DOCTOR OF PHILOSOPHY

Temporal variation, occurrence and factors controlling the production and concentrations of volatile organic compounds (VOCs) in the marine environment

Bravo-Linares, Claudio

Award date:
2007

Awarding institution:
University of Wales, Bangor

Temporal variation, occurrence and factors controlling the production and concentrations of Volatile Organic Compounds (VOCs) in the marine environment.

Thesis submitted for the degree of Doctor of Philosophy

By

Claudio M. Bravo-Linares

School of Ocean Sciences
University of Wales, Bangor
Menai Bridge
Anglesey
LL59 5AB
United Kingdom

August 2007.

Dedicated to my
wife Julia and our
dearest son, Dylan

Abstract

The atmosphere contains VOCs which are both man-made (anthropogenic) and those produced by natural sources (biogenics). The biological production of volatile organic compounds, especially in the marine environment, constitutes an important source of gases into the atmosphere. Marine organisms can produce different kinds of trace gases, such as halocarbons, dimethylsulphide (DMS), nonmethane hydrocarbons (NMHCs) and others that are exchanged across the ocean-atmosphere boundary. Their contribution, particularly for halocarbons, has a direct influence in the composition and reactivity of the atmosphere. For instance, some of these compounds have been shown to deplete stratospheric ozone, typically referred to as ozone depleting substances (ODSs). However, they are also potent greenhouse gases, exceeding the values of the greenhouse effect of some gases such as carbon dioxide, methane and nitrogen-oxide compounds. Recognizing the harmful effects of these compounds on the ozone layer, many governments signed the Montreal Protocol in 1987 on substances that deplete the ozone layer. This limits the production and the importation of a number of halogenated compounds. Recently, the natural production of those compounds has become an important topic of research, studying their production in a variety of environments and conditions.

This thesis focuses on how external factors such as meteorology, physico-chemistry and biology drive the production and release of VOCs in the marine environment, and how individual sources contribute to the total amount of VOCs measured. The relatively new technique of solid-phase microextraction (SPME) coupled with GC-MS analysis was used for VOCs identification and quantification. Two marine environments were studied including The Menai Strait and Liverpool Bay. Multivariate analysis including Principal Component Analysis (PCA) and Partial Least Squares (PLS) was used to find relationships between VOC production and release with external factors.

Three potential natural contributors of VOCs were studied in the Menai Strait such as sediments, macroalgae and microalgae. Analysis of sediment-derived gases had 61 different compounds classified into groups as halogenated (<0.1 – 13,435 pg g^{-1} w/w), sulphur containing compounds (1.1 – 5,671 pg g^{-1} w/w), aldehydes (1.4 – 462 pg g^{-1} w/w), BTEXs and monoaromatic compounds (<0.1 – 886 pg g^{-1} w/w) and aliphatic hydrocarbons (<0.1 – 195 pg g^{-1} w/w). Results of PCA showed that the chemical composition of extracted gas is influenced primarily by sediment type. Muddy/anoxic sediments were

dominated by halogenated and sulphur containing compounds and sandy sediments had more aldehydes and BTEXs.

A range of intertidal macroalgae produced 47 different compounds: the algae studied were *Ascophyllum nodosum, Fucus vesiculosus*, *Fucus serratus*, *Laminaria digitata*, *Ulva lactuca*, *Enteromorpha sp*, *Palmaria palmata* and *Grifithsia flocculosa.* The main compound quantified was bromoform followed by dibromomethane, tetrachloroethene, chloroform, dichloromethane, diiodomethane, iodoethane, bromodichloromethane, dimethyl sulphide (DMS) and dimethyldisulphide (DMS_2). Results showed that production of VOCs increased after long immersion experiments and this production was enhanced when algae were exposed to desiccation, especially those living at low intertidal levels such as kelps.

The microalgae investigation principally focused on one species (*Skeletonema costatum*) and was used to obtain a characteristic VOC signature appropriate to the algal blooms in the Menai Strait during April. Key compounds obtained from it were iodomethane, 1-iodobutane, diiodomethane, 1,1,2-trichloroethene, 2-chloropropane, chloroiodomethane, dibromochloromethane, 1-bromopentane, 1-bromopropane, linear hydrocarbons C_5 to C_8, DMS, DMS_2, hexanal and 2,4-dimethylfurane.

A one year time series of VOC in seawater was conducted in the Menai Strait. 64 different VOCs were quantified including halogenated ($<$LoD to 906 ng L^{-1}), non-methane hydrocarbons (NMHC) ($<$LoD to 1539 ng L^{-1}), mono-aromatics ($<$LoD to 4,232 ng L^{-1}), oxygenated ($<$LoD to 1,539 ng L^{-1}) and sulphur containing compounds ($<$LoD to 160 ng L^{-1}). Pigments such as chlorophyll *a* correlated with halogenated compounds (*e.g.* chloroform and dichloromethane) and DMS was maximal during the spring bloom. Multivariate statistical analyses demonstrated the seasonal changes in the VOC signature (more BTEX and alkanes in the winter and halocarbons in the summer). PCA analysis demonstrated that physico-chemical and meteorological factors such as wind speed, water temperature can influence the detection of VOCs in surface waters as well their productions. A PLS analysis was conducted with all the signatures from the three potential sources. Signatures analysis highlighted the importance of the microalgae signature in spring while macroalgae and sediments dominated at other times. Short term variability in concentrations and fluxes was due to such factors such as tidal state, wind speed and seawater temperature.

The survey conducted in the Irish Sea and Liverpool Bay area showed a suite of compounds that can be classified as halogenated (0.2 – 1,400 ng L^{-1}), BTEXs and mono-

aromatics (1.5 - 2,900 ng L^{-1}), aliphatic hydrocarbons and others (0.6 - 15,800 ng L^{-1}). Day and night sampling was performed at a single station and suggested that factors such as sunlight and tide effect the presence of many of these compounds. Sample variability was very high under different weather conditions at the same station. Poor correlations were found with marine pigments and some selected VOCs. PCA analysis showed that chlorinated compounds such as 1,2-dichloroethane, 1,1,1-trichloroethane, trichloroethene, tetrachloroethene and carbon tetrachloride were predominantly anthropogenic in origin and originated from the River Mersey. Brominated and iodinated compounds were likely to be from biogenic sources with presence of novel marine compounds such as 2-chloropropane, 1-bromoethane and 1-chlorobutane.

In conclusion, VOCs concentrations are governed by external factors influencing their production, release and degradation in complex ways: there are factors effecting long time scale variations and also factors having an effect on a daily base. The presence of VOCs in the marine environment is the result of a combined production of natural and anthropogenic sources.

Acknowledgements

I would like to thank my supervisor Dr. Stephen Mudge for his constant and encouraging help and friendship during this thesis.

I would like to thank the technicians and secretaries of the SOS for their kindness and useful help, especially to Vivienne Ellis, Ian Pritchard, Gwyn Hughes, John East and Gillian Roberts.

I would like to thank a very special person who gave me all her support and friendship. I refer to Lynn Yule (the landlady!!!).

I would like to thank all my friends who made me feel at home during my three years in the UK.

Thanks to my family for their constant support from the distance and to all the members of the church "Ebenezer" and of course to God for giving me the opportunity to achieve my biggest dream.

I would like to acknowledge the support of my Scholarship funded by the European Community through the ALβan programme code E03D00781CL.

Thanks to my faithful mate, my beloved wife "Julia" and to our dearest son "Dylan" for giving me all their love through this thesis.

Contents

List of Figures

Chapter 1.

Chapter 2.

Chapter 3.

Page

Chapter 4.

Page

Chapter 5.

Page

Chapter 6.

List of Tables

Chapter 2:

Chapter 3.

Chapter 4.

Chapter 5.

Chapter 6.

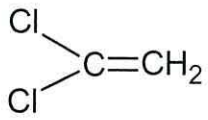
CHAPTER 1: GENERAL INTRODUCTION

1.1 Introduction

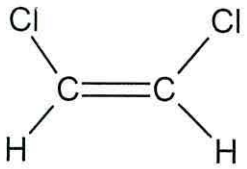
The atmosphere contains halocarbons which are both man-made (anthropogenic) and those produced by natural sources (biogenics). The biological production of volatile organic compounds (VOCs), especially in the marine environment, constitutes an important source of gases into the atmosphere. Marine organisms can produce different kinds of trace gases, such as halocarbons and other gases that are exchanged across the ocean-atmosphere boundary. Their contribution, particularly for halocarbons, has a direct influence in the composition and reactivity of the atmosphere. For instance, some of these compounds have been shown to deplete stratospheric ozone, typically referred to as ozone depleting substances (ODSs). However, they are also potent greenhouse gases, exceeding the values of the greenhouse effect of some gases such as carbon dioxide, methane and nitrogen-oxide compounds. Recognizing the harmful effects of these compounds on the ozone layer, many governments signed the Montreal Protocol in 1987 on substances that deplete the Ozone layer. This limits man-made production and the importation of a number of chlorofluorocarbons (CFCs) and other halogenated compounds. Recently, the natural production of those compounds has become an important topic of research, with studies of their production in a variety of environments and conditions.

1.2 Volatile Halogenated Organic Compounds (Halocarbons)

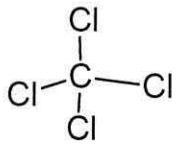
The kinds of compounds known as volatile halogenated organic compounds (VHOCs) are a group of compounds produced by natural and anthropogenic sources comprised principally of halogen atoms (chlorine, bromine and iodine), carbon and hydrogen; at ambient temperatures and atmospheric pressure they are in a gaseous phase. The VHOCs have mainly 1 to 4 carbon atoms and their natural production and concentration in seawater and air are at trace levels. The source of VOCs can be divided according to their origin into two basic groups: man-made sources and naturally occurring sources (Kuran and Sojak, 1996). Some structures of halogenated compounds produced in the marine environment are shown in Figure 1.1.



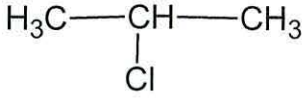
1,1-dichloroethene



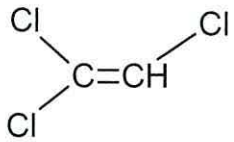
Cis-1,2-dichloroethene



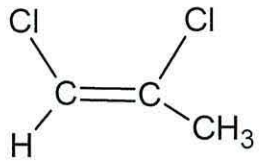
Carbon tetrachloride



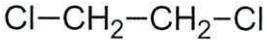
2-chloropropane



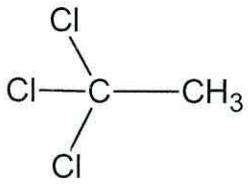
1,1,2-trichloroethene



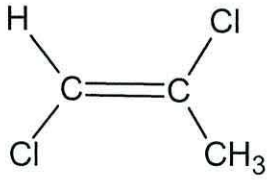
Cis-1,2-dichloropropene



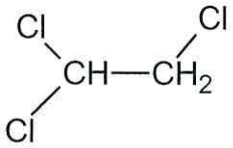
1,2-dichloroethane



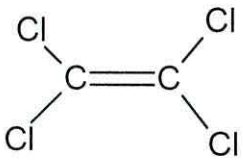
1,1,1-trichloroethane



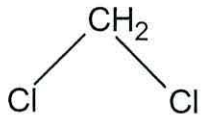
Trans-1,2-dichloropropene



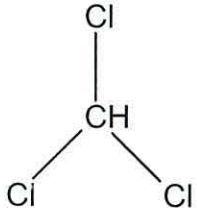
1,1,2-dichloroethane



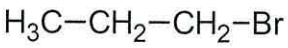
Tetrachloroethene



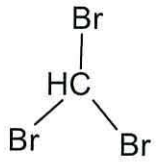
Dichloromethane



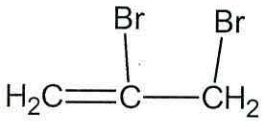
Chloroform



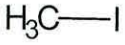
1-bromopropane



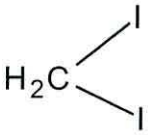
Bromoform



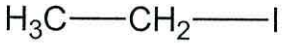
2,3-dibromopropene



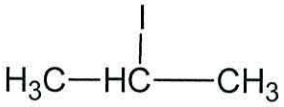
Iodomethane



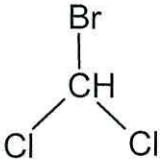
Diiodomethane



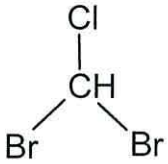
Iodoethane



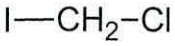
2-iodopropane



Bromodichloromethane



Dibromochloromethane



Chloroiodomethane

Figure 1.1. Structures for some halogenated compounds produced in the marine environment.

