coli* and artificial sweeteners, with no significant differences $P > 0.05$ except for Ba downstream of Site 2 (Table 8.1). The concentrations similarities between upstream and downstream for Site 2 were particularly observed at sampling time 3 where stream discharge was at its greatest (Figure S8.2).

Figure 8.1 shows selected microbial and chemical concentrations for STE, upstream and downstream of the source for Site 1 and Site 2 separately against the normalised discharge (Q_t/\hat{Q}), where Q_t is

the stream discharge of the day during sampling time and \hat{Q} is the mean stream discharge for all 4 sampling events for each site. The normalised discharge was used to better illustrate the data throughout the sampling periods and to facilitate comparisons between the two sites. Figure 8.1 shows that downstream waters for Site 1 had elevated concentration of Zn, total coliforms, caffeine and saccharin compared to the more diluted downstream at Site 2. It also shows catchment influence on the upstream concentrations of Site 2 for Zn and saccharin.

A canonical variate analysis (CVA) plot of the data of both sites combined (Supplementary material Figure S8.3) showed a clear separation between STE and up and downstream waters. Although there was a small proportion of overlapping of the regions of the 95% confidence intervals for up and downstream waters, downstream samples were closer to septic effluent composition. The data position in CVA was influenced by loading weightings CV1 (Ba 14.5, B 7.1, saccharin 6.3, Zn -20.5, TN -13.6 and K -6.6) and CV2 (Ba 17.8, DOC 4.7, saccharin 3.3, Zn -12.9, TN -7.4 and K -6.8) (Figure S8.3).

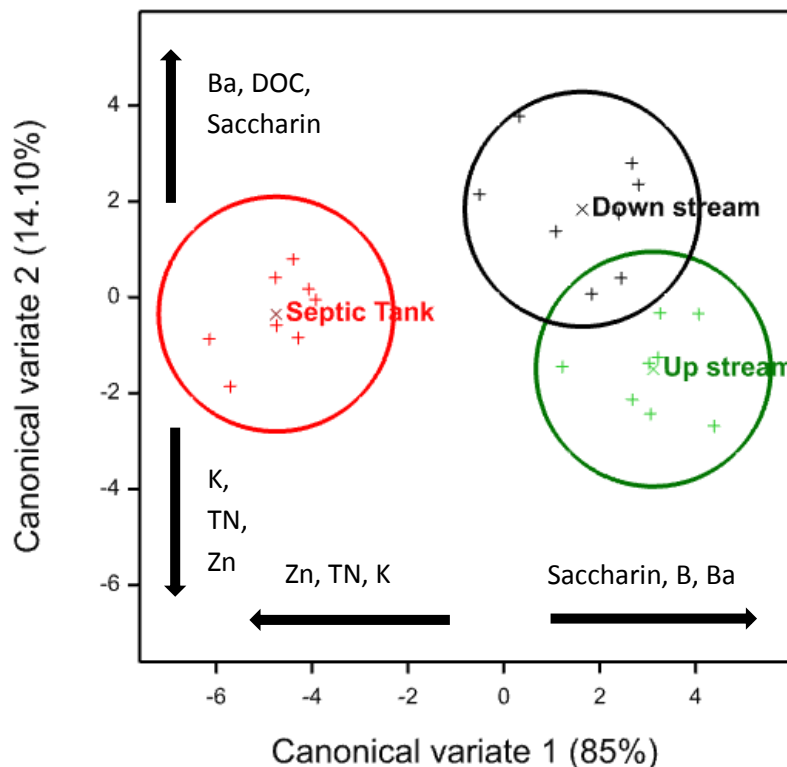


Figure S8.3: Canonical Variates plot of CV1 and 2 for septic tank effluent (STE) and adjacent upstream and downstream water with 95% confidence bands. The axes indicate greatest loadings of variates in positive and negative directions.

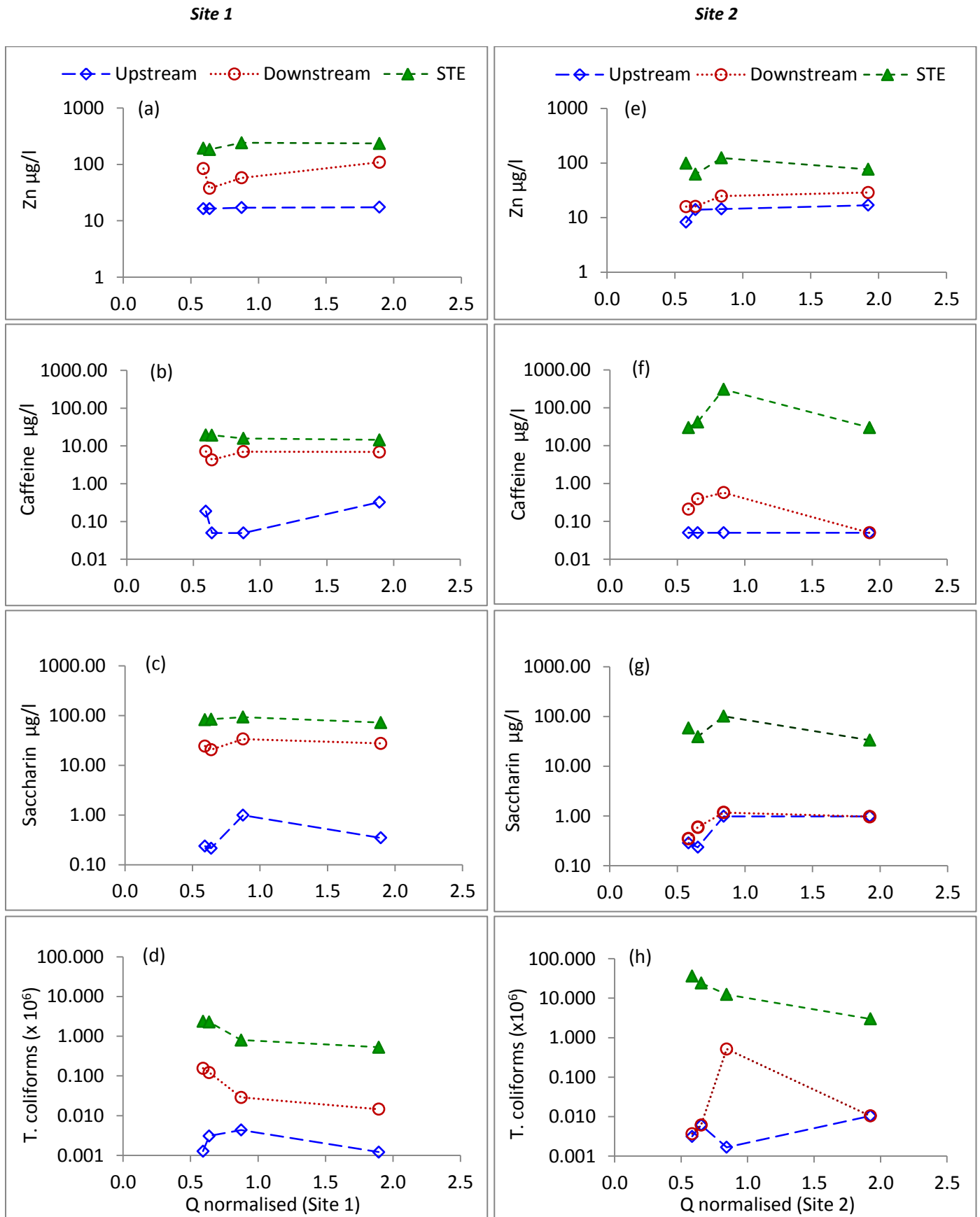


Figure 8.1: Parameter indicators for the septic tank effluent (STE), upstream and downstream water for Site 1 (a to d) and Site 2 (e to h) against normalised stream discharge (Q_i/\bar{Q}), where Q_i is the stream discharge at sampling time and \bar{Q} is the mean stream discharge for all 4 sampling events for each site.

8.3.3 Assessing tracers' behaviours in stream water

8.3.3.1 Microbial tracers

Microbial abundance in water samples downstream from the source was greater in concentration relative to upstream for both sites (Table 8.1). Faecal coliforms concentrations were 3 and 1 orders of magnitude greater downstream relative to upstream waters in Site 1 and Site 2, respectively. Faecal coliforms were positively correlated ($P < 0.05$) with effluent indicators (B, Ba, K and Zn) for Site 1 and (caffeine, total coliforms and *E. coli*) for Site 2 in stream water when upstream and downstream were ANOVA grouping factor (Table 8.2).

8.3.3.2 Dissolved inorganic substances and metals

Table 8.1 shows that Ba concentrations were greater downstream from the source for both sites separately, and were significantly different ($P < 0.05$) for up and downstream waters, suggesting a potential role of Ba as a tracer for effluent discharge. Other elements and indicators such as K, Zn, TSS, TN and turbidity were significantly greater downstream ($P < 0.05$) for Site 1 only. The mass ratio of a conservative tracer such as Cl to other chemical indicators (Table 8.3) revealed that the mass ratio of Cl/Ba, Cl/Zn, Cl/ $\text{NH}_4\text{-N}$, Cl/turbidity, Cl/TN, Cl/TSS, Cl/EC and Cl/total coliforms were significantly different ($P < 0.05$) in receiving waters relative to upstream waters for Site 1 only. Conversely, the ratios of Cl to other elements were not statistically significant ($P > 0.05$) between upstream and downstream in Site 2, therefore were not included as potential tracers.