1.3 Halocarbon Properties

In order to understand the processes in which halocarbons are involved when they are released from biological sources, it is necessary to understand some physical and physico-chemical parameters that affect such processes.

1.3.1 Lifetime

The lifetime of a greenhouse gas, also known as residence time, is the approximate amount of time a compound will spend in the atmosphere before either being converted into another compound or being taken out of the atmosphere via a sink (WMO, 2002). This time depends on the pollutant's sources and sinks as well as its reactivity. Lifetime affects the mixing of chemicals in the atmosphere; a long lifetime will allow the chemical to mix well in the atmosphere. Average lifetimes can vary from one day (nitrogen dioxide) to more than a century (CFCs, carbon dioxide, oxygen) and beyond.

The lifetime of halocarbons in the atmosphere depends on photochemical reactions and transformation, along with reactions with the OH radical or other species, temperature, radiation and oxidant concentration. In seawater, their lifetimes are dependent on temperature and biodegradation. The lifetimes of some halocarbons have been published by different authors (Table 1.1). The values differ due to the methodologies employed to calculate it; some methodologies or expressions to calculate the lifetime are as follows:

1. Lifetimes derived from a model calculated from distributions and sink loss frequencies.
2. Lifetimes inferred by inverse methods from direct observations of halocarbon abundance with high precision and accuracy over multiyear periods and requiring varying degrees of knowledge about actual emissions.
3. Lifetimes determined relative to a reference species with an independently derived lifetime through observations of species correlations or knowledge of relative kinetic rate parameters.
4. Lifetimes determined from some combination of the above three techniques, where the total lifetime is determined as the combination of individual process lifetimes.

Table 1.1. Atmospheric, global and seawater lifetimes of some halocarbons.

Compound	Lifetime	Reference
	Chlorinated	
CH_3Cl	G: 1.3 years A: 1.1-1.5; 1.0-1.3; 1.55; 0.37 years	WMO (2002) Keene *et al.* (1999); Tokarczyk *et al.* (2003); Louis *et al.* (2001); Cox *et al.* (1976)
CH_2Cl_2	G: 0.38 years A: 0.41-0.5; 0.46; 0.30 years	WMO (2002) Keene *et al.* (1999); Louis *et al.* (2001); Cox *et al.* (1976)
$CHCl_3$	G: 0.41 years A: 0.5; 0.51; 0.19 years	WMO (2002) Keene *et al.* (1999); Louis *et al.* (2001); Cox *et al.* (1976)
CCl_4	G: 26 years A: 500; 40; 330; 50 years S: 30; 3-5 years	WMO (2002) Bullister and Wisegarver (1998); Simmonds *et al.* (1983) and Simmonds *et al.* (1988); Cox *et al.* (1976); Prather and Watson (1990) Huhn *et al.* (2001); Wallace *et al.* (1994)
CH_3CH_2Cl	G: 0.11 years	WMO (2002)
CH_2ClCH_2Cl	G: 0.19 years	WMO (2002)
CH_3CCl_3	G: 5 years A: 4.8; 1.1; 6.0; 4.8-5.4 years	WMO (2002) Prinn *et al.* (1995); Cox *et al.* (1976); Prather and Watson (1990); Rudolph *et al.* (2000)
$CH_3CH_2CH_2Cl$	G: 0.06 years	WMO (2002)
	Brominated	
CH_3Br	G: 0.7 years A: 0.7; 2.1; 1.3; 0.17; 1.97; 0.7; 3 years A: 14; 35 days S: 21 days	WMO (2002) Yvon and Butler (1996); Zhang *et al.* (1992); Mellouki *et al.* (1992); Orkin *et al.* (1997); Louis *et al.* (2001); Yvon-Lewis and Butler (1997); Lobert *et al.* (1995). McGivern *et al.* (2002); Penkett *et al.* (1985) Elliott and Rowland (1993)
CH_2Br_2	G: 0.33 years A: 0.41; 0.42 years	WMO (2002) Orkin *et al.* (1997); Louis *et al.* (2001)
$CHBr_3$	G: 0.6-1.4; 0.07 years S: 2.4-6.5 years	Yvon and Butler (1996); WMO (2002) Yvon and Butler (1996)
$CH_3CH_2CH_2Br$	G: 0.04 years	WMO (2002)
$CH_2BrCH_2CH_3$	A: 14 days	Kozlov *et al.* (2003)
$CH_3CHBrCH_3$	A: 19 days	Kozlov *et al.* (2003)
	Iodinated	
CH_3I	G: 4; 0.02 days A: 2.5; 4.8; 5 days	Keene *et al.* (1999) and Fahr *et al.* (1995); WMO (2002) Fahr *et al.* (1995); Solomon *et al.* (1994); Blake *et al.* (1996) and Bey *et al.* (2001)
CH_2I_2	G: Few minutes	WMO (2002)
CH_2CH_2I	A: 4 days	Keene *et al.* (1999)
$CH_3CH_2CH_2I$	G: 1.1 days	WMO (2002)
CH_3CHICH_3	G: 1.1 days	WMO (2002)
	Mixed halogen	
CH_2ClI	G: Few hours	WMO (2002)

	A: 100 minutes	Keene *et al.* (1999)
CH_2BrCl	G: 0.37 years	WMO (2002)
	A: 0.21; 0.49 years	Mellouki *et al.* (1992); Louis *et al.* (2001)
	S: 0.42 years	Mellouki *et al.* (1992)
$CHBr_2Cl$	G: 0.19 years	WMO (2002)
	A: 0.16 years	Louis *et al.* (2001)
$CHBrCl_2$	G: 0.21 years	WMO (2002)
	A: 0.16 years	Louis *et al.* (2001)

Where G: Global, A: Atmospheric and S: Seawater lifetimes.

1.3.2 Reactions in the atmosphere and their subsequent effects

The marine boundary layer, which may consist of up to 25% of the total atmosphere by mass, is an ideal place to study the basic processes that drive atmospheric photochemistry and the relationships between free-radical sources and sinks, owing to its stable and chemically simple nature (Monks, 2000).

Many iodine and bromine containing halocarbons can be broken down by sunlight in the troposphere (the lower layer of the atmosphere) to form very reactive halogen radicals. In this way they differ from chlorofluorocarbons (CFCs) which are man-made halogen containing chemical compounds. CFCs can only be broken down to halogen radicals by ultra-violet radiation in the stratosphere (the upper atmosphere).

Halogen radicals are extremely reactive and one of their most important reactions is the destruction of ozone (Figure 1.2). In the troposphere, ozone is harmful to human health and also acts as a very strong greenhouse gas (responsible for about 15% of the enhanced greenhouse effect). Therefore, the emission of halocarbons from the sea may lower tropospheric ozone levels and reduce global warming. However, lowering ozone amounts also reduces the concentration of hydroxyl radicals in the troposphere (Cho *et al.*, 2003). Because these hydroxyl radicals clean the air of harmful chemicals, lower concentrations may reduce the air quality. The hydroxyl radical is formed by the reaction with UV radiation on O_3 and H_2O at wavelengths below 315 nm (Crutzen and Bruhl, 1993).

$$O_3 + h\nu \longrightarrow O(^1D) + O_2 \quad (<315\ \text{nm})$$
$$O(^1D) + H_2O \longrightarrow 2OH^{\cdot}$$

Biogenic halocarbons compounds participate in atmospheric photochemical reactions and they may be partially involved in the depletion of the stratospheric ozone layer (Scarratt and Moore, 1998; Thunis and Cuvelier, 2000; Abrahamsson *et al.*, 2003). Bromocarbons are the major reactive halocompounds; in addition, bromoform is estimated to be 40 to 100 times more effective in depleting stratospheric ozone than chloroform (Solomon *et al.*, 1994). However, for the same concentration in the stratosphere, iodine is most efficient in removing ozone, followed by bromine and chlorine. The estimated efficiency factor relative to chlorine (~150-300) is still higher than that of bromine (~45) (WMO, 2002). Another compound of interest is bromomethane; this compound is the

major carrier of ozone-destroying bromine to the stratosphere, and the quantities produced annually in seawater are comparable to the amount entering the atmosphere each year from natural (terrestrial) and anthropogenic sources (Anbar *et al.*, 1996). The work of Ramacher *et al.* (1999) in the Arctic Ocean expedition revealed that free bromine atoms in the atmosphere appear to be the major cause of ozone depletion (more than 92%) and the chlorine atoms contribution to the loss of ozone is of the order of 1% or less.

While iodine-containing halocarbons are photolyzed in the troposphere and interact with the photo-oxidant cycle (Solomon *et al.*, 1994), chloride- and bromide-containing halocarbons have long enough lifetimes to reach the stratosphere. There they are photolytically degraded to produce halide free radicals, which can then participate in ozone destruction.

Marine aerosol contributes significantly to the global aerosol load and consequently has an important impact on both the Earth's albedo and climate. So far, much of the focus on marine aerosol has centred on the production of aerosol from sea-salt and non-sea-salt sulphates. Recent field experiments, however, have shown that known aerosol production processes for inorganic species cannot account for the entire aerosol mass that occurs in submicrometre sizes (McInnes *et al.*, 1996). Several experimental studies have pointed to the presence of significant concentrations of organic matter in marine aerosol (Kleefeld *et al.*, 2002). There is some information available about the composition of organic matter, but the contribution of organic matter to marine aerosol, as a function of aerosol size, as well as its characterization as hydrophilic or hydrophobic, has been lacking. Findings of O'Dowd *et al.* (2004) measured the physical and chemical characteristics of submicrometre marine aerosol over the North Atlantic Ocean during plankton blooms progressing from spring through to autumn. They found that during bloom periods, the organic fraction dominates and contributes 63% to the submicrometre aerosol mass (about 45% is water-insoluble and about 18% water-soluble). In winter, when biological activity is at its lowest, the organic fraction decreases to 15%. Their model simulations indicated that organic matter can enhance the cloud droplet concentration by 15% to more than 100% and is therefore an important component of the aerosol–cloud–climate feedback system involving marine biota.

Results of particles measurements done by Greenfell et al. (1999) showed that the occurrence of nucleation events coincides with low tide and solar irradiation, suggesting a tidal-biological source of the aerosol precursors. Alkyl iodides are known to be produced by seaweed and they have a rapid photodissociation during day time (Carpenter *et al.*,

1999). One of the main iodinated compounds produced by macroalgaes is diiodomethane (CH_2I_2), this compound is photo dissociated according to the following reactions and being associated to nucleation burst in the coastal boundary layer (Hoffmann *et al.*, 2001).

$$CH_2I_2 + h\upsilon \rightarrow I + CH_2I \quad (1)$$

$$I + O_3 \rightarrow IO + O_2 \quad (2)$$

$$IO + IO \rightarrow OIO + I \quad (3)$$

Where reaction 1 and 2 are the photodissociation of alkyl iodides to produce I atoms followed by a rapid reaction of I with ozone to form IO radicals. However, based on the equation presented above is possible to suggest that IOI is not only removed from gas-phase by heterogeneous uptake on existing particles, but also might be the source of observed nucleation events in coastal areas by self-reaction of IOI as follow:

$$OIO + OIO \rightarrow I_2O_4 \text{ (or } [IO]^+[IO_3]^-)$$

$$I_2O_4 + n\,OIO \rightarrow [-I - O - IO2 - O -]_{1+n/2}$$

Once the VOCs are released into the atmosphere they take part of different atmospheric reactions, and some of them like halogenated compounds and dimethyl sulphide are believed to be involved in what is called cloud condensation nuclei (CCN) formation. CCN can be defined as hygroscopic aerosol particles that can serve as nuclei of atmospheric cloud droplets, that is, particles on which water condenses (activates) at supersaturations typical of atmospheric cloud formation (fraction of one to a few percent, depending on cloud type)

Sulphate aerosol (SO_4^{2-}) and methanesulphonic acid droplets act as CCNs. These sulphate aerosols form partly from the dimethyl sulphide (DMS) produced by phytoplankton in the open ocean (Kloster, 2006).

1.3.2.1 Very Short-Lived Halogen Substances (VSLH)

In accordance with the lifetime, some halocarbons are defined as Very Short-Lived Halogen Substances (VSLH). These substances have chemical lifetimes of a few months or less, comparable with tropospheric transport time scales, with the result that the steady-state mixing ratio of the substance in the troposphere depends on where and when (time of the year) it is released.

The most efficient route for irreversible transport of VSLH source gases and their degradation products from the surface to the stratosphere is in the tropics, as the vertical transport times from the surface to the upper troposphere are short, and air that enters the stratosphere through the tropical tropopause remains there for more than a year.

These compounds might be degraded in the atmosphere and converted in precursors of important quantities of inorganic substances, such as inorganic chlorine, bromine and iodine (Dvortsov *et al.*, 1999). Platt and Honninger (2003) suggested that the VSLH probably are precursors of free tropospheric BrO and coastal IO, and other chemical species potential depressors of stratospheric ozone. The scheme showing the reaction pathways is presented in the Figure 1.3.

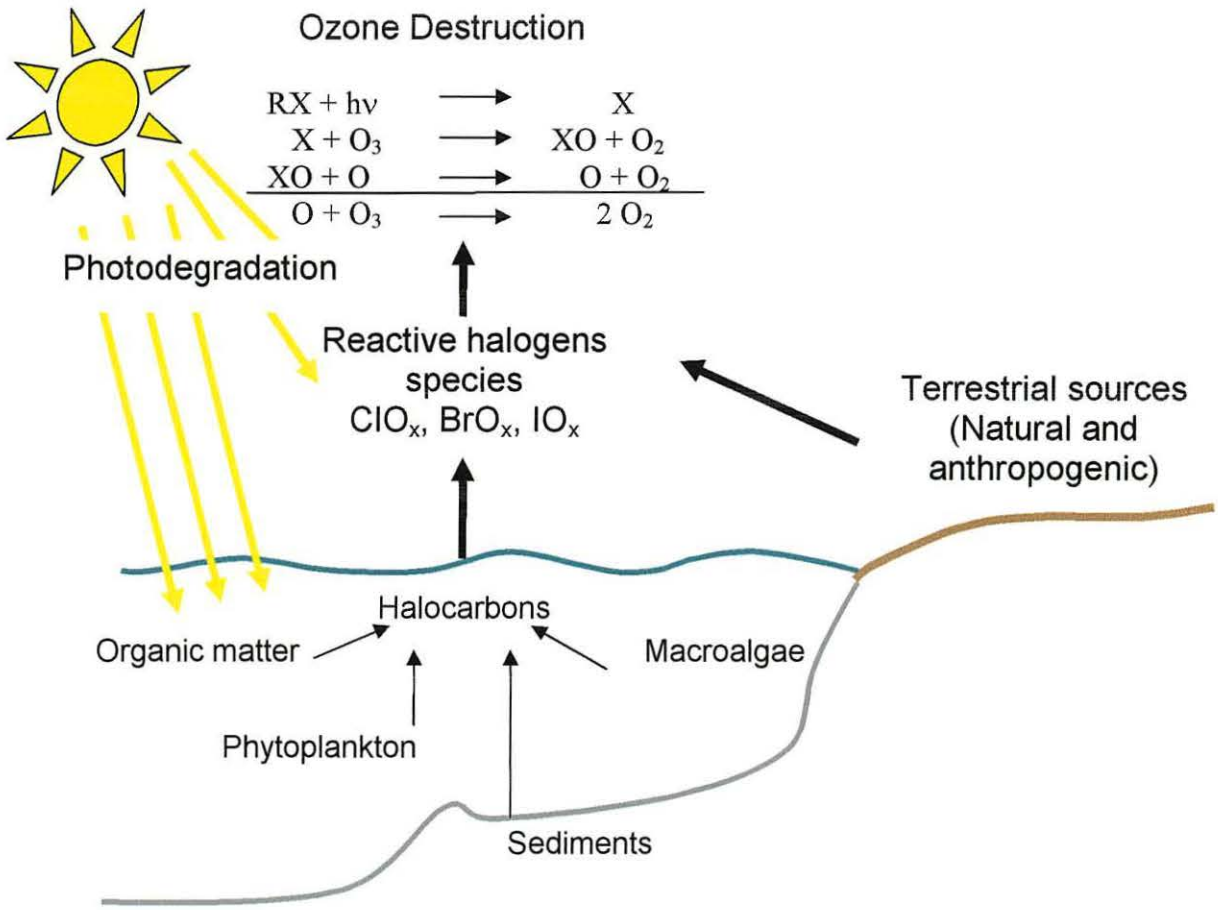


Figure 1.2. Production and pathways of halocarbons and subsequent destruction of atmospheric ozone. X= Cl, Br and I.

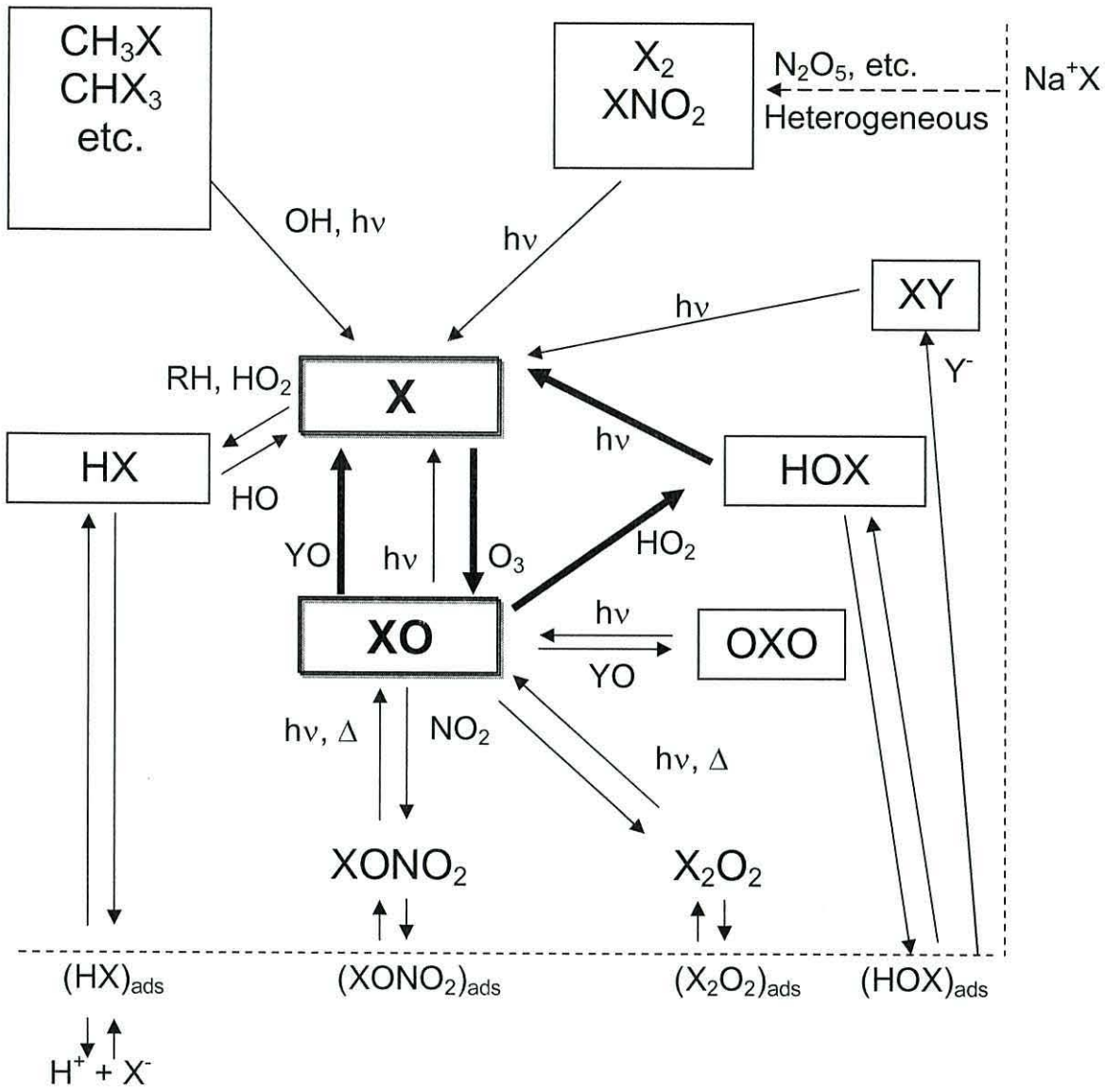


Figure 1.3. Scheme of the inorganic halogen reactions in the boundary layer (X, Y=Cl, Br, I). Taken from Platt and Honninger (2003).

The removal mechanisms of VSLH are mainly through oxidation with the OH radical, photolytic reactions (Yamamoto *et al.*, 2001) and/or UV dissociation (280-315 nm) (Erickson III *et al.*, 2000). Table 1.2 shows the VSLH, dominant loss processes and main degradation products.

Table 1.2. Dominant loss processes and product formation by different degradation pathways of VSLH.

Compound type	Dominant loss process	Products
Bromine and chlorine containing Photo-labile compounds Brominated and iodoalkanes	OH radical	Carbonyl halides Peroxynitrates Hydroxyhalomethanes Haloperoxy acids
Alkyl iodides (RI +hν → R +I) Multiple substituted halomethanes	UV photo-dissociation or photolysis.	Formyl halides Halo-oxides

1.3.2.2 Ozone Depletion Potential

The Ozone Depletion Potential (ODP) of a halogen source gas X (ODP(X, X_e,T_e)) is defined as the time-integrated effect on stratospheric ozone caused by emission of X at location X_e and time T_e relative to the time-integrated effect on stratospheric ozone from the same mass emission of CFC-11 (CCl_3F) at the same location and time (WMO, 2002).

The ODP is an integrative quantity, distinct for each halocarbon source species, that represents the extent of ozone depletion in the stratosphere expected from the halocarbon on a mass-for-mass basis, relative to CFC-11. The formal definition of ODP is the ratio of integrated perturbations to total ozone, for a differential mass emission of a particular compound relative to an equal emission of CFC-11. Some values are shown in Table 1.3.

Table 1.3. Ozone Depletion Potentials for long-lived halocarbons. Taken from WMO (2002).

Halocarbon	WMO (2002) Updated Semiempirical	Schauffler *et al.* (2002) Semiempirical	WMO (1999) Model	WMO (1999) Semiempirical	Montreal Protocol (1987)	Average
CCl_4	0.73	0.78	1.20	-	1.1	**0.95**
CH_3CCl_3	0.12	0.15	0.11	0.12	0.1	**0.12**
CH_3Cl	0.02	-		-	-	**0.02**
CH_3Br	0.38	-	0.37	0.37	0.6	**0.43**
CCl_3F (CFC-11)	1	-		-	-	**1**
$CBrF_3$ (Halon-1301)	12	-	12	12	13	**12.25**

1.3.2.3 Global Warming Potential

Global Warming Potentials (GWPs) are used to estimate the integrated climate forcing of various greenhouse gases compared with a reference gas, usually chosen to be carbon dioxide (CO_2). They provide a simple way to gauge how decisions affecting greenhouse gas emissions (*e.g.* in the Kyoto Protocol) may influence our future climate in a relative sense. Furthermore, they allow the effects of these potential actions to be roughly assessed in terms of a "carbon dioxide equivalent" emission. Some values of GWP are listed in table 1.4 for selected halocarbons and other greenhouse gases in order to compare the fact that halocarbons are several times more effective than other greenhouse gases, such as carbon dioxide, in the Global Warming Effect.

Table 1.4. Direct Global Warming Potentials (mass basis) for gases that have adequately characterize lifetimes. Taken from WMO (2002) and IPCC (2001).

Compound	Source	Global Warming Potential for Given Time Horizon		
		20 years	100 years	500 years
CH_3CCl_3	WMO	476	144	45
CCl_4	WMO	2,540	1,380	437
CH_3Cl	WMO	56	17	5
CH_3Br	WMO	16	5	1
$CHCl_3$	IPCC	*	140	*
CO_2	IPCC	1	1	1
CH_4	IPCC	62	23	7
N_2O	IPCC	275	296	156
SF_6	IPCC	15,100	22,200	32,400

*: No data

1.3.3 Sea/air gas exchange

The atmosphere is the major source of gases to sea water. The atmosphere itself consists of a mixture of major, minor and trace gases. The ocean can act as either a sink for atmospheric gases or a source of those gases to the atmosphere (Chester, 1990). The gases enter or leave the ocean via exchange across the air/sea interface, and are transported within the ocean reservoir by a physical process (Chester, 1990).