Table 8.2: Pearson correlation coefficients and the significant difference (asterisks) between faecal coliforms, *E. coli*, soluble reactive P (SRP) and other indicators in stream water for Site 1 and Site 2. Correlation coefficient value >0.5 but not significant (P>0.05) is denoted ns and correlation coefficient value <0.5 represented by (-) is not included.

Indicator	Faecal coliforms		<i>E. Coli</i>		SRP	
	Pearson correlation coefficient		Pearson correlation coefficient		Pearson correlation coefficient	
	Site 1	Site 2	Site 1	site 2	Site 1	Site 2
Saccharin	ns	ns	0.88**	ns	0.97***	-
Sucralose	ns	-	0.87**	-	0.97***	0.88**
Acesulfame K	ns	-	0.92**	-	0.99***	0.83*
Caffeine	ns	0.81*	0.89**	0.81*	0.99***	0.76*
B	0.86**	ns	ns	ns	0.88**	-
Ba	0.86**	ns	ns	ns	0.84**	-
K	0.74*	-	0.81*	-	0.95**	-
Zn	0.84**	ns	ns	ns	0.86**	-
TP	ns	-	0.91**	-	0.99**	-
SRP	ns	-	0.95***	-		
TN	ns	-	0.94***	-	0.99***	-
Tryptophan	-	-	0.92***	-	0.94***	-
Total coliforms	ns	0.99***	0.75*	0.99***	0.75*	-
Faecal coliforms			-	0.99***	ns	-
<i>E. coli</i>	ns	0.99***			0.95***	-

* P-value <0.05, **<0.01 and ***<0.001

Table 8.3: The ANOVA significant difference (P-values) of stream water indicators concentration ratios Cl/indicators for Site 1 (upstream and downstream was ANOVA grouping factor). There were no significant differences in these ratios for the highly diluted Site 2.

Indicator ratio	P-value
Cl/Ba	***
Cl/Zn	***
Cl/B	**
Cl/NH ₄ -N	**
Cl/K	*
Cl/TN	*
Cl/TSS	*
Cl/alkalinity	*
Cl/EC	*
Cl/turbidity	*
Cl/total coliforms	*
Cl/ faecal coliforms	*
Cl/humic	*
Cl/saccharin	*

* P-value <0.05, **<0.01 and ***<0.001

8.3.3.3 Fluorescence as an effluent tracer

Characterisation of OM in STE and stream waters by fluorescence spectroscopy produced excitation emission matrices (EEMs) showing two peaks in the UV region: a tryptophan-like peak (T) at excitation/emission (Ex 270-290/Em 330-360 nm), which was present in all STE for Site 1 and 2, and a tyrosine-like peak (B) at (Ex 270-290/Em 290-320 nm), which was only present in STE from Site 1 throughout sampling period (Figure 8.2b). Two extra peaks were detected in Site 1 effluent in the visible light fluorescence region: humic-like peak (A) and fulvic-like peak (C) at (Ex 280-310/Em 380-430 nm) and (Ex 320-370/Em 390-450 nm), respectively. Fluorescence of stream waters detected the presence of humic-like and fulvic-like peaks in up and downstream waters of both sites at (Ex 240-270/Em 390-460 nm) and (Ex 290-350/Em 390-450 nm) for peak A and C, respectively. However, tyrosine-like and tryptophan-like peaks were not detected in upstream water samples (Figure 8.2a) for both sites. The anthropogenic input in the form of tryptophan-like peak was positively correlated with stream *E. coli* and SRP (Pearson correlation coefficient 0.92 and 0.94, respectively, $P < 0.05$), (Table 8.2), suggesting tryptophan's potential role to trace FIOs and effluent P.

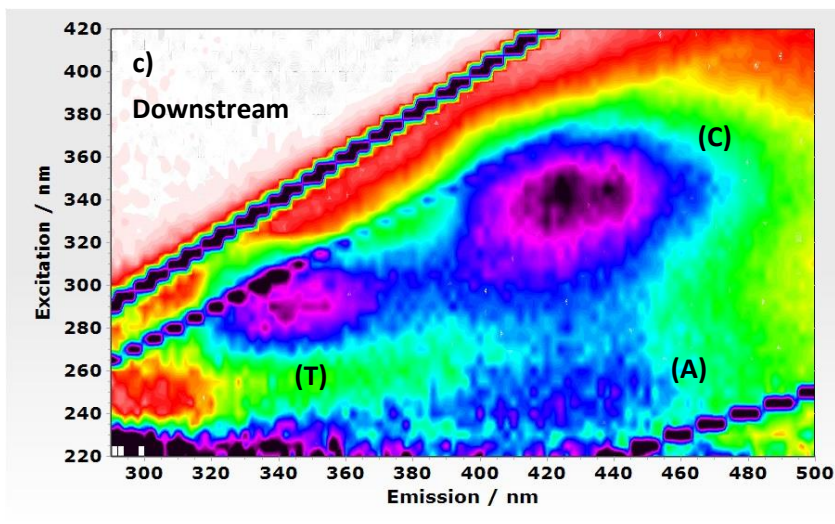
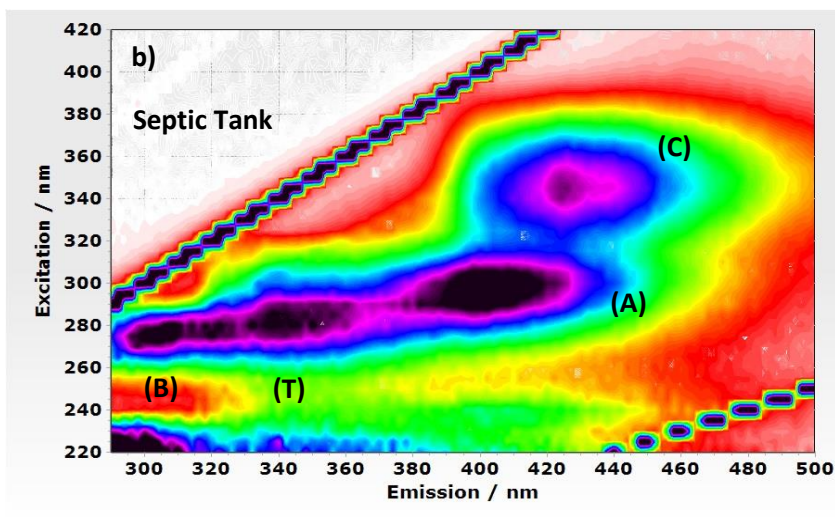
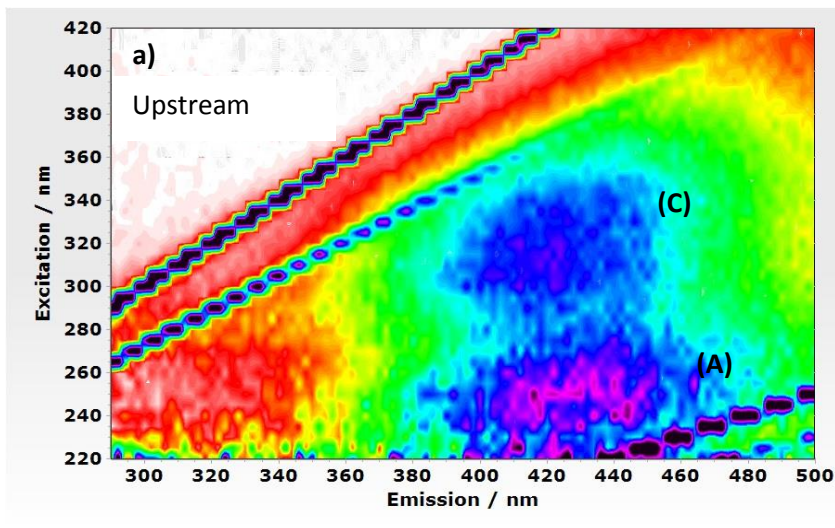


Figure 8.2: Fluorescence spectra tracking septic tank effluent (STE) discharge to stream water at site 1: a) Upstream from effluent discharge showing only humic and fulvic-like peaks A and C; b) Septic effluent at the source showing humic-like peak A, fulvic-like peak C, tyrosine-like peak B and tryptophan-like peak T; c) Downstream from the source showing the anthropogenic indicator tryptophan-like peak T that is not present upstream from septic tank source.

8.3.3.4 Caffeine and artificial sweeteners as indicators of STE discharge

Septic tank effluent concentrations of caffeine and artificial sweeteners were elevated downstream of ST discharge for both sites. The mass ratios of Cl/saccharin (Table 8.3) was significantly different ($P < 0.05$) downstream of the STE input at Site 1. However, the upstream concentrations of saccharin, sucralose and acesulfame K were under detection limits for Site 1 and relatively low for Site 2 compared to downstream waters (Table 8.1). Caffeine and artificial sweeteners in stream waters were positively correlated with stream faecal coliforms and with *E. coli* (Pearson correlation coefficient 0.81-0.92, $P < 0.05$), (Table 8.2), suggesting their potential role to trace FIOs. Caffeine and artificial sweeteners also correlated with SRP having Pearson correlation coefficient values of 0.76-0.99 and correlation significance of $P < 0.05$, suggesting their potential use as tracers for phosphorus released from septic tank discharge.