The large surface area of the global ocean results in the chemistry of the remote marine boundary layer being sensitive to the surface emission/uptake processes occurring in the underlying ocean. Many of the gases which undergo surface exchange processes, such as carbon dioxide (CO_2) and dimethylsulphide (DMS) are related very closely to the abundance of specific primary producers. Other gases, such as carbon monoxide (CO), halocarbons, non-methane hydrocarbons (NMHCs) and other relatively low molecular weight trace gases, are more strongly related to photochemical reactions in surface seawater (Zepp and Ritmiller, 1995), further influenced by the biological exudates of primary producers, bacteria and other marine organisms (Erickson and Eaton, 1993; Doney *et al.*, 1996). Furthermore, the equilibrium solubilities of trace gases in the non-polar nature of the surface seawater are a function of temperature and salinity. The air/sea boundary is not a simply connected surface. Bubbles in the water and droplets in the air extend the area of interaction between those fluids. The entrainment of air bubbles provides a major source for dissolved oxygen, carbon dioxide and other gases in the oceans. The spray drops form marine aerosols contain an inordinate amount of organic and inorganic substances (Kraus, 1972). For most gases, the surface region of the ocean, especially the top (100 μm or so), is the most relevant region for gas exchange between the ocean and the atmosphere (Jones, 1980).

1.3.3.1 Physical properties

The physical parameters are one of the most important parameters that govern the sea/air gas exchange. These parameters for halocarbons are studied and reported mainly in fresh water; few measurements have been done in seawater. This requires urgent attention, as oceans constitute over 70% of the earth surface, significantly greater than fresh water bodies. Some parameters that have been studied are, for example, the Henry's constant, diffusivity and solubility.

1.3.3.2 Henry's Constant

Henry's law constant (the concentration in air divided by that in water at equilibrium) is a basic parameter used to determine the partitioning of VOCs between various environmental compartments. This constant is used in environmental applications (air-stripping process to remediate VOCs in contaminated waters), analytical applications (headspace gas chromatography), determination of surface seawater gas saturation and for the calculation of exchange velocity or fluxes. This constant determines the extent to which resistance to transfer occurs in the gas across the liquid phase. High values mean that the gas has a low solubility in the liquid phase and low values mean that the gas has a high solubility in the liquid phase, such as halocarbons in seawater.

Temperature and salinity are the parameters that have been considered to affect the values of Henry's constant of some halocarbons in seawater. Some equations to obtain the Henry's constant in seawater (~35 psu) were determined by Hunter-Smith *et al.* (1983) in the function of surface water temperature, the equations are as follows:

Methyl chloroform	$\ln H = -3905/T + 13.04$
Carbon tetrachloride	$\ln H = -3230/T + 11.27$
Chloroform	$\ln H = -3649/T + 10.63$
Iodomethane	$\ln H = -3541/T + 10.34$ (determined only in distilled water)

Henry's constants (dimensionless) for halocompounds as a function of temperature are presented in Table 1.5.

Table 1.5. Henry's constant (dimensionless) measured in different temperatures in sea water.

Compound	Temperature (°C)	Henry's constant (Dimensionless)	Reference
		Chlorinated	
Chloromethane CH_3Cl	0	0.17; 0.17	Elliott and Rowland (1993); Moore *et al.* (1995)
	3	0.20	Moore *et al.* (1995)
	6	0.22; 0.08	Moore *et al.* (1995); Schwarzenbach *et al.* (1993)
	10	0.06	Gossett (1987)
	17	0.10	Gossett (1987)
	22	0.36	Elliott and Rowland (1993)
	25	0.15	Gossett (1987)
	35	0.22	Gossett (1987)
Dichloromethane CH_2Cl_2	6	0.11	Dewulf *et al.* (1995)
	10	0.05	Gossett (1987)
	17	0.05	Gossett (1987)
	25	0.25; 0.09	Dewulf *et al.* (1995); Gossett (1987)
	35	0.13	Gossett (1987)
Chloroform $CHCl_3$	0	0.056	Moore *et al.* (1995)
	10	0.09; 0.1; 0.06	Moore *et al.* (1995); Hunter-Smith *et al.* (1983); Gossett (1987)
	17	0.1	Gossett (1987)
	20	0.14; 0.16	Moore *et al.* (1995); Hunter-Smith *et al.* (1983)
	25	0.15	Gossett (1987)
	35	0.22	Gossett (1987)
Carbon tetrachloride CCl_4	6	0.58	Dewulf *et al.* (1995)
	10	0.57	Gossett (1987)
	17	0.88	Gossett (1987)
	25	1.36; 1.24; 1.5	Dewulf *et al.* (1995); Gossett (1987); Schwarzenbach *et al.* (1993)
	35	1.82	Gossett (1987)
1,2-Dichloroethane CH_2ClCH_2Cl	6	0.0241	Dewulf *et al.* (1995)
	25	0.0495	Dewulf *et al.* (1995)
1,1,2-trichloroethene $CCl_2{=}CHCl$	6	0.16	Dewulf *et al.* (1995)
	10	0.29	Gossett (1987)
	17	0.49	Gossett (1987)
	25	0.43; 0.72	(Dewulf *et al.*, 1995); Gossett (1987)
	35	1.12	Gossett (1987)
1,1,1-trichloethane CCl_3CH_3	6	0.345	Dewulf *et al.* (1995)
	25	0.811; 0.94	Dewulf *et al.* (1995); Schwarzenbach *et al.* (1993)
Tetrachloroethene $CCl_2{=}CCl_2$	6	0.309	Dewulf *et al.* (1995)
	10	0.29	Gossett (1987)
	17	0.49	Gossett (1987)

	25	0.775; 0.72	Dewulf *et al.* (1995); Gossett (1987)
	35	1.12	Gossett (1987)
Brominated			
Methyl Bromide	0	0.11	Elliott and Rowland (1993)
CH_3Br	22	0.24	Elliott and Rowland (1993)
Dibromomethane	0	0.01	Moore *et al.* (1995)
CH_2Br_2	10	0.02	Moore *et al.* (1995)
	20	0.03	Moore *et al.* (1995)
Bromoform	0	0.006	Moore *et al.* (1995)
$CHBr_3$	10	0.01	Moore *et al.* (1995)
	20	0.02	Moore *et al.* (1995)
Iodinated			
	0	0.1; 0.08	Elliott and Rowland (1993); Moore *et al.* (1995)
Iodomethane	10	0.14	Moore *et al.* (1995)
CH_3I	20	0.22	Moore *et al.* (1995)
	22	0.22	Moore *et al.* (1995)
Diiodomethane	0	0.004	Moore *et al.* (1995)
CH_2I_2	10	0.01	Moore *et al.* (1995)
	20	0.01	Moore *et al.* (1995)
Mixed halogen			
Dichlorobromomethane	0	0.02	Moore *et al.* (1995)
$CHBrCl_2$	10	0.04	Moore *et al.* (1995)
	20	0.08	Moore *et al.* (1995)
Iodochloromethane	0	0.01	Moore *et al.* (1995)
CHClI	10	0.02	Moore *et al.* (1995)
	20	0.03	Moore *et al.* (1995)
Chlorodibromomethane	0	0.01	Moore *et al.* (1995)
$CHBr_2Cl$	10	0.02	Moore *et al.* (1995)
	20	0.04	Moore *et al.* (1995)

According to Dewulf *et al.* (1995), the dependency of H upon temperature and salinity is expected to be:

$$\ln H = a\,(1/\boldsymbol{T}) + b$$

$$\ln H = c\,(\boldsymbol{Z}) + d$$

Where a, b, c and d are constants, $\boldsymbol{T}$ is the temperature (K) and $\boldsymbol{Z}$ the salt concentration (ppt).

Although, apparently salinity is not a parameter that affects the Henry's constant. Moore *et al.* (1995) reported that the effect of ionic strength on the apparent Henry's

constants appears to be minimal. These results show that the solubilities of halocarbons should be mainly affected by seawater temperature rather than seawater salinity.

1.3.3.3 Sea/air flux and exchange

The exchange of mass across the air/sea boundary is of fundamental importance in a number of essential oceanic and atmospheric processes. These processes include the mass transfer of anthropogenic and biogenic trace gases, such as halocarbons, NMHC, dimethyl sulphide and other gases (Asher, 1988). Calculation of the flux of a particular species requires knowledge of its atmospheric and marine phase concentrations and its transport rate. All of these parameters may be affected by chemical and biological processes. These compounds may then form organic films at the air/sea interface and those films may have a dramatic effect on gas/liquid transport rates. Transport rates, or fluxes, are also affected by physical parameters such as wind speed, friction velocity and/or turbulence intensity. There may also be interesting chemistry within the oceanic surface films themselves caused by air/sea exchange. Because these films are at the surface, they are exposed to reactive atmospheric compounds, such as OH radicals and photochemically produced organic oxidants. If the flux of these species across the air/sea interface is large enough, and they react with the organic compounds which make up the film, these reactive compounds may cause the chemical and dynamic parameters of the film to change with time.

The ocean is a major source of a number of volatile halogenated methanes to the atmosphere, where the compounds can play a significant chemical role. The normal procedure for estimating ocean-atmosphere exchange for these compounds is to determine the level of saturation in ocean water and to convert this to a flux by applying an average gas exchange velocity appropriate to the average windspeed and temperature (Moore *et al.*, 1995). The air/sea exchange calculations are based on measured concentration at the interface, wind speed relationships and liquid-phase diffusivities in seawater. For low-solubility gases, the gas-liquid flux can be expressed by the followed relationship proposed by Liss *et al.* (1994):

$$F = K_{(T)\,w}\,(\Delta C) \qquad \Delta C = (C_a\,H^{-1}) - C_w$$

Where F is the flux of gas, C_a is the concentration of gas in the air, C_w is the concentration of the species in water, *H* is the Henry's law constant of the gas (C_a/C_w) and $K_{(T)\,w}$ is the gas transfer velocity (cm h^{-1}) which links the flux and the concentration difference, as the dimension of a velocity and may be termed the transfer coefficient, transfer velocity (cm h^{-1}) or piston velocity (cm h^{-1}).

1.3.3.4 Sea/air transfer velocity

The total transfer velocity can be expressed as:

$$1/K_{(T)\,w} = 1/\alpha\, kw + 1/H\, ka$$

Where *ka* and *kw* are the individual transfer velocities for gases in the air and water respectively. α is the factor that quantifies any enhancement of gas transfer in the water as a result of chemical reactions, and *H* is the Henry's law constant. In this context, the next equation can be expressed in terms of resistance to gas transfer when $1/K_{(T)\,w} = R_{(T)\,w}$, $1/\alpha\, kw = r_w$ and $1/H\, ka = r_a$; thus

$$R_{(T)\,w} = r_w + r_a$$

On this basis, the gases can be divided into:

a. Gases for which $r_a \gg r_w$; these gases generally have high water solubility (low values of *H*).

b. Gases for which $r_w \gg r_a$; Thus r_w is the dominant resistance to transfer. These gases have low water solubility (high values of *H*). Liss and Merlivat (1986) pointed out that the majority of gases that are important in geochemical cycling, therefore, fall into this category.

Liss and Merlivat (1986) proposed a three-line relationship to describe the behaviour of transfer velocity as a function of wind speed. The equations are as the following:

$K_{(T)\,w} = 1.17\,\upsilon$; $\upsilon \leq 3.6$ (waves with a low intensity)

$K_{(T)\,w} = 2.85\,\upsilon - 9.65$; $3.6 < \upsilon \leq 13$ (waves with a medium intensity)

$K_{(T)\,w} = 1.17\,\upsilon - 49.3$; $\upsilon > 13$ (waves with a high intensity and bubble formation)

Where, $K_{(T)\,w}$: water phase transfer velocity (cm h^{-1}) and υ: wind speed (m s^{-1})

The transfer velocity is dependent on the diffusivity of the compound and the viscosity of the solvent, often described by the Smith Number (Sc), which is the quotient of the kinematic viscosity of the solvent (ν) in $cm^2\ s^{-1}$ and the diffusion coefficient (D) in $cm^2\ s^{-1}$ of the compound. These are directly dependent on temperature and with a minor influence on salinity (Quack and Wallace, 2003).