8.3.3.5 Downstream attenuation

The dilution plot of nutrient and indicators/Cl mass ratios (Figure 8.3) showed that EC and alkalinity behaved conservatively similar to the conservative element Cl. Also, the attenuation curve for saccharin and sucralose indicated a small degree of reactivity and mixing in receiving waters, while the attenuation curves for SRP and NH₄-N indicated that NH₄-N was the most reactive compound followed by SRP in stream waters. Figure 8.3 also revealed that caffeine attenuation curve was comparable with that of SRP attenuation.

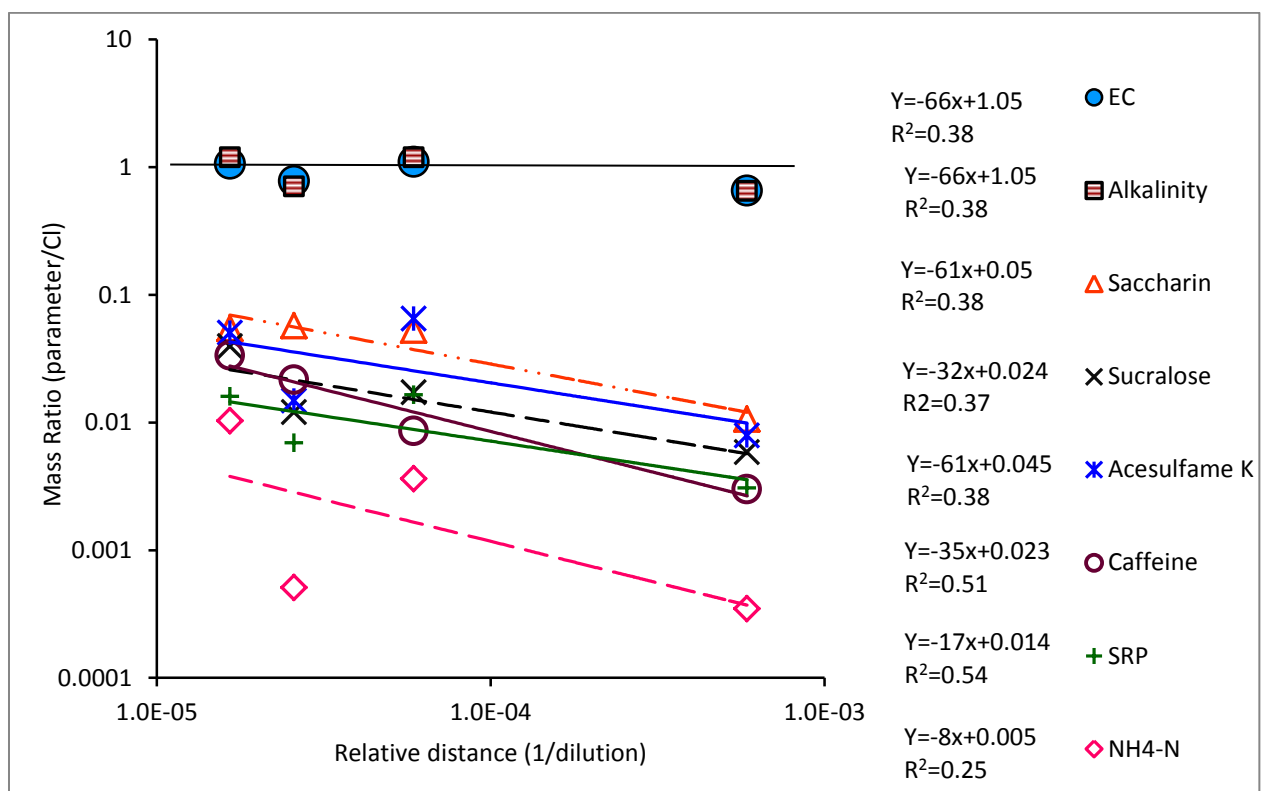


Figure 8.3: The relative removal/loss of determinants compared to the conservative element chloride (Cl), where values increasingly <1 show combined abiotic and biotic loss pathways (ie greater in stream reactivity).

8.4 Discussion

Data on direct discharges from ST to nearby watercourses are seldom documented or reported as it is difficult to identify the presence of STE discharge, to quantify their contribution, to locate and trace the source. In this work, the ST discharge to two streams (low flow rate and low level of dilution: Site 1, and higher flow rate and higher level of dilution: Site 2) was investigated to track STE output, for effluent pollution presence and movement in receiving waters through effluent in situ tracers. Effluent potency on downstream water was particularly apparent in the stream with low level of dilution at Site 1, which exhibited significantly elevated concentrations in all parameters tested ($P < 0.05$) relative to upstream water. Nutrient concentrations such as TP and $\text{NH}_4\text{-N}$ were elevated downstream for Site 1 (mean 0.99 and 5.22 mg/l, respectively) and for Site 2 (mean 0.06 and 0.08 mg/l, respectively).

8.4.1 The presence and evaluation of effluent in situ tracers

8.4.1.1 The viability of effluent FIO role as effluent tracers

Microbial contamination of a faecal origin from ST or sewage treatment works to surface and ground waters is a concerning matter as a potential risk of outbreaks of waterborne diseases (US EPA, 2002a; 2002b; 2003). Yates (1985) suggested that the majority of ground water related disease outbreaks in the USA are caused by bacteria and viruses present in domestic sewage, while Bradley et al. (1999) suggested that the presence of microbial indicators in watercourses infers the presence of viruses and pathogens of faecal origin. Faecal coliform bacteria are one of the target pollutants and often used to indicate sewage discharge as they are not naturally present in catchment soil sources and can be differentiated from other soil bacteria (i.e. they grow at elevated temperature (44°C) on a selective media), and in theory should be an ideal tracer for anthropogenic activity.

There are two major criteria for microbial presence and concentrations to be a suitable tracer for effluent discharge (Bitton, 2005): 1) their concentration should be high enough for detection and; 2) their presence should be maintained in water courses to track the source. In this current work, catchment difference between sites did not seem to have influenced faecal coliforms concentrations upstream of either site (Table 8.1). However, faecal coliforms were tracked downstream from ST with concentration of 3 and 1 order of magnitude greater relative to upstream waters for Site 1 and

Site 2, respectively. Nevertheless, microbial organisms have natural attenuation and decline with time (die off time) and with dilution in water courses (Collins and Rutherford, 2004; Anderson, 2010). Another disadvantage of using faecal coliforms as a single tracer of STE discharge is the difficulty in differentiating between human, animal or bird sources (Carson et al., 2001). Thus, while the presence of faecal coliforms in water courses may suggest contamination; it may not necessarily indicate human input from STE and an additional indicator may be required before assuming anthropogenic contamination. A more reasonable approach is to use additional chemical indicators naturally found in domestic wastewaters that are easy to detect and identify.

8.4.1.2 The viability of dissolved substances as STE tracers

Dissolved nutrient concentrations in surface waters are often used as indicators of wastewater contamination since they are present in high concentration in human wastes (Cornin et al., 2006; Anderson et al., 2010; Withers et al., 2011; Williams et al., 2013). In this work, nutrient concentrations downstream from the source were elevated, however, the relative concentration increases and the significance between upstream and downstream varied between the two sites in accordance with their flow rates (Table 8.1). Conversely, the presence of high concentrations of nutrients such as $\text{NH}_4\text{-N}$ or P in surface waters can be indicative of both sewage contamination as well as agriculture runoff contamination (Lehmann and Schroth, 2003). Therefore, relying on elevated nutrients concentration alone as an indicator for STE discharge may not reveal the true source of contamination.

Chloride is considered as a conservative element, which is often used as a tracer for sewage effluent and for groundwater tracing studies (Wilson and Mackay, 1993; Zellweger, 2006; Gill et al., 2009; Singha et al., 2011; Jarvie et al., 2012) to evaluate origin and transport of contaminants. In this work the ratio of Cl to effluent indicators in upstream and downstream waters revealed that ratio of Cl/most indicators (Table 8.3) upstream from the source was greater and significantly different ($P < 0.05$) from downstream for Site 1. Therefore, Cl ratios between Ba, Zn, B, TSS, alkalinity, EC, Turbidity and saccharin stand out as potential tracers for STE discharge in streams with low level of dilution. Katz et al. (2011) used Cl/Br ratio to identify ST input to ground waters, however, in this current work Cl/Br ratios statistically had no significant difference between upstream and downstream ($P > 0.05$) as Br concentration was similar for both up and downstream waters.

This study found no statistical significant difference in B concentration upstream and downstream for Site 2 while in Site 1, B concentration in downstream water exceeded that of the effluent from the ST. This highlighted that an additional unknown source may have contributed to B concentration downstream of Site 1 or B movement may have been restricted and not mixed with receiving water of the smaller stream.

8.4.1.3 Fluorescence of effluent dissolved OM to track SET

Domestic wastewater contains a collection of anthropogenic OM including proteins, fats and carbohydrates, which possess fluorescence properties (Hudson et al., 2008). The fluorescence of OM in STE and stream waters of this work, revealed the presence of the tryptophan-like peak in the effluent with high intensity (Table 8.1), which was also detected downstream at Site 1 but was not present upstream from ST discharge (Figure 8.2 and Table 8.1). Thus, the presence of tryptophan-like peak in receiving waters may potentially be used to track STE discharge. However, the anthropogenic input in the form of tryptophan-like peak was only detected in downstream water of Site 1 and was not present in Site 2. Thus, the results suggest that fluorescence spectroscopy's ability to be used as a tracer for effluent discharge can be limited to a low dilution nature of water courses or to a situation where stream discharge is extremely low. The strong positive correlation between tryptophan, *E. coli* and SRP for Site 1 was indicative of the similar behaviour (Table 8.2 and Figure S8.4) and demonstrates the potential of tryptophan fluorescence to track a discharge of a faecal origin and may act as a surrogate indicator for effluent SRP. This is in agreement with Baker et al. (2015) and with a study by Sorensen et al. (2015) in which the authors declared that tryptophan-like peak can be an effective indicator of faecal enteric bacteria in drinking water supply. To increase fluorescence data resolution, and to validate this finding, more work is required.

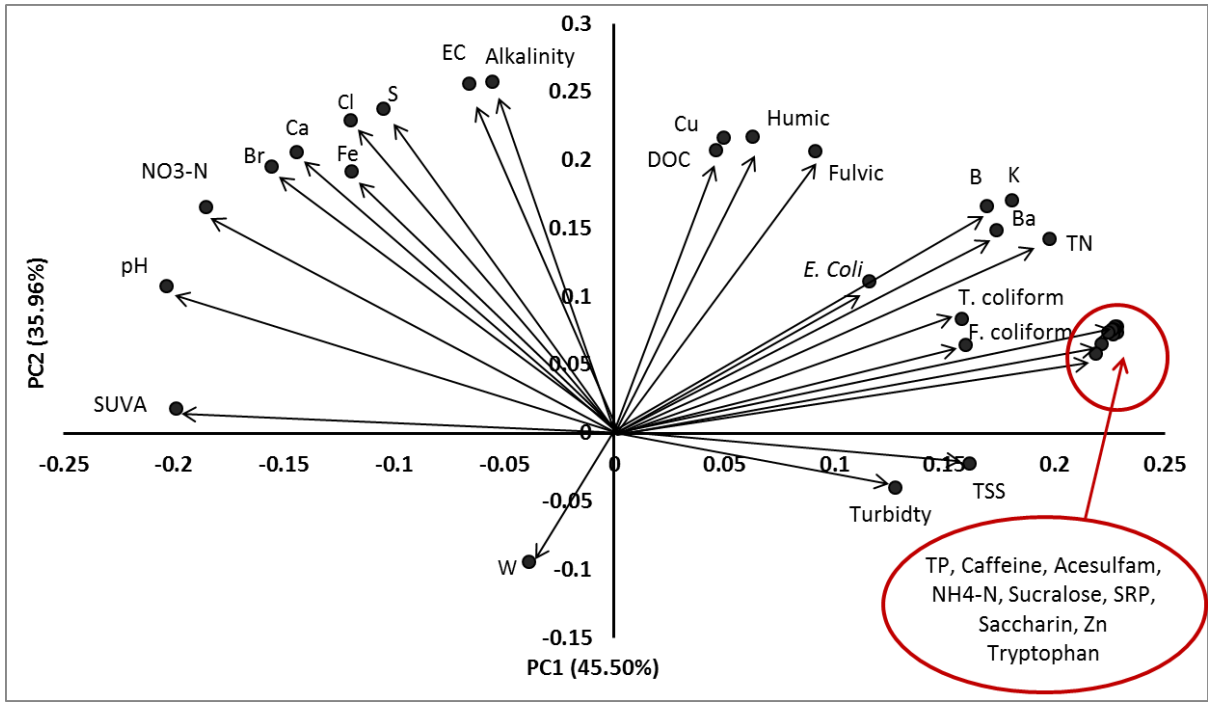


Figure S8.4: Loading plot of weights assigned to stream water indicator variables including artificial sweeteners and caffeine which explain 81.46% of the total variance. Arrows represent the weight and the direction of each parameter in relation to others.

8.4.1.4 The capability of trace organic compounds to track STE

Organic compounds such as caffeine and artificial sweeteners originate from anthropogenic sources such as food, drinks, medicines, toothpaste, and are therefore present in sewage waters through human consumption then excretion in the un-hydrolysed form (Spoelstra et al., 2013). Caffeine and artificial sweeteners are uniquely specific to domestic wastewater and their resistance to breakdown during sewage treatment make them ideal tracers for sewage discharge if detected and quantified in the environment (Seiler et al., 1999; Robertson et al., 2013). In this work, the concentrations of caffeine and artificial sweeteners downstream from the source were elevated relative to upstream waters (Table 8.1), and their concentrations upstream of Site 1 were below detection limits. The artificial sweetener acesulfame K concentration of 19 µg/l found in downstream waters at Site 1 is comparable to 12 µg/l reported by Robertson et al. (2013) for ground water and is indicative of artificial sweeteners tendency to accumulate in aquatic systems. Buerge et al. (2009) suggested that acesulfame K can be the ideal tracer of wastewater in environmental samples due to its resistance to degradation in wastewater treatment plants (WWTP). Conversely, Scheurer et al. (2009) reported that saccharin was more easily degraded during WWTP processes (Soh et al., 2011). However, in this work saccharin concentration downstream from the ST had the greatest concentration compared to other sweeteners tested (Table 8.1). This can imply that, while saccharin is easily degradable by WWTP processes, it may have a conservative nature in STE and that ST processes contribute little to saccharin degradation. Therefore, saccharin may be considered as a potential marker for STE in environmental samples. Furthermore, the positive correlation between caffeine and artificial sweeteners with faecal coliforms and *E. coli* in stream waters (Table 8.2) demonstrates the potential of these organic markers to track a discharge of a faecal origin and highlight the risks of waterborne diseases. Although the presence of caffeine and artificial sweeteners in stream waters can be an indication of contamination, their detection requires a complex and expensive technique such as SPE-LC-MS/MS (Zwir-Ference and Biziuk, 2006).

8.4.2 Using effluent tracers to indicate P sourced from septic tank

Phosphorus in receiving waters in rural catchments has many sources: agricultural runoff, farm wastes, sewage treatment works (STW) and septic tank discharges (Johnston and Dawson, 2005; Withers et al., 2009). Therefore, direct measurement of P contribution from ST to watercourses can be a difficult process and hence the use of tracers to estimate ST contribution of P is often

necessary. A number of studies have used tracer techniques to quantify effluent from STW discharges (Alhajjar et al., 1990; Vengosh and Pankratove, 1998; Nael et al., 2010), which can differ in composition and concentration from ST discharges (Lowe et al., 2009). In this study a number of tracers that were naturally present in STE were explored for the possibility of being used as a surrogate indicator for P from STE. As STE contained a large concentration of SRP (Withers et al., 2011; Richards et al. 2016), it was appropriate to investigate STE indicators that behave in a similar way and positively correlate with SRP in stream waters including caffeine and artificial sweeteners (Table 8.2). The correlation coefficients ranged 0.97-0.99 and were indicative of the similar behaviour of these indicators and SRP for both sites. Moreover, the loading scatter plot of SRP and potential tracer indicators (Figure S8.4) confirmed the strong positive correlation between TP, SRP, caffeine, artificial sweeteners, $\text{NH}_4\text{-N}$, Zn, tryptophan, faecal coliforms and total coliforms, indicating their potential to track effluent P. Nutrient attenuation behaviour in downstream water (Figure 8.3), highlighted the reactivity of SRP and $\text{NH}_4\text{-N}$, and also suggested the similarity in the attenuation behaviour of SRP, caffeine and artificial sweeteners. Therefore, the presence of these indicators in stream waters not only can indicate sewage and STE contamination, but also may act as a marker for effluent P.

8.4.3 A Combined tracing approach

The ability to track contaminants movement and transport in watercourses is essential to monitor their presence to remediate impacted waterbodies. The simplest step of effluent traceability is the initial visual and physical parameters encountered during field screening activities such as odour, colouration, turbidity, floating deposits and signs of lush vegetation indicating sewage effluent discharge. Following from that is the microbial and physicochemical characterisation of stream waters including hydrological factors such as stream dilution caused by rainfall and stream discharge, which may influence the degree of pollution and the choice of tracing method in waterbodies. For watercourses with low effluent dilution level, it was found that a number of effluent parameters and markers combined such as fluorescence intensity of tryptophan-like peak, microbial population and elevated nutrient concentrations as well as Cl/indicators ratios may be used to track STE discharges. Conversely, for watercourses with high dilution levels, more complex methods to track STE discharge, such as SPE-LC/MS/MS analysis of stream waters, can be employed to detect organic compounds used only by humans and present in STE (e.g. caffeine and artificial sweeteners). Caffeine and artificial sweeteners were positively correlated with FIO such as coliforms

and *E. coli* abundances and with TP and SRP in stream waters, suggesting their potential role as reliable tracers of effluent discharges and effluent P. This study agrees with Barrett et al. (1999) and Cronin et al. (2006) that a combination of multiple tracers and indicators are the most indicative way of tracking STE discharge and that factors such as rainfall, stream discharge and volume are important to consider before choosing a tracer and assuming STE contamination.