1.3.3.5 Saturation percentage

Once a gas is dissolved in seawater, *i.e.* it has diffused across the interface into the liquid phase, the process that determines its oceanic distribution depends on the nature of the gas itself. The distributions of those gases which are generally regarded as being non-reactive in seawater are controlled by physical processes as a temperature and salinity on their solubility. It is usual to express variation in non-reactive gases in terms of their percentage saturation. To do this, the observed concentration of the gas in the sea is given as a percentage of its solubility in pure water of the same temperature and salinity. Thus:

$$\text{Saturation (\%)} = 100 \times C/C`$$

Where C is the observed gas content in seawater and C`: is the solubility of the gas in pure water at the observed temperature, pressure and salinity.

1.3.3.6 Diffusivity and solubility

The results of DeBruyn and Saltzman (1997) on diffusivity of bromomethane show that in pure water are 9.85×10^{-6} $cm^2 s^{-1}$ at 5℃ and 1.50×10^{-5} $cm^2 s^{-1}$ at 19.4 ℃ and the diffusivity in salt water (3.5% NaCl) at 13 ℃ is very similar to the results in pure water.

Solubility is also an important factor; the findings of DeBruyn and Saltzman (1997) with bromomethane solubility in pure, sea and salt water as a function of temperature are shown in Table 1.6. Results showed that the methyl bromide in more soluble in pure water than seawater or NaCl 3.5 %.

Table 1.7 shows the different halocarbon solubilities, those values in pure water are useful in saturation percentage calculations.

Table 1.6. Solubility measurements for methyl bromide in pure water, seawater and NaCl 3.5% solution. From DeBruyn and Saltzman (1997).

Temperature (°C)	Solubility (mol L^{-1})		
	Pure water	**Seawater**	**NaCl 3.5%**
1.1	0.49	0.40	0.40
5.0	0.39	0.31	0.32
10.0	0.30	0.24	0.24
13.4	0.27	0.21	0.22
18.0	0.23	0.19	-
19.4	0.22	-	0.19
21.2	0.20	-	0.18
25.0	0.17	0.14	0.15
30.5	0.15	0.12	0.13

Table 1.7. Pure water solubilities of selected halocarbons at 25°C.

Compound	Solubility (g L^{-1})	Reference
	Chlorinated	
Chloromethane	5.25	Schwarzenbach *et al.* (1993)
Dichloromethane	19.5	Schwarzenbach *et al.* (1993)
Chloroform	7.68	Schwarzenbach *et al.* (1993)
Carbon tetrachloride	0.92	Schwarzenbach *et al.* (1993)
1,1-dichloroethane	4.95	Schwarzenbach *et al.* (1993)
1,2-dichloroethane	8.41	Schwarzenbach *et al.* (1993)
1,1,1-Trichloroethane	1.06	Schwarzenbach *et al.* (1993)
1,1,2-Trichloroethane	4.40	Murphy and Morrison (2002)
1,1-dichloroethene	5.10	Murphy and Morrison (2002)
Cis-1,2,dichloroethene	3.50	Murphy and Morrison (2002)
Trans-1,2,dichloroethene	6.30	Murphy and Morrison (2002)
1,2-dichloropropane	2.80	Murphy and Morrison (2002)
Chloroethene	2.81	Schwarzenbach *et al.* (1993)
Trichloroethene	1.18	Schwarzenbach *et al.* (1993)
Tetrachloroethene	0.15	Schwarzenbach *et al.* (1993)
	Brominated	
Bromomethane	15.39	Schwarzenbach *et al.* (1993)
Bromoform	3.02	Schwarzenbach *et al.* (1993)
1,2-dibromoethane	4.20	Murphy and Morrison (2002)
1,2-dibromomethane	1.69	Schwarzenbach *et al.* (1993)
	Mixed halogen	
Bromodichloromethane	4.50	Murphy and Morrison (2002)

Other gases have been studied in terms of solubility in seawater, such as sulphur hexachloride "SF_6" (Bullister *et al.*, 2002) and some chlorofluorocarbons (Bu and Warner, 1995; Scharlin and Battino, 1995).

1.4 Sources of halogenated compounds

1.4.1 Anthropogenic contribution and emissions

Man-made halocarbons have a considerable impact on the environment. Chlorine- and bromine-containing organic compounds, such as chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs) are responsible for the decline of stratospheric and tropospheric ozone and their use has, therefore, been regulated under the Montreal Protocol. Fluoro-containing halocarbons are not regulated within this treaty, but as all halocarbons act as greenhouse gases; this group of compounds was included in the Kyoto Protocol.

The identified emissions of the halogenated compounds come predominantly from their use and production in industrial and commercial processes. The main halocarbon compounds reported in the literature from an origin anthropogenic are the chlorofluorocarbons (CFCs), chlorinated and brominated compounds. Meanwhile, iodo compounds are rarely reported as man-made halocarbon pollutants.

The anthropogenic sources of some halo-compounds are, for example, the industrial production of flame retardants, the use of bromomethane and bromoethane as fumigants, the utilization of 1,2-dibromoethane as a anti-knock agent, the use of chlorine for the chlorination of water and industrial bleaching processes (Class *et al.*, 1986) and the use and production of trichloroethene and tetrachloroethane as by-products of gasoline, coal combustion and industrial production (McCulloch *et al.*, 1999). Further information can be found in Table 1.8, such as halocarbon properties, uses and fates. Their uses nowadays have been restricted and reduced after the Montreal and Kyoto Protocols.

Table 1.8. Production and historical uses of man-made halocarbons.

Compound	Anthropogenic production and uses
	Chlorinated
Chloromethane CH_3Cl	Medication, anaesthetic, aerosol propellant, foaming agent in the plastics industry, methylating agent, manufacture of silicone resins and rubbers, as a refrigerant.
Dichloromethane CH_2Cl_2	Solvent for cellulose acetate, medication, cleaning and industrial solvent, fumigant, used in aerosol formulations, in solid phase peptide synthesis.
Chloroform $CHCl_3$	Solvent, fire extinguishers, insecticidal, fumigant extraction and solvent purification.
Carbon tetrachloride CCl_4	Additives in refrigerants, grain fumigant, Solvent, cleaning agent, in synthesis of nylon-7 and other organic chlorination processes, use in polymer technology as a reaction medium, catalyst in organic synthesis for chlorination of organic compounds; in soap perfumery and insecticides.
Chloroethane CH_3CH_2Cl	Refrigerant, solvent, alkylating agent, synthesis, insecticides, use in manufacture of dyes and drugs, use as a propellant in aerosols, use in manufacture of perfumes.
1,1-dichloroethane CH_3CHCl_2	Solvent of plastics, oil and fats; as a fumigant and insecticide spray, fire extinguishing, medical, extractant for heat-sensitive substances, manufacture of high vacuum rubber, coupling agent in antiknock gasoline; in paint, varnish & paint removers; in ore flotation.
1,2-dichloroethane CH_2ClCH_2Cl	Manufacture of acetyl cellulose, tobacco extract, in paint, varnish and finish removers, soaps and scouring compounds, wetting and penetrating agents, ore flotation, lead scavenger in antiknock gasoline, fumigant, industrial solvent and cleaner, catalyst, in photography, xerography, and water softening and in the production of cosmetics.
Trichloroethene $CHCl{=}CCl_2$	Degreasing; dry cleaning, pharmaceuticals, industrial solvent, wool-fabric scouring, extractant for spice oleoresins,

	Intermediate in the production of pentachloroethane, carrier solvent for the active ingredients of insecticides and fungicides, medication, former use.
Tetrachloroethene $CCl_2=CCl_2$	Used in the textile industry for dry-cleaning, processing and finishing; used in both cold cleaning and vapour degreasing of metals; chemical intermediate in the synthesis of fluorocarbon 113, 114, 115, and 116; textile manufacturer, medication.
Brominated	
Bromomethane CH_3Br	Soil fumigant, refrigerant and in fire extinguishers, solvent in aniline dyes, methylating agent, medicinal agent to destroy malignant tissue and as an anesthetic in dentistry; fungicide, nematicide, herbicide, insecticide and miticide, organic synthesis, extraction solvent for vegetable oils.
Dibromomethane CH_2Br_2	Organic synthesis, solvent, ingredient of fire extinguishing, gage fluid.
Bromoform $CHBr_3$	Pharmaceutical uses, ingredient in fire-resistant chemicals, industrial solvent, in medicine, mineral flotation, catalyst, initiator or sensitizer in polymer reactions, and in vulcanization of rubber.
1,2-dibromoethane CH_2BrCH_2Br	Catalyst, solvent for resins, gums, and waxes; chemical intermediate in the synthesis of dyes and pharmaceuticals; fumigant, insecticide, nematicide, former uses scavenger for lead in gasoline, general solvent, water proofing preparations, organic synthesis, in antiknock gasoline.
Mixed halogen	
Bromodichloromethane $CHBrCl_2$	Fire retardant, solvent, intermediate in synthesis of other compounds, fire-extinguisher fluid ingredient, Heavy liquid for mineral and salt separations and laboratory use.
Dibromochloromethane $CHBr_2Cl$	Organic synthesis, as a chemical intermediate in the manufacture of fire extinguishing agents, aerosol propellants, refrigerants, and pesticides.
Bromochloromethane CH_2BrCl	Chemical intermediate in industrial processes and fire extinguishing agent.

Contrasts of estimated annual fluxes of some halocarbons from anthropogenic and biogenic sources are shown in figure 1.4.

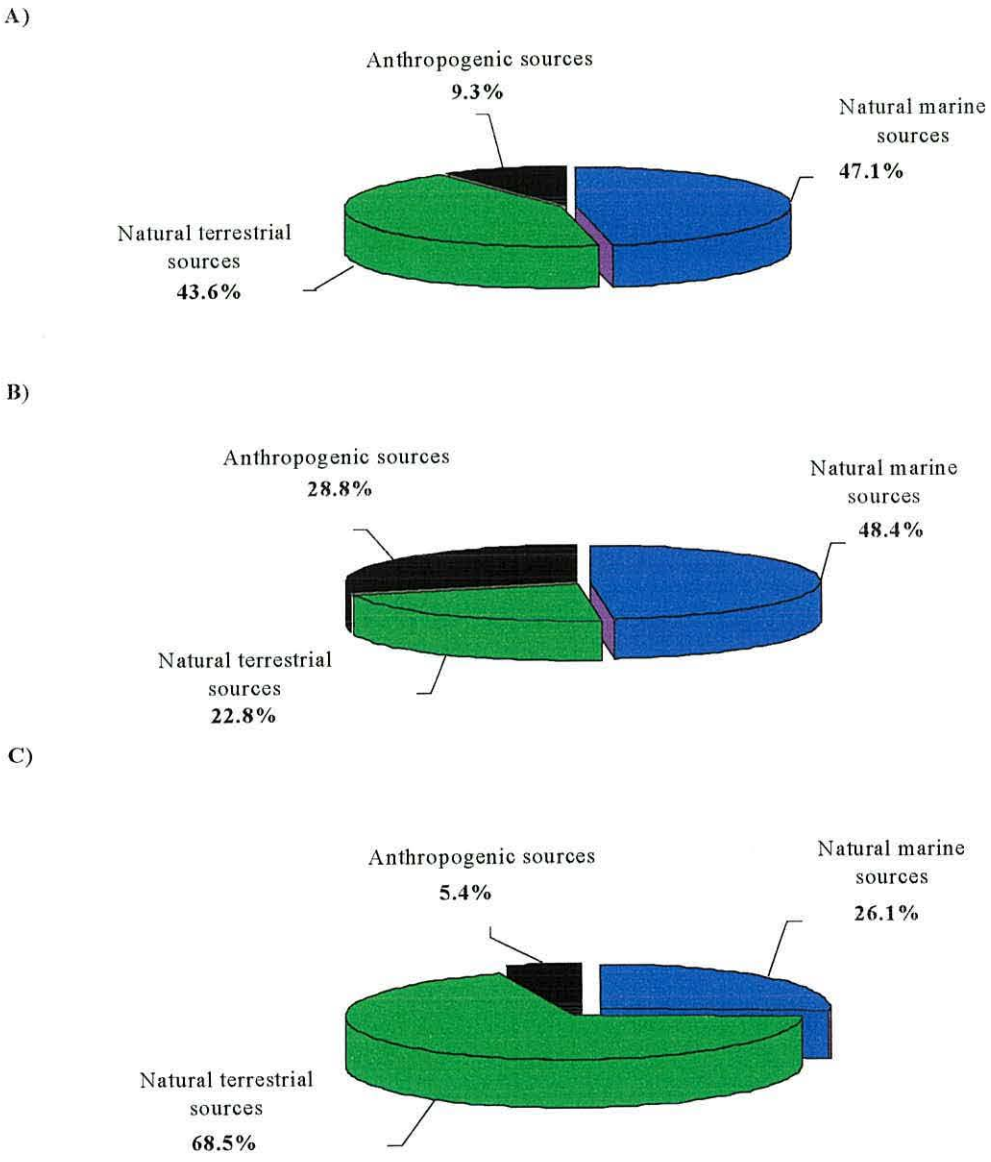


Figure 1.4. Percentage distribution of annual global emissions by anthropogenic and biogenic sources of A) chloroform, B) methyl bromide and C) methyl chloride. Data were taken from Laturnus *et al.* (2002) and WMO (2002).