8.5 Conclusion

The aim of this work was to investigate STE discharge in stream waters through effluent in situ tracers in streams with low and high level of effluent dilution. This work revealed that a combination of multiple tracers and indicators are the most indicative way of tracking STE discharge, and that factors such as rainfall, stream discharge should be considered before choosing a tracer to evaluate STE contamination. This study revealed that catchment difference between sites caused elevated alkalinity, EC, TN, B and Ba, however, these elevations did not influence downstream concentrations at the highly diluted stream. Moreover, catchment differences did not seem to have influenced microbial or nutrients concentrations for upstream at both sites relative to downstream waters. Septic tank effluent parameters were elevated downstream adjacent to the source relative to upstream water in both stream systems, though to a lesser extent in the stream with high level of effluent dilution. Tracking effluent discharge using the ratio of a conservative element such as Cl and effluent indicators revealed that of Cl/Ba, Cl/Zn, Cl/B, Cl/ NH₄-N, Cl/turbidity, Cl/TN, Cl/TSS, Cl/EC and Cl/total coliforms (greater upstream) stood out as potential tracers for STE discharge in streams with low level of dilution. The results also revealed that fluorescence of tryptophan-like peak can be used to track a discharge of a faecal origin and may act as a surrogate indicator for effluent SRP. However, fluorescence detection of the anthropogenic input can be limited to water courses with low level of dilution or to streams with extreme low discharge. For stream with high level of dilution, tracking STE discharges using caffeine and artificial sweeteners as tracers can be employed, which involved complex and expensive detection and pre-concentration techniques (LC-MS/MS). This work revealed that artificial sweeteners can be a suitable tracer for effluent discharge and that ST processes contribute little to saccharin degradation and may be considered as a potential marker for STE. Caffeine and artificial sweeteners were positively correlated with faecal coliforms, *E. coli* and SRP, which suggests their potential to track discharges for key regulatory targets such as microbial and P pollution.

Supplementary material: Detailed method for artificial sweeteners and caffeine detection:

This analytical procedure describes the sample preparation of received samples and specifies a liquid chromatography tandem mass spectrometry (LC-MSMS) method for the determination of four separate artificial sweeteners and Caffeine.

450µl of sample was transferred to an LC vial and 50µl of a 1µg/ml mixed internal standard solution containing Acesulfame K-d₄, Cyclamic acid-d₁₁, Saccharin-¹³C₆, Sucralose-d₆ and Caffeine-d₉ added.

Analysis was carried out using an Agilent 1100 series LC system interfaced to a Waters Quattro Ultima Platinum triple quadrupole mass spectrometer operating in both positive and negative electrospray ionisation (ESI) modes. The HPLC-MS/MS system was controlled by MassLynx™ software and data processing was carried out using MassLynx™ 4.1 software (both from Waters).

The HPLC column was a Waters XSELECT CSH C18 3.5µm x 2.1mm x 150mm. The mobile phase consisted of 95% methanol/5% water/10 mM ammonium acetate in channel A and 95% water/5% methanol/10 mM ammonium acetate in channel B at a constant flow rate of 0.2 ml/min. The HPLC was programmed to hold 95% channel B for 2 minutes followed by a linear decrease to 50% channel B over 5 minutes, then held at 50% for 8minutes before returning to 95% with a runtime of 22minutes. The injection volume was 5µl.

The electrospray voltage was set at 3.0 and 1.0 kV for positive and negative modes respectively. The desolvation and source temperatures were set at 350 °C and 120 °C in positive mode and 400 °C and 120 °C respectively in negative mode. Nitrogen was employed as the desolvation and cone gas with a flow rate set to 500 L h⁻¹ and 70L h⁻¹ respectively. The collision gas was argon at a pressure of 2.7 x 10⁻³ mBar.

Ions monitored in –ve mode

Ions monitored	Cone voltage	Collision energy	Compound
161.80 > 77.80	40	13.0	Acesulfame K
161.80 > 81.90	35	10.0	Acesulfame K
165.70 > 85.90	40	13.0	Acesulfame K-d ₄ (3,4-Dihydro-6-methyl-1,2,3-oxathiazin-4-one-d ₄ 2,2-Dioxide Potassium Salt)
178.00 > 79.90	35	17.0	Sodium cyclamate
189.00 > 79.70	35	17.0	Cyclamic acid-d ₁₁ (N-(Cyclohexyl-d ₁₁)sulfamic Acid)
181.90 > 62.00	40	13.0	Saccharin
181.90 > 105.80	55	14.0	Saccharin
187.80 > 105.60	55	14.0	Saccharin- ¹³ C ₆ (1,2-(Benzisothiazol-13C ₆)-3(2H)-one 1,1-Dioxide)
394.60 > 358.60	45	10.0	Sucralose
396.60 > 360.60	50	10.0	Sucralose
400.90 > 364.80	45	10.0	Sucralose-d ₆ (1,6-Dichloro-1,6-dideoxy-β-D-fructofuranosyl-4-chloro-4- deoxy -α-D-galactopyranoside-d ₆)

Ions monitored in +ve mode

Ions monitored	Cone voltage	Collision energy	Compound
194.90 > 110.10	40	19.0	Caffeine
195.10 > 138.10	60	15.0	Caffiene
203.80 > 143.80	60	15.0	Caffeine-d ₉ (1,3,7-Trimethyl-d ₉)

Chapter 9

Summary, Conclusion and Future Work

Septic tank systems (STS) are the most widely used systems around the world for treatment and disposal of domestic wastewater where connection to the mains sewerage network system is not available. The preferred use of STS stems from their relative simplicity, low costs and treatment capabilities, however, the performances of STS is highly variable and hence, they often produce effluent with varied quality. The quality and concentration of STE parameters depends on household habits, water and detergents use. Septic tank systems often fail due to aging, users neglect and lack of maintenance, posing risks to the environment. Domestic wastewaters contain a wide variety of pollutants including pathogens, faecal bacteria, phosphorus (P), nitrogen (N), organic matter (OM), biochemical oxygen demand (BOD) and suspended solids (SS) as well as pharmaceutical organic compounds and household detergents and chemicals. Although most modern STS discharge their effluent to soil systems for contaminants removal in the soakaway/drainage field, soil treatment is also highly variable. Moreover, some tanks were designed to discharge directly to watercourses without secondary soil treatment, and in the case of failing systems, contaminants often reach surface and groundwaters posing ecological impacts on water quality and human health.

9.1 Detergents phosphorus contributions to ST discharges

Septic tank pollution is often evaluated in terms of the annual load of an environmentally targeted element such as P for its contribution to eutrophication of surface waters. Unlike Waste Water Treatment Plants (WWTP), STs are not designed to remove pollutants such as P from the effluent before discharging to the environment. A proportion of the readily available P in household wastes originates from modern detergents (16-19%, Chapter 7) in the form of tripolyphosphates (TPP) that if not removed or reduced, may eventually reach surface and groundwaters. In this study, the P load from detergents to domestic waste water was found to be 0.154 kgP/person/year, of which, the dishwasher contribution alone was 0.147 kgP/person/year (Chapter 3). This dishwasher P contribution was 20 times greater than that of laundry detergents of 0.007 kgP/person/year. The

small P loading from laundry detergents was a result of detergent manufacturers entering a voluntary agreement to reduce TPP or to use alternative builders such as zeolite A. In a survey conducted during this study (Appendix 1), it was revealed that a small proportion of ST users have tried and used P reduced detergents (eco-products) at some point and then switched back to regular P-based detergents as they were deemed to be not as effective, more expensive and not widely available. This research estimated a reduction of >90% of detergents P load could be achieved if only non-phosphate based detergents were used, especially dishwasher products. The UK Detergents Regulations 2010 (SI 2010 740), which came into force in January 2015 and restricted phosphate content in domestic laundry detergents to no greater than 0.4% of detergent's weight, but currently this does not cover dishwasher detergents (coming into force in 2017 for dishwashers). Given that the detergent P loads in this study were dominated by P from dishwashers, the restriction of P content should extend to dishwasher detergents in order to reduce the P load in sewage effluents and improve surface water quality. To achieve this goal, eco and low phosphate based detergents need to be made more attractive to consumers by increasing their cleaning efficiency, availability and affordability. A validation of the effectiveness of detergents regulations is needed in terms of detergents P load before and after the regulations came into force.

9.2 Characterisation of septic tank effluent discharge

Septic tank systems are often capable of treating domestic wastes at low cost if they are designed, sited, managed and maintained appropriately. However, due to their limited capability of removing nutrients and pathogens, their use often poses environmental and human health risks. The first full characterisation of STE in the UK (Chapter 4) revealed that, not only was STE rich in bacteria, nutrients, OM and metals, but also high proportions of most parameters were present in the soluble reactive forms. Factors such as tank condition, tank maintenance, frequency of desludging, use of dishwasher and number of tank users significantly influenced the quality of STE. This research showed that tank drainage system design (receiving roof runoff) played a critical role in effluent quality, causing nitrification of ammonium-N, reducing effluent retention time in the tank with the risk of discharging untreated effluent to the environment. Infrequent desludging of the tank was linked to increased concentrations of PN, P, OM, alkalinity and bacterial abundance. Dishwasher use produced effluent with increased suspended solids and particulate P, while tanks that served larger numbers of users had effluents with greater bacterial abundance, elevated dissolved P and N concentrations. Although most STs discharged their effluents to soil soakaways for secondary

treatment, 10% of STS tested in this research discharged their effluents and contaminants directly to surface waters and 12% of STS discharged to soakaways that were sited too close to watercourses (2-30 m; Chapter 3, Section 3.3.3). A better tank design, installation and maintenance are required, possibly reinforced by legislation to remove direct connections to streams and to consider an additional treatment for STE before discharge to the environment. This would be beneficial in protecting and improving stream water quality and guarding against human health impacts.

9.3 Consistency of septic tank effluent discharge

Septic tank discharges to watercourses are persistent throughout the year and can influence surface and groundwater quality particularly during ecologically sensitive periods of elevated temperature and low flow. This research examined the consistency of STE discharges throughout the year and revealed that domestic effluent composition exhibited some seasonal variation (Chapter 5). Effluent produced in the spring and the summer was compositionally similar but different from effluent produced in the autumn and the winter. Effluent BOD concentrations were particularly greater in the spring and the summer and suggest increased effluent organic matter in warmer months. Nutrients such as P and N as well as barium (Ba) in STE were also elevated in the spring and the summer. These seasonal variations may be due to a change in water and detergent use, diets or shorter effluent retention time during warmer months (more frequent washings and showering). This work has highlighted that STE discharges are a key factor influencing adjacent downstream water quality as stream waters adjacent to ST discharges had exceeded eutrophic conditions in some parameters such as alkalinity, P and N, although concentrations for these parameters were not particularly enhanced in a certain season over another. A longer term study on temporal variation in STE composition is required to validate and enhance data resolution.

9.4 The attenuation of effluent P, caffeine and saccharin in soil

The high abundance of microorganisms and high concentrations of metals and nutrients normally present in STE are expected to be removed by filtration, precipitation and adsorption to soakaway soil systems. However, many old STS are sited on unsuitable soils and the ability of soakaway soils to remove effluent pollutants becomes increasingly exhausted over time causing contaminants to

move further away from the soakaway, which may reach ground and surface waters. This research revealed that complete removal of pollutants in soil does not occur and contaminants such as P and compounds such as caffeine and artificial sweeteners have the potential to reach watercourses. Sorption and desorption data for P, caffeine and saccharin (present in STE) on the test soil, revealed that 80% of saccharin and 33% of caffeine removal was associated with soil microbial activities rather than sorption processes (Chapter 6). A complete attenuation for saccharin and caffeine did not occur, suggesting that these substances may leach from the soil. Conversely, P removal was dominated by precipitation and adsorption processes, however, only 14-35% of effluent P was removed by soil (Chapter 6) which can infer that a large concentration of effluent P was not removed and may pose risk to surface and groundwaters. The attenuation behaviour of P, caffeine and saccharin from the effluent differed from that of aqueous solution. Phosphorus removal from an aqueous solution matrix was greater than that when the matrix was STE, suggesting that the complex composition of STE allowed other substances present in the effluent (e.g. bacteria, metals, DOC) to compete over soil binding sites. Desorption data suggested that P had the greatest leaching potential followed by caffeine, which indicating the likelihood of the adsorbed P and caffeine to become leached from the soils during rain events. Thus, the presence of saccharin and caffeine in surface and groundwaters may indicate anthropogenic activity and may be considered as tracers for domestic sewage effluent in watercourses. However, more research on STE pollutants sorption to soil is needed to validate substance removal in different types of soils and for a wider variety of organic compounds found in STE.

9.5 Annual phosphorus loading from STE discharge

Although eutrophication of watercourses is driven by N, P, elevated temperature and low flow, it is P that is considered the limiting factor in this process. Thus, it is important to estimate P loads from STE input to watercourses to assess the impacts to prioritise and target the effective mitigation measures. Annual phosphorus load *per capita* from STE was estimated using mean concentration of P (14.55 mg/l), to be 0.797 kgP/person/year for water use of 150 l/person/day and effluent retention time of 24 h. Detergent contribution of P load in the effluent was found to be 0.154 kg/person/year (Chapter 3, Section 3.3.3). The amount of P loading was increased when water use was 180 l/person/day to be 0.956 kgP/person/year. When considering the spatial and the temporal variations of STE P concentrations, it was revealed that the top 5 percentile would have P loadings of 1.67 and 2.00 kgP/person/year from water use of 150 and 180 l/person/day, respectively. When

annual P loadings were modelled on median P concentration, P loadings were 0.60 and 0.71 kg/person/year, while P loadings for the lower 5 percentile were 0.29 and 0.35 kg/person/year for water use of 150 and 180 l/person/day, respectively. The estimation of P load at these current values based on the assumption that STS were functioning and the soakaway soil was not saturated with effluent contaminants. Phosphorus load would be much greater if retention time inside the tank was reduced due to increased water use or if STS was failing and raw sewage was released to the environment. Approximately 35 and 14% of effluent P was adsorbed by soil (batch equilibrium and column experiment, respectively; Chapter 6) and 10% of P loadings are released to watercourses as direct discharge (Chapter 4). Thus, a considerable proportion of P may reach surface and groundwaters untreated. However, more work is needed for P loads estimation in different type of soils and different flow scenarios. This study also revealed that STE influence soil properties, where soils received sewage effluents had increased acidity and elevated bioavailable P concentrations relative to soils that did not receive effluents. These soils may become P leaching source relative to soils and sediment situated before the tank.

9.6 Tracing STE using in situ effluent tracers

Pollution from small point sources such as ST can be difficult to identify and apportion impacts relative to other catchment sources in order to prioritise remedial actions. Septic tank effluent in-situ tracers can be a useful tool to determine the source of pollutants in natural waters, however individual tracers have limitations. Therefore, a combination of multiple tracers and indicators are the most indicative way of tracking STE discharge. Effluent microbial indicators were found in large concentrations downstream from the source, however, their presence may not necessarily indicate human input. The mass ratios of chloride (Cl) to other effluent indicators in up and downstream waters, such as Cl/EC, Cl/NH₄-N, Cl/TN, Cl/TSS, Cl/turbidity, Cl/total coliforms, Cl/saccharin and Cl/Zn can be useful indicators for STE discharge but were only effective in streams with low levels of dilution. This research also revealed that fluorescence detection of the amino acid tryptophan-like excitation/emission peaks can be used to track a discharge of a faecal origin and may act as a surrogate indicator for effluent SRP, but was also limited to watercourses with low levels of dilution. However, caffeine and artificial sweeteners proved more suitable tracers for effluent discharges for streams with low and high levels of dilution and that processes inside the tank had little effect on saccharin in the effluent and may be considered as a potential marker for STE. Factors such as stream discharge should be considered before choosing a tracer to evaluate STE contamination.

Caffeine and artificial sweeteners were positively correlated with faecal coliforms, *E. coli* and SRP, suggesting their potential to trace discharges for key regulatory targets such as microbial and P pollution. However, more research is needed to validate and enhance the data on the use of caffeine and artificial sweeteners to track STE discharge. To date, a reliable single tracer for STE discharge does not exist, rather this study suggest that a composite multiple tracer approach is the most cost-effective way of tracking STE discharge. Table 9.1 summarising research hypothesis, key questions, results and conclusions.

9.7 Research recommendations to policy makers

This research highlighted that effluent discharges from both functional and failing ST pose risks to water quality, particularly for watercourses with low level of dilutions. Suggestions and recommendations to stakeholders to improve water quality and reduce ST impacts are:

- To include ST observations among other (agricultural) catchment inspection walks on an individual site basis to monitor tank failure, condition, and maintenance to identify problematic hot spots and to target mitigation processes.
- To increase legislative pressure on ST owners to apply and incorporate measures to reduce ST discharge emission such as, replacing aging and failing tanks, re-directing ST discharge to appropriate soakaway areas or installing additional units for microbial and nutrients removal before discharging to the environment. Since these measures are costly, though they should be done on a risk basis and potentially with funding.
- To encourage householders to manage and maintain existing tanks more effectively by using low phosphorus based detergents, ST friendly products as well as increasing the frequency of tank desludging.
- To continue promoting a reduction in water use and effort must be made to make ST user aware of STE influence on water quality.
- When replacing an old ST and installing a new unit, tank size should accommodate the maximum possible number of current and future property occupants to maintain effluent retention time inside the tank.

- A comprehensive but more costly way to reduce ST impacts on water quality is to reduce the number of STs in the catchments by extending sewage mains treatment connection to cover critical and wider areas with high densities of STs.