1.4.2 Natural sources of halocarbons

The natural production of halocompounds is not exclusively from marine sources; evidence has shown that halocarbon can be produced, for example, by fungus (Hoekstra *et al.*, 1998; Saxena *et al.*, 1998), soil (Hoekstra *et al.*, 1998), minerals and rocks (Prilepsky *et al.*, 1998; Harnisch *et al.*, 2000), volcanic activities (Jordan *et al.*, 2000), degradation of organic matter (Keppler *et al.*, 2001), bacteria (Amachi *et al.*, 2001; Miller *et al.*, 2001), terrestrial plants (Saini *et al.*, 1995; Smith and Bridges, 1996; Hamilton *et al.*, 2003), peatlands (Dimmer *et al.*, 2001), biomass burning (Rudolph *et al.*, 1995; Blake *et al.*, 1996; Ferek *et al.*, 1998; Blake *et al.*, 1999; Brunke *et al.*, 2001), trees (Brown *et al.*, 1999) and others sources that may not have been found yet.

Evidence that halocarbon natural production is not always from biogenic sources, is provided by Prilepsky *et al.* (1998), who found production of halocarbons, especially methyl chloride, with the reaction of methane and halogen containing minerals under irradiation, possible mediated by photochemical reactions. Other evidence is provided by Hoekstra *et al.* (1998), who found conclusive support that chloroform, bromoform and chlorodibromomethane are naturally produced in the soil top layer by different biogenic and inorganic sources. The degradation of organic matter in soil may be an interesting source of abiotic halocarbons, for example, compounds produced by wood-degrading areas and soils with humic acids (Hoekstra *et al.*, 2001) or probably the reaction mechanism induced by the oxidation of organic matter by iron (III) (Keppler *et al.*, 2001), suggesting that the soil is an important source of natural iodide into the atmosphere (Keppler *et al.*, 2003). Volcanic activity can produce some halocarbons, including some CFCs; the report of Jordan *et al.* (2000) has shown a wide diversity of halocarbons produced in different volcanoes.

However, biological contributions are important too, such as the formation of halocarbons by marine and terrestrial bacteria; the findings of Amachi *et al.* (2001) suggest that the bacteria contribute to iodine transfer from terrestrial and marine ecosystems into the atmosphere. Fungi are an important source of natural halocarbons, producing an elevated concentration of chloroform in soil (Hoekstra *et al.*, 1998). Basidiomycetes are an important contributors of halomethanes, halogenated aromatics and haloaliphatic compounds, producing near to 53 varieties of halogenated metabolites (Field *et al.*, 1995). Terrestrial plants and trees are capable of producing halocompounds, producing mainly chlorinated compounds. The release of these compounds by terrestrial sources would be

increased with the elevated temperature, potentially those due to climate changes (Peñuelas and Llusia, 2003).

Another important natural source of halocarbons is biomass burning; globally, fire emissions are divided into two categories: hot/low emission fires (savanna fires, agricultural residue fires) and cool/high emission fires (forest fires, fuel wood burning). Estimated annual global emissions from biomass burning are 2 Gg of chloroform, mainly emitted by savannah fires (38% of the global emission) and wood and charcoal burning (24% of the global emission) with 64% released in the Northern Hemisphere (Laturnus *et al.*, 2002). Biomass burning is a major source of many atmospheric trace constituents and about 90% of today's biomass burning appears to be induced by humans. Some compounds produced by biomass burning are, for example, chloroform (Lobert *et al.*, 1999) and different methyl halides (Andreae *et al.*, 1996). Some authors have found evidence that halocarbons are produced by biomass combustion and they found good correlations with the carbon monoxide (CO) concentration (Andreae *et al.*, 1996; Ferek *et al.*, 1998).

Table 1.9 presents a listing of the halocarbon concentrations, their ranges and fluxes from a series of anthropogenic and biological measurements in different environments.

Table 1.9. Halocarbon global production from the literature.

Source/Location	Flux		Compound	Reference
	Range Flux ($Gg\ Yr^{-1}$)	Mean Flux ($Gg\ Yr^{-1}$)		
Global Sources production				
Global production		1,490	$CHBr_3$	Nielsen and Douglass (2001)
Global production	240-1,760 24-88	800	Bromine natural Bromine anthropogenic (Sea-air flux)	Quack and Wallace (2003)
Global production		122 3,500 6,000 470	CH_3Br CH_3Cl CH_2Cl_2 $CHCl_3$	Kurylo and Rodriguez (1998, 1999)
Global production		5,000	CH_3Cl	Gribble (1992)
Global production	23-119 4.8-48 0-10 10-40 2.3-9.2	63 40.8 5 20 4.6	CH_3Br Ocean CH_3Br Fumigation CH_3Br Gasoline CH_3Br Biomass Burning CH_3Br Wetlands	WMO (2002)

	7-29	14	CH_3Br Salt marshes	
	0.5-2	1	CH_3Br Shrublands	
	4.8-8.4	6.6	CH_3Br Rape seed	
	0.5-2.5	1.5	CH_3Br Rice Fields	
	0.5-5.2	1.7	CH_3Br Fungus	
	0.1-3.3	0.9	CH_3Br Peatlands	
Global Production	325-1,300	600	CH_3Cl Ocean	WMO (2002)
	655-1,125	911	CH_3Cl Biomass Burning	
	820-8,200	910	CH_3Cl Tropical plants	
	43-470	160	CH_3Cl Fungi	
	65-440	170	CH_3Cl Salt marshes	
	6-270	40	CH_3Cl Wetlands	
	5-205	105	CH_3Cl Coal combustion	
	15-75	45	CH_3Cl Incineration	
		10	CH_3Cl Industrial	
		5	CH_3Cl Rice Fields	
Global production		300	$CHBr_3$	Dvortsov *et al.* (1999)
Global production		600	CH_3Cl	Kurylo and Rodriguez (1998, 1999)
From ocean		200	CH_2Cl_2	

sources		450	$CHCl_3$	
Global production from ocean sources		460 320 160 20 20	CH_3Cl $CHCl_3$ CH_2Cl_2 $CHCl{=}CCl_2$ $CCl_2{=}CCl_2$	Khalil *et al.* (1999)
Global production from Sea-air flux transfer	300-1,300	~14	CH_3I CCl_4	Chester (1990)
Global production from Land-based emissions		100 200	CH_3Cl $CHCl_3$	Khalil *et al.* (1999)
Marine Seawater Production				
Arctic Ocean		1	$CHBr_3$	Krysell (1991)
Southern North Sea		0.11 0.07	CH_3I sea-air flux Iodine deposition flux rain	Campos *et al.* (1996)
British Estuary	$5x10^{-6}$-$1.17x10^{-4}$		$CHCl_3$	Bianchi and Varney (1998)
Kattegatt area		0.25	$CHBr_3$ anthropogenic	Fogelqvist and Krysell (1991)

between Sweden and Denmark		0.35	$CHBr_3$ Biogenic	
Southern California	70-100 10-200		Bromine anthropogenic Bromine marine algae	Goodwin *et al.* (1997)
North-west Atlantic and Pacific Ocean	403-554 101-252 151-453		CH_3Cl efflux CH_3Cl influx CH_3Cl global ocean source	Moore *et al.* (1996)
East Pacific Ocean		105.6 18 27.6 151.2	CH_3Br Open ocean CH_3Br Coastal CH_3Br Upwelling CH_3Br Total production	Lobert *et al.* (1995)
Coast East Atlantic		220	$CHBr_3$ Macroalgae global production	Carpenter and Liss (2000)
Algae Production				
Temperate marine macroalgae		~10 ~1 ~1000	Bromine from macroalgae Iodine from macroalgae CH_3I phytoplankton	Gschwend *et al.* (1985)
Marine sources	0.01-0.1 0.1-1		Iodine from macroalgae Bromine from macroalgae	Giese *et al.* (1999)

	100-1,000 10-1,000		Total Iodine emission Total Bromine emission	
Various marine phytoplankton	33.5 110.34	0.37-190 0.12-42.3	CH_3Cl CH_3Br	Scarratt and Moore (1998)
Polar Regions	0.1-10 0.01-0.1		Bromine Macroalgae global production Iodine Macroalgae global production	Laturnus (2001)
Ice algal communities	4.7-70 5.3-80		$CHBr_3$ Arctic ice algae $CHBr_3$ Antarctic ice algae	Sturges *et al.* (1992)
			Other Sources	
Biomass burning		14	CH_3CCl_3	Rudolph *et al.* (1995)
Biomass burning		2.5	CH_3CCl_3	Rudolph *et al.* (2000)
Biomass burning		640 49 1.8 13 6,350	CH_3Cl CH_2Cl_2 $CHCl_3$ CH_3CCl_3 Total volatile-inorganic and particulate chlorine	Lobert *et al.* (1999)
Global volcanogenic		$9.8x10^{-4}$ $9.49x10^{-2}$	CH_3Br CH_3Cl	Schwandner *et al.* (2004)

sources		3.41×10^{-3}	CCl_4	
Irish peatlands ecosystem	0.1-151.9 0.1-3.3 0.9-43.4 0.1-12.8	4.7 0.9 5.5 1.4	$CHCl_3$ CH_3Br CH_3Cl CH_3I	Dimmer *et al.* (2001)
			Anthropogenic Sources	
Anthropogenic emissions		30 19 13	$CHCl_3$ Pulp and paper $CHCl_3$ Water treatment $CHCl_3$ Manufacturing	Aucott *et al.* (1999)
Asian emissions year 1999		241 366 583	$CHCl{=}CCl_2$ industrial release $CCl_2{=}CCl_2$ industrial release CH_2Cl_2 industrial release	McCulloch *et al.* (1999)
Asian Continental outflow		4.7 167	CH_3Br CH_3Cl	Blake *et al.* (2003)
Anthropogenic emissions		30 19 13 62	$CHCl_3$ Pulp and paper manufacturing $CHCl_3$ Water treatment $CHCl_3$ Other sources $CHCl_3$ total emission	Aucott *et al.* (1999)

Anthropogenic emissions (Eastern Asian)		21.5	CCl_4	Palmer *et al.* (2003)
Atmospheric input		~50	CH_3Br fumigant	Gschwend *et al.* (1985)
Atmospheric input		3,032	$CHBr_3$	Penkett *et al.* (1985)

1.5 Degradation and Fates

It seems clear that the source of the halogens is the large concentrations of these elements which exist as their anions in seawater; the average concentrations are 19,000 mg L^{-1} Cl^-, 65 mg L^{-1} Br^- and 0.06 mg L^{-1} I^- (Fenical, 1981). Iodine compounds are found in modest amounts in marine environment. The reasons are that iodine compounds are thermodynamically unstable in seawater and may be depleted by photolysis (Carpenter *et al.*, 2000) or suffer nucleophilic substitutions with chloride (Manley and delaCuesta, 1997) and its chemical fate is kinetically controlled (Gagosian and Lee, 1981).

The degradation of halocarbons by biological and chemical mechanisms has been reported by some authors. Tokarczyk *et al.* (2003) pointed out that chloromethane is rapidly degraded in coastal water by microbial activity. Other evidences of halocarbon degradation by biological pathways has been found in the Pacific Ocean, the Atlantic Ocean and the Caribbean Sea using isotopic techniques (Tokarczyk *et al.*, 2001; Tokarczyk and Saltzman, 2001; Tokarczyk *et al.*, 2003).