9.8 Potential areas for future scientific work

This research highlighted a few aspects in which future work would be beneficial:

- A long term study on STE consistency and temporal variation would be beneficial to validate and enhance STE temporal understanding.
- More research on pollutant sorption to soils is needed to investigate substance removal in different types of soils and for a wide variety of organic compounds found in STE.
- More work is needed to validate STE phosphorus load estimations for different type of soils and different effluent flow scenarios.
- More research is needed on the use of trace organic compounds found in STE to track STE discharges.
- More work is needed to validate the effectiveness of detergents legislation in reducing detergents phosphorus load.
- More work is needed to evaluate the fate of nitrogen in soakaway soil.
- Studies are required on the prolonged effect of sewage effluent release to soil on soil chemical and physical properties required.
- Research is required to assess methods of soakaway soil enhancement to increase its capability to remove effluent pollutants.

Table 9.1: Summarising research hypothesis, key questions, results and conclusions.

Hypothesis	Key Questions	Results	Conclusion
STE discharge to surface waters can pose risks to water quality as small inputs of multiple pollutants. These risks can vary with human factors such as tank design, maintenance, use of dishwasher and number of users.	What are the current physicochemical and microbial properties of STE?	STE is enriched in bacteria, nutrients, organic matter and metals relative to stream waters and large proportion of nutrients were present in the soluble reactive forms (Table 4.1 and 4.2).	The hypothesis was proven. Discharges from STE pose risks to water quality and these risks vary with human and tank factors associated with the tank.
	What are the enrichment potential of STE to stream waters?	The enrichment potential of STE was greatest for NH ₄ -N, microbial populations, P, SS, turbidity and Cu compared to stream waters (Table 4.1 and 4.2).	
	Does STE composition change with the tank design, maintenance or number of users?	Tank design, maintenance and number of users influence effluent quality. Receiving roof runoff was linked to reduction in effluent retention time, infrequent desludging linked to increase OM, P, alkalinity and bacteria. Dishwasher use caused increased SS, TPP. Tanks serving large number of users had effluent with elevated P, N and bacteria (Figure 4.2 and Table 4.3) in combination with other indices.	
	Can effluent parameters be used to indicate effluent discharge?	The presence of a tryptophan-like fluorescence peak downstream from the source may be used to indicate effluent discharge (Figure 4.3).	
STE compositions would vary in different seasons and thus may have different potential ecological impact on water quality during different seasons, for example during the low flow sensitive periods.	Are STE properties consistent throughout the year?	STE was not consistent throughout the year. Effluent compositions exhibited seasonal variation in BOD, As, Ba, Co, Cr, Mn, Sr, Ti, W and Zn (P<0.05) (Table 5.1 and Figure 5.1).	STE varied during different seasons. Stream waters also exhibited seasonal variation, but was not necessarily associated with effluent seasonal variation.
	Does STE concentration vary during different seasons?	Effluent composition were similar in warmer months (spring/summer) and were different from colder months (autumn/winter) P<0.05 (Table 5.1, 5.2 and Figure 5.1).	
	Does stream water show seasonal variation associated with that of STE?	Receiving stream waters showed significant seasonal variation (P≤0.05) in alkalinity, BOD, dissolved organic carbon, sulphate, sulphur, lithium, W, Zn and <i>E. coli</i> abundance (Table 5.2 and Figure 5.3), which may not be associated with STE.	
	What are the impacts of STE discharges on downstream waters?	There was a clear significant influence of STE on downstream waters relative to upstream from the source (P<0.05) for BOD, TSS, TPP, NH ₄ -N and TPN, coliforms and <i>E. coli</i> (Table 5.3 and Figure 5.3).	

Table 9.1: Continue.

Hypothesis	Key Questions	Results	Conclusion
Detergents and household chemicals that enter the septic tank contain large quantities of P despite manufacturers' voluntary agreements and potential legislation to reduce detergents P.	What are P concentrations in household detergents and cleaning products?	The greatest P concentrations were found for regular dishwasher detergents (43-131 mg P/g detergent). Other household cleaning groups contained relatively smaller P concentrations (Table 3.1, 3.2 and Figure 3.2).	The hypothesis was proven: Detergents, particularly for dishwashers contained large quantity of P as a builder in the form of TPP, which enters septic tank (>70% of home owners use a dishwasher).
	What are detergents P loading scenarios if only regular or reduced-P detergents were used?	P load from detergent use was 0.154 kg P/person/year of which the dishwasher contribution was 0.147 kgP/person/year. P loading from P-reduced detergents was estimated to be 0.007 kgP/person/year.	
	Can major or trace elements found in detergents act as a tracer for effluent discharges?	Na, P, SRP and B were positively correlated with each other, indicating their potential use as a tracer suite for STE in combination with other STE indices such as EC, alkalinity, turbidity and microbial abundance (Figure 3.3).	
P and other STE organic molecules (Caffeine and saccharin) are expected to be locked in the soil system. The attenuation and the degradation of these compounds may not be completed in the soil.	What is the mass removed of these substances found in STE by soil treatment?	Approximately, 91 µgP/g soil was adsorbed from the effluent. For caffeine, 6 µg/g soil was removed and for saccharin 2.8 µg/g soil was removed from the effluent during 24 h (Table 6.1 and Figure 6.2) batch equilibrium.	Large proportions of phosphorus present in septic tank effluent were not removed by soil treatment. A small proportion of caffeine and saccharin were attenuated by soil. Hypothesis was proven. These substances would leach from the soil readily.
	Does the attenuation of these substances similar in STE and in aqueous solution?	The attenuation of all 3 substances in the aqueous solution was greater than in STE, suggesting that the complex composition of STE reduced the adsorption of the tested substance and that other substances present in STE may be competing over soil binding sites (Table 6.1, Figure 6.2 and S6.1).	
	Does a complete degradation of these substances occur in soil?	A complete attenuation did not occur during the 24 h, suggesting that phosphorus, saccharin and caffeine may be leached to surface and groundwaters. Only 35% of effluent P was sorbed by soil (Figure 6.1 and 6.2).	
	What is the dominant process of the degradation /attenuation?	Phosphorus attenuation was dominated by adsorption processes. 80% of saccharin attenuation was associated with microbial activities rather than adsorption processes (Figure 6.2).	
	Can caffeine and saccharin found in STE be indicator for an environmentally targeted element such as P?	Caffeine exhibited similar behaviour to effluent P. The presence of saccharin and caffeine in watercourses can indicate anthropogenic activity and may be considered as tracers for sewage effluent in watercourses (Figure 6.1).	

Table 9.1: Continue.

Hypothesis	Key Questions	Results	Conclusion
Phosphorus annual loadings from STE can be considerable values and the release of sewage effluent to soakaway soil may cause changes in the soil property.	What are the annual P and N loadings from STE discharge?	Annual P loadings from STE to soakaway soil were 0.797 and 0.956 KgP/person/year for water use of 150 and 180 l/person/day, respectively. (Table 7.1 and Figure 7.3).	P annual load from STE alone is substantial 0.8 - 1.0 kgP/person/year. Soakaway soil acidity and bioavailable P concentration were increased when irrigated with sewage effluent.
	What is the effect of effluent irrigation on soakaway soil?	Soil acidity was increased in soakaway soil relative to soil not receiving effluent. Bioavailable phosphorus concentrations in soil and sediments situated after receiving STE were elevated, soils were P enriched and may become P leaching source relative to soils and sediment situated before the tank (Figure 7.1).	
Certain effluent parameters concentrations are much higher compared to stream waters and thus may be used to indicate effluent discharge and may contribute to source tracking methodologies.	Can effluent in-situ indicators be used to trace effluent discharge?	A single individual tracer alone was not sufficient to evaluate STE contamination, but a combination of multiple chemical and physical tracing approaches would help to identify STE inputs to stream water.	Effluent in-situ indicators can be used to track ST discharge in waterbodies, most effectively where levels of dilution are low. For waterbodies with high levels of dilution, indicators such as caffeine and artificial sweeteners can be used to track effluent discharge.
	Are these potential in-situ tracers effective in different flow scenarios?	Tracer concentration ratios Cl/EC, Cl/NH ₄ -N, Cl/TN, Cl/TSS, Cl/turbidity, Cl/total coliforms, Cl/sucralose, Cl/saccharin and Cl/Zn had potential as tracers only in the stream with low dilution level.	
	Can detection of tryptophan-like peak downstream from the source indicate of effluent discharge?	Fluorescence spectroscopy could detect STE inputs through the presence of the tryptophan-like peak, but this was limited to watercourses with low level of dilution (Figure 8.2).	
	Can STE caffeine and artificial sweeteners be used as tracking tool for effluent discharge and act as surrogate tracers for effluent P?	Concentration of caffeine and the artificial sweeteners were positively correlated with faecal coliforms, <i>E. coli</i> , TP and SRP, indicating their potential to trace discharge of a faecal origin and to be a marker for effluent P. Caffeine and SRP had similar attenuation behaviour in the receiving stream waters suggesting caffeine's potential role as a surrogate indicator for the behaviour of P downstream of effluent inputs (Table 8.3 and Figure 8.3).	

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Appendix 1

SURVEY OF SEPTIC TANK SYSTEM FOR ON-SITE WASTEWATER TREATMENT

The James Hutton Institute and Bangor University
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Please answer all questions as well as you can and put crosses in boxes where applicable. If you do not know the answer to a question, please put (nk) for not known.