Chemical degradation may be through different pathways (See the equations below). The work of Tanhua *et al.* (1996) with some halocarbons in the Black Sea revealed evidence that the concentration of halocarbons decrease rapidly in anoxic areas.

These reactions represent the transformation mechanism of methyl halides in seawater:

$$CH_3X \longrightarrow CH_3X_{(g)} \quad (1.1)$$

$$CH_3X + Y^- \longrightarrow CH_3Y + X^- \quad (1.2)$$

$$CH_3X + H_2O \longrightarrow CH_3OH + X^- + H^+ \quad (1.3)$$

$$RX + H^+ + 2e^- \longrightarrow RH + X^- \quad (1.4)$$

$$RX\text{-}RX + 2e^- \longrightarrow R{=}R + 2X^- \quad (1.5)$$

$$2RX + 2e^- \longrightarrow R\text{-}R + 2X^- \quad (1.6)$$

$$X\text{-}CH_2\text{-}X + HS^-(H_2S) \longrightarrow X\text{-}CH_2\text{-}SH + X^- (+H+) \quad (1.7)$$

Where $X = Cl^-, Br^-, I^-$ and $Y = Cl^-, Br^-, I^-$ or another arbitrary ion.

Equation 1.1 represents vaporization, 1.2 represents the nucleophilic substitution reaction with other halide, 1.3 represents the possible reaction between halocompounds with water and the subsequent hydrolysis to methanol and the equations 1.4, 1.5 and 1.6

represent different pathways of the reduction process: hydrogenolysis, dihalo-elimination and coupling respectively; and finally equation 1.7 proposed by Roberts *et al.* (1992) represents the nucleophilic attack of dihalomethanes by sulphide species in solution. Some possible ways and fates of halocarbons in seawater are represented in Figure 1.5.

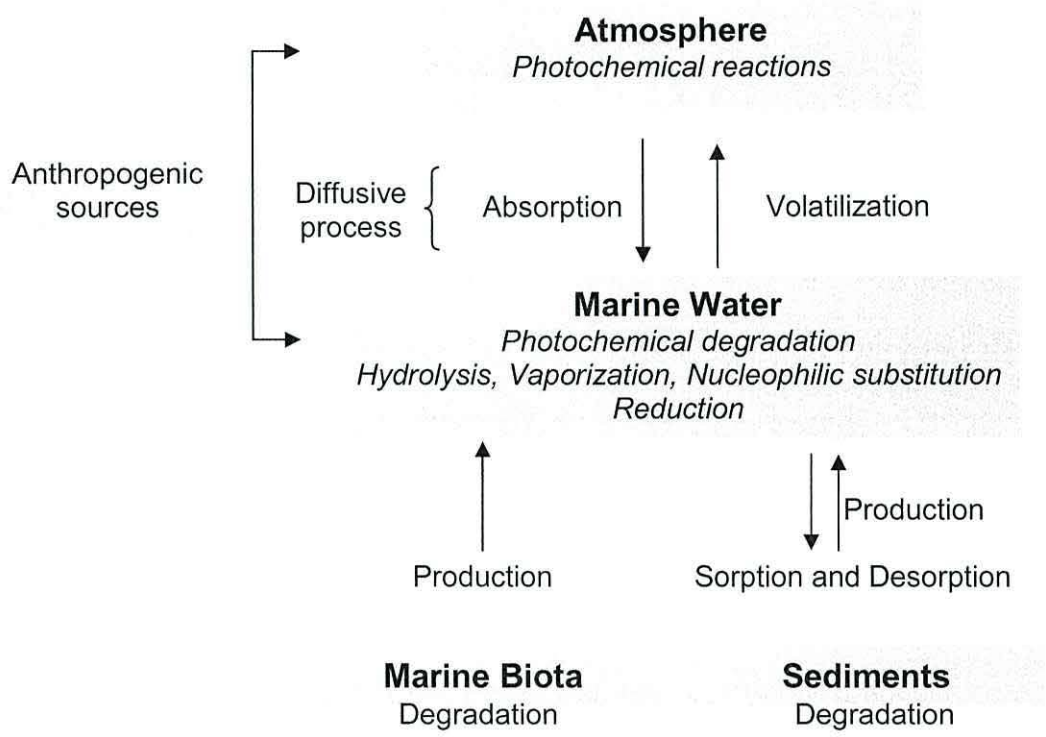


Figure 1.5. Schematic representation of the sources and fates of halogenated VOCs. Modified from Dewulf and VanLangenhove (1997).

1.6 Multivariate analysis

Environmental data are generally a large and complex data set of variables and observations. To analyze large numbers of data it is necessary to have a tool able to summarize and find relationships among the data set. Multivariate statistical analysis has become within the last few years a widely technique applied to analyze large data sets.

Two useful analyses in environmental chemometrics and forensics are principal component analysis (PCA) and partial least squares (PLS). Those techniques are helpful tools to analyze the data, for example to find out the spatial and temporal variability in the occurrence and productions of VOCs and also to find a relationship between the variables and observations (Glenn, 2002).

1.6.1 Principal component analysis (PCA)

PCA is a quite commonly employed statistical tool to evaluate the underlying dimensionality of the data and also to get an overview of the dominant patterns and major trends in the data (Eriksson *et al.*, 1999). To feed the analysis is necessary to have data or matrix, comprising N rows (observations) and K columns (variables) as shown in Figure 1.6. Variables can be, as in this specific study, the compounds found for each analyzed sample and the, observations the samples collected for a particular place or time.

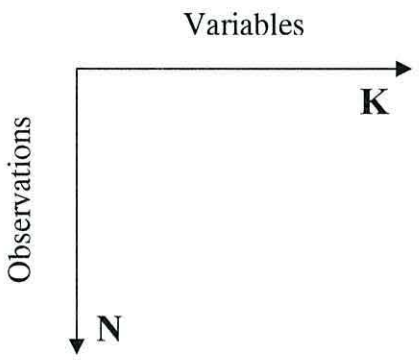


Figure 1.6. Matrix representation in a PCA analysis.

The most important use of PCA is to represent a multivariate data table in a low dimensional space, usually 2 to 4 dimensions, allowing an overview of data. This overview may reveal groups of data with similar properties and associations and also be able to find relationships among variables as well with observations associated to them.

1.6.1.1 Pre-treatment of data

Data is not always ready to be analyzed and for this reason is necessary to pre-treat it. Pre-treatment is done in order to transform the data in the most suitable way for analysis. There are several tools to pre-treat the data. The two more common are mean-centring and scaling.

Mean-centering is done calculating the average value for each variable and then subtracted from the data. After mean-centering and unit variance scaling all variables will have equal "length" and mean value "zero".

A common problem with data is the different scales or magnitudes obtained. There are several ways of scaling, but the most employed is unit variance scaling, also known as auto-scaling. This consist on determine the standard deviation (S_k) calculated for each variable and then the inverse of the standard deviation ($1/ S_k$) multiplies each variable. The idea of using it is to avoid the domination of some variables due to the differences in numerical ranges.

1.6.1.2 Geometric interpretation of PCA

A good way of understanding how PCA does work, is through a geometrical interpretation. The next figures will summarize the steps followed to obtain the model. Figure 1.7 represents the geometrical interpretation of a PCA model. The steps shown to obtain the model are explained as follows:

A) Each observation of the table is plotted in the K-dimensional variable space. The dimension shown in this example corresponds to a model with 3 variables (to simplify the data dimension and be able to show it graphically) and 14 observations (n=14). It is also important to notice that observations are always positive values, and for instance are distributed among the positives regions of the respective dimensions (variables). Then the model calculates the average for all observations shown as shadowed spot.

B) Effects on the matrix of the pre-treatment process using unit variance scaling and mean centering. This corresponds to a re-positioning of the coordinate system, such that the origin now passes through the average point (shadowed spot).

C) Now the process of calculation of the first two components. The calculation to the first component (PC1) corresponds to a line in the K dimensional space that best approximate the data in a least square sense. This line goes through the average point in the origin. Now, each observation is projected onto this line, but some of them might not. This new coordinate value is known as a ***score***. The second component (PC2) is calculated to represent more adequately the variation of the data set. The second component also passes through the average point and is orthogonal to PC1. It improves the approximation of the data set as much as possible, explaining the variance in a higher proportion combined with PC1. Generally, no more than 2 to 4 components are necessary to explain much of the variance in a model (Eriksson *et al.*, 1999). However, infinite principal components can be calculated and very high explanations of the variance obtained. On the other hand, calculating several components can be detrimental to the prediction ability of the model. This will be explained later on.

D) When two principal components have been derived they define a plane, a window into a K-dimensional variable space. Each observation may be projected onto this plane in order to get new co-ordinate values (scores) in the co-ordinate system. The plane generated is called ***score plot***.

F) To interpret the meaning of the scores is useful to use the ***loadings***. The direction of PC1 in relation to the original variables is given by the cosine of the angles α_{x1}, α_{x2} and α_{x3}. The values indicate how the original variables x1, x2 and x3 load or contribute to PC1. The same is needed for PC2, so six values of loadings are minimally required to understand how the model is positioned in a variable space. They express the orientation of the obtained model plane inside the K-dimensional variable space.

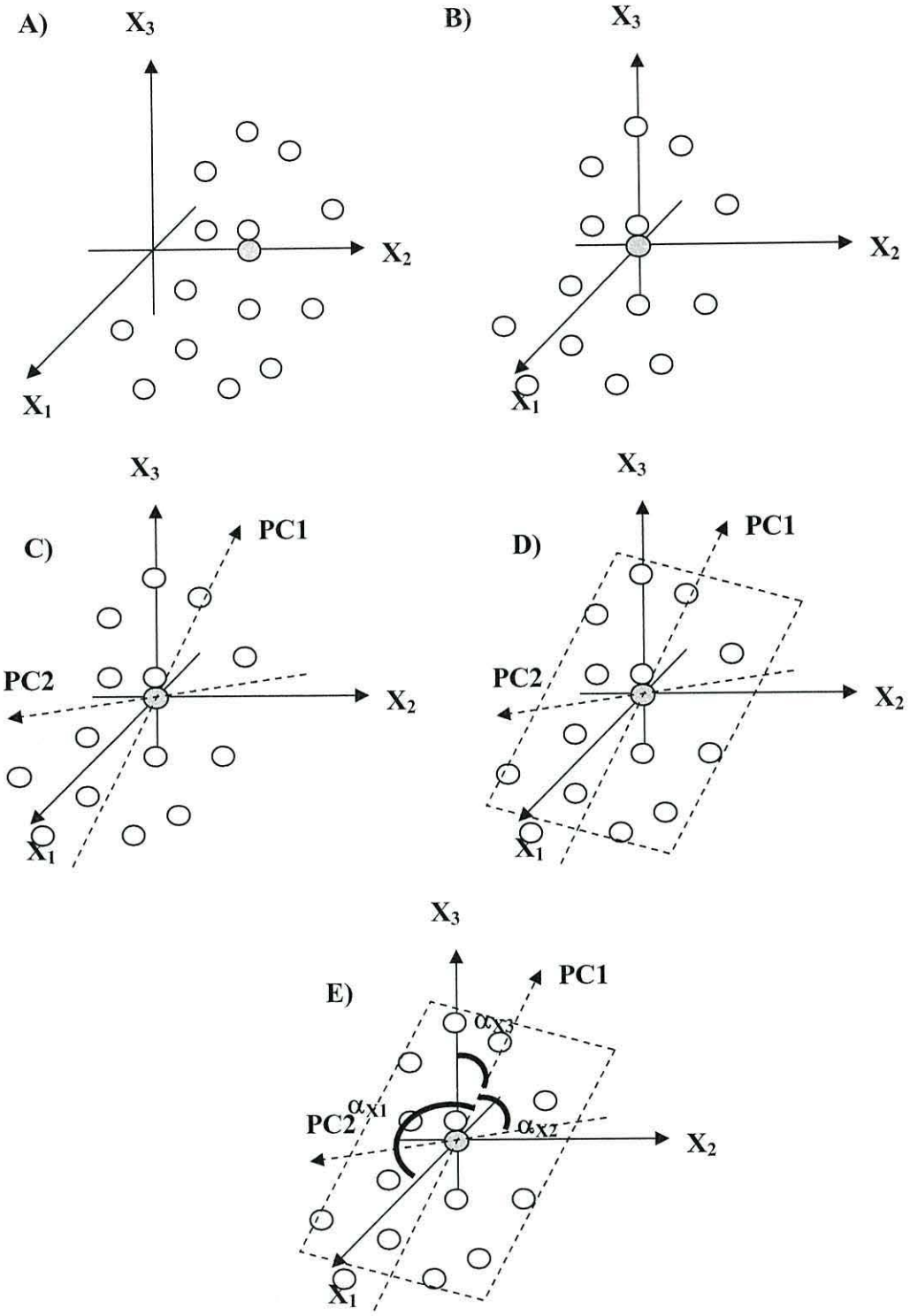


Figure 1.7. Geometrical interpretation of PCA analysis.