QUESTIONS ON OCCUPANCY IN YOUR HOME TO INDICATE WATER VOLUME ENTERING THE TANK:

Number of people living in your home _____

Number of bedrooms in your home _____

What is the capacity (volume or size) of your septic tank? _____

Do you live here all year round? Yes No

If no, how many months of the year do you live here _____

Has the house been enlarged since septic tank was installed? Yes No

QUESTIONS ON THE DAILY ACTIVITIES IN YOUR HOME THAT LINK TO YOUR SEPTIC TANK SYSTEM:

Do you use a washing machine? Yes No

If yes, does the washing machine drain into the septic tank? _____

What is the wash load capacity of your washing machine?

- Less than 7 kg washing
- 7 kg washing
- 8 kg washing
- 9 kg washing
- Do not know

What washing machine detergents do you use? (You can put as many as you use)

In what form are your laundry detergents?

Liquid Powder Tablets All

Do you measure the amount of detergent used? Yes No

Roughly, how much detergent is used each time?

Tablets scoops capfuls

How many washing loads do you on average use in one week? _____

Have you used eco detergents? Yes No

Have you considered using eco detergents? Yes No

If you have, what do you think of their performances, prices and availability?

Do you use fabric softener? Yes No

What fabric softener do you use?

Do you use a dishwasher? Yes No

If yes, does the dishwasher drain into the septic tank? _____

What is the capacity of your dishwasher?

8 setting 12 setting More than 12 setting

Do not know

What dishwasher detergents do you normally use? _____

In what form are your dishwasher detergents?

Liquid Powder Tablets All

If not tablets, roughly, how much dishwashing detergent per use? _____

Scoops Capfuls

How many dishwasher loads are usually done in a week? _____

Have you used eco detergents? Yes No

Have you considered using eco detergents? Yes No

If you have, what do you think of their performance, prices and availability?

Do you use bleach? Yes No

If yes what is the amount of bleach you use per week? _____

QUESTIONS ON YOUR SEPTIC SYSTEM:

How old is your septic tank? _____

What type is your septic tank? _____

Has the septic system been replaced since you have been in this property? _____

If it has been replaced, in what year was it replaced? _____

What were the reasons for replacing your old system? _____

Does your septic tank drain to a soakaway or a drainage area?

Yes No Do not know

Do you know exactly where the septic tank and the soakaway are located?

Yes No

Are they accessible for observation and sampling?

Yes No Do not know

Has your drainage field/soakaway ever flooded after heavy rain? Yes No

When was the last time your septic tank was emptied?

On average, how many times has your septic tank been emptied in the last 10 years?

Do you have well/spring water or public water? _____

If you answered well water, do you use water softener for your drinking water?

Yes No

Have you ever had any problems with your septic tank system – either the tank or the soakaway?

Yes No

If yes, what was the problem and how was it resolved:

Is the septic tank or drainage field within 20 meters of a ditch, stream, lake or river?

Yes No Do not know

If yes, how far is the water course from the septic tank or drainage field?

Is your septic tank registered with SEPA? Yes No Do not know

If we need to conduct a follow up data collection of tank effluent and soakaway soil, would you be willing to participate and allow me to sample effluent and soakaway soil?

Yes No

If yes, please fill in the name and address

Your Name: Mr, Mrs, Miss _____

Mailing address:

If yes, what is the best means of contacting you?

Mail e-mail Phone

If by phone, when is the best time of the day to contact you? _____

Phone Number: _____ home/work/mobile

Additional Phone Number: _____ home/work/mobile

If by e-mail, e-mail address: _____

Any comments or additional information that you think it could help in this study:

Date _____

Thank you.

Appendix 2

Summary of septic tank survey results:

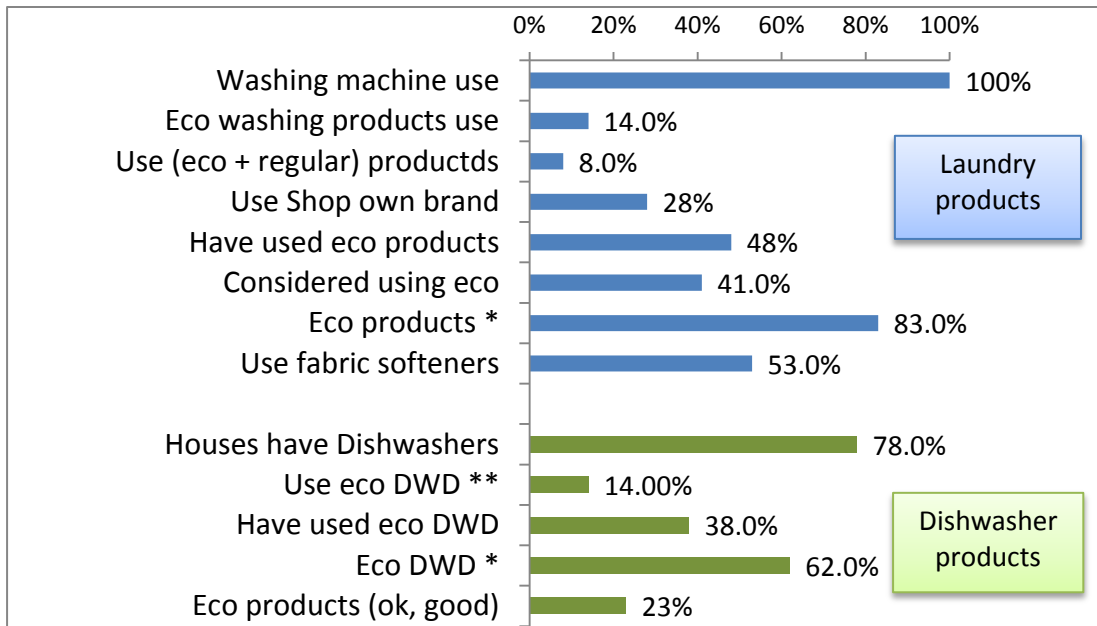


Figure A1: Survey stats on washing machine and dishwasher detergents.

* Eco products are considered by consumers as expensive, not available and not effective.

** Dishwasher detergents.

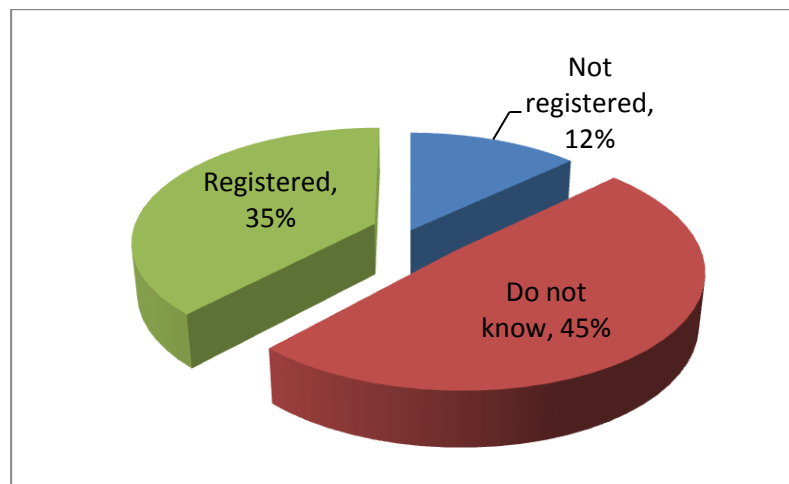


Figure A2: Septic tank% registered with SEPA.

Septic tank problems reported by tank users and listed in the survey

- Tank drains direct to a ditch (no soakaway) and ditch got blocked once causing back up of sewage and flooding of neighbouring field/ flooded and backfilled tank, we believe washing out some of the contents.
- During renovations, builder discovered that the clay pipes connecting house soil pipe to tank was ruptured, probably decades ago so the waste was not reaching tank so the connection was remade with plastic drainage pipes.
- The soakaway drains into a field that produced dark smelly patches among the grass with increased nettle growth. We dug up the ground and found broken pipes and replaced them. So this problem is now appearing in other places.
- Occasional problem with pipe work leading into the tank.
- Can be smelly in the summer.
- Threw a dead rabbit into the tank (road kill).
- Outflow was blocked - Excavated and cleared.
- It doesn't soak away well, so is often full with water; the matter has not been resolved.
- Blockage at outflow - cleared by hand several times. It tends to smell in the Summer.
- Tree roots lifted and broke the soakaway pipe and had to be dug up and pipe replaced.
- Blockage, smelly, empty eight years ago.
- Problem of flooding - Problem located to septic tank being incorrectly installed.
- We had problems with blockage to the septic tank and drain devil has used pressure to clear it.
- Blocked twice inlet into tank.
- On-going maintenance.
- ST backed up, assumed to be full of solids subsequently emptied and OK ever since.
- The septic tank and soakaway are currently broken due to be fixed and replaced this autumn.
- Outflow blocked, dug down to the pipe and removed the blockage.
- The soakaway was blocked when a new cattle court was built - now resolved.
- Blockage in input to tank - excess paper plus paper kitchen towels (from mopping up after cat!!).