1.6.1.3 Outliers

Using PCA is possible to detect strong and moderate outliers. The outliers are the observations that are not possible to fit very well with the PCA model. Strong outliers are found in plots of PC-scores and moderate are found by inspecting the model residuals. The detection tool for strong outliers is called ***Hotelling's T^2***. This statistic is a multivariate generalization of student's t-test, and provides a check for observation adhering to multivariate normality (Eriksson *et al.*, 1999). The *Hotelling's T^2* when used together with a score plot defines the normal operating area corresponding to a 95 to 99% tolerance. For instance, every observation which is plotted out of the ellipse generated by *Hotelling's T^2* can be considered as a strong outliers and for instance modify completely the interpretation of the model itself. With a level of confidence of 95%, and having "N" observations and multiplying 0.05*N is possible obtain more and less how many observation are expected to be outside of *Hotelling's T^2* tolerance ellipse.

Moderate outliers are found by inspecting the residuals for each observation. These outliers do not affect the model as strong do. Due to the fact that the software SIMCA will be employed to do these analyses, most of the terminologies employed will be according to this particular software. The detection of moderate outliers using SIMCA is called DmodX (distance to the model in X-space). A critical deviation distance for the data set can be given (Dcrit). Normally, if a value exceeds this Dcrit value, it can be interpreted as a moderate outlier.

1.6.1.4 Variable diagnostics

When the PCs are created, some of the variability in the dataset is explained by this model. This explanation is represented by "R^2" and ranges from 0 (no explanation) to 1 (perfect explanation). With increasing numbers of principal component it is possible to obtain a better explanation of some variables. Not all the variables are well explained by the model, so this diagnostic helps to take decision in this way of calculating more principal components.

1.6.1.5 Model diagnostics

It is always difficult to decide how many principal components are really needed to explain the variables in a data set. Calculating more principal components is possible obtain a good explanation for the variables (R^2 =the explained variation). However, the predictive ability of the model (Q^2=the predicted variation) may get worse. The relation between R^2 and Q^2 is not always the same and depends of the dataset, but generally has the following behaviour represented in figure 1.8.

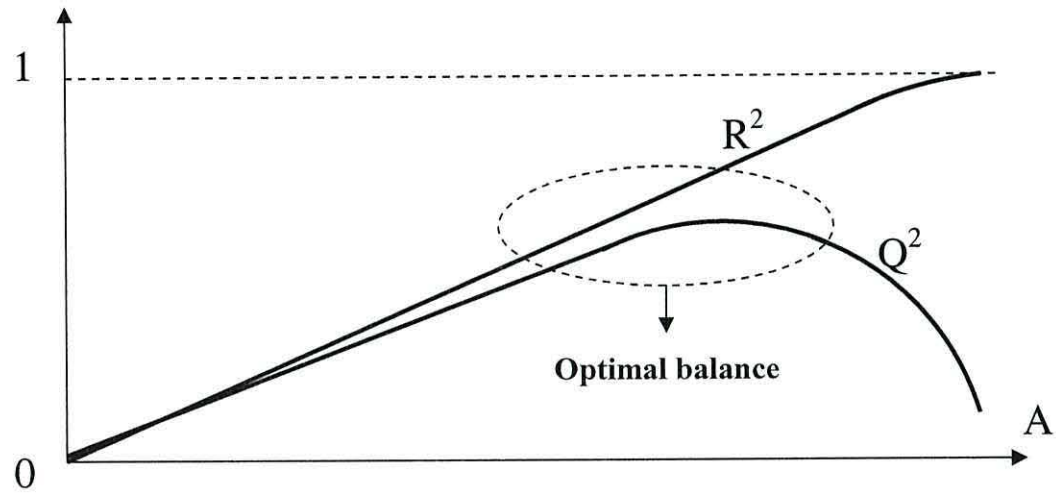


Figure 1.8. Trends of R^2 and Q^2 showing the optimal balance in which the model is well explained and predicted. For a model with "A" number of principal components.

There is a way of validating the model. It is called cross-validation (CV), this consists of dividing the data into "G" groups, typically between 5 to 10, then one of the group is deleted and predicted by the model. This is done in order to simulate the predictive power of the model. In SIMCA the validation is done using the R^2 and Q^2. Generally a $Q^2 > 0.5$ is considered good and a $Q^2 > 0.9$ is excellent, but these considerations are extremely dependent of the application and the origin of the dataset. Moreover, it is important that coherence exists between R^2 and Q^2. It is desirable not have a large difference between them, and preferably not above 0.2-0.3 (Eriksson *et al.*, 1999).

1.6.2 Partial least squares (PLS)

PLS is a regression extension of PCA; it is used when it is necessary to connect the information of two blocks of variables (X and Y) by a linear multivariate model. This technique was developed by Wold *et al.* (1984). It has been employed widely in environmental forensic in order to find signatures and find sources of chemical compounds (Yunker *et al.*, 1995). Generally, the X-block of dataset are chemical, physical or biological parameters, whose origin ideally is a pure source or a sample with high proportion of a single source (Mudge, 2002). This block then can be used to explain the environmental data (Y-block).

Figure 1.9 represents the geometrical interpretation of a PLS model for multiple responses

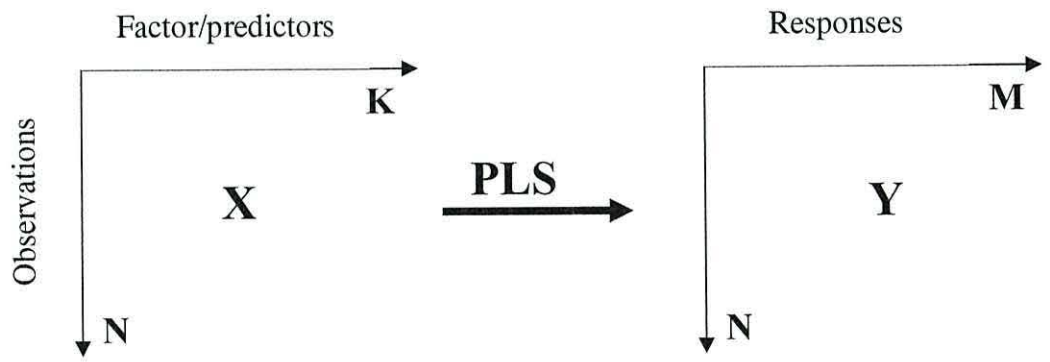


Figure 1.9. Matrices representation in a PLS analysis.

A good way of understanding how PLS does operate is through a geometrical interpretation. The next figure (1.10) will summarize the steps followed to obtain the model. The steps shown to obtain the model are explained for a multiple response model with (K=3 predictors, and M=3 responses) as follows:

A) As PCA, the data prior to analysis is pre-treated by unit variance scaling and mean-centring in both matrices. The average point passes through the origin.

B) The first PLS component is calculated now, and one line is inserted in the X-space and other in the Y-space. The lines are calculated in order to well estimate the observation in both matrices and also to provide a good correlation between them. By projecting the

observation to those lines the scores for both matrices (X and Y) are obtained (t_1 and u_1 respectively).

C) After that, the second PLS component is calculated. Two lines are projected in each matrix passing through the origin and orthogonal to the first two (not being always this for the Y matrix). The lines improve the approximation and explanation of the dataset. By projecting the observations onto these planes, the PLS scores t_1 and t_2 in X and u_1 and u_2 in Y are obtained.

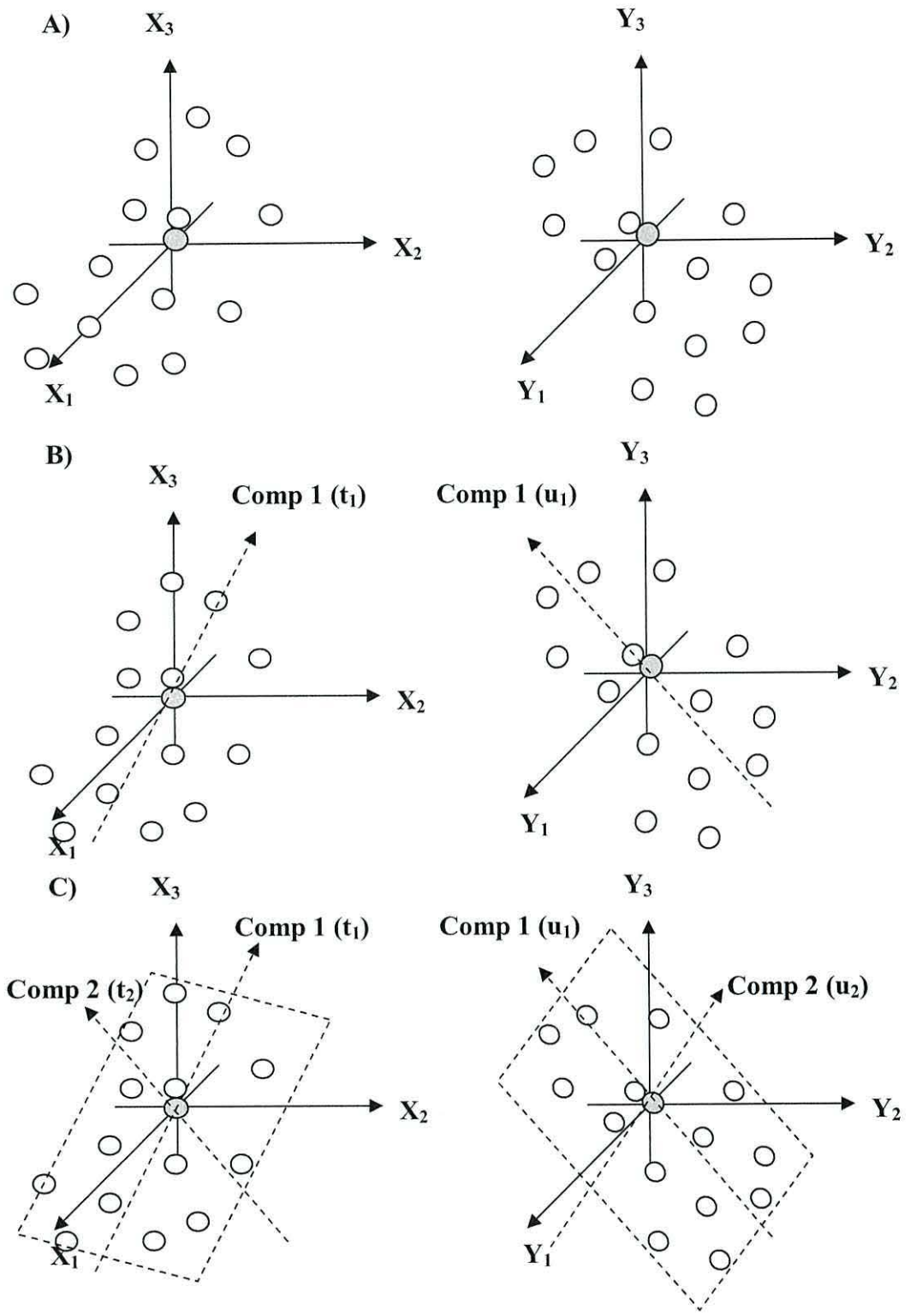


Figure 1.10. Geometrical interpretation of PLS analysis.

To better interpret the relationship between the PLS matrices, the variables associated to them can be employed. They are usually called ***weights*** (w*c). The weights obtained for X and Y might be plotted in the plot and can be interpreted in the same way as PCA loadings. The plot might show which variable contribute to the PLS model and which do not and also help to understand the relationships between X and Y data.

1.6.2.1 PLS type 1 and 2.

Those types of PLS analysis are performed for different situations. PLS type 1 is done when the variables used in the X and Y matrices are different. Whereas, PLS type 2 is done when both matrices contain the same sort of variables. The next figure (1.11) exemplifies the uses of these two types of PLS analysis giving as a case the analyses in this thesis.

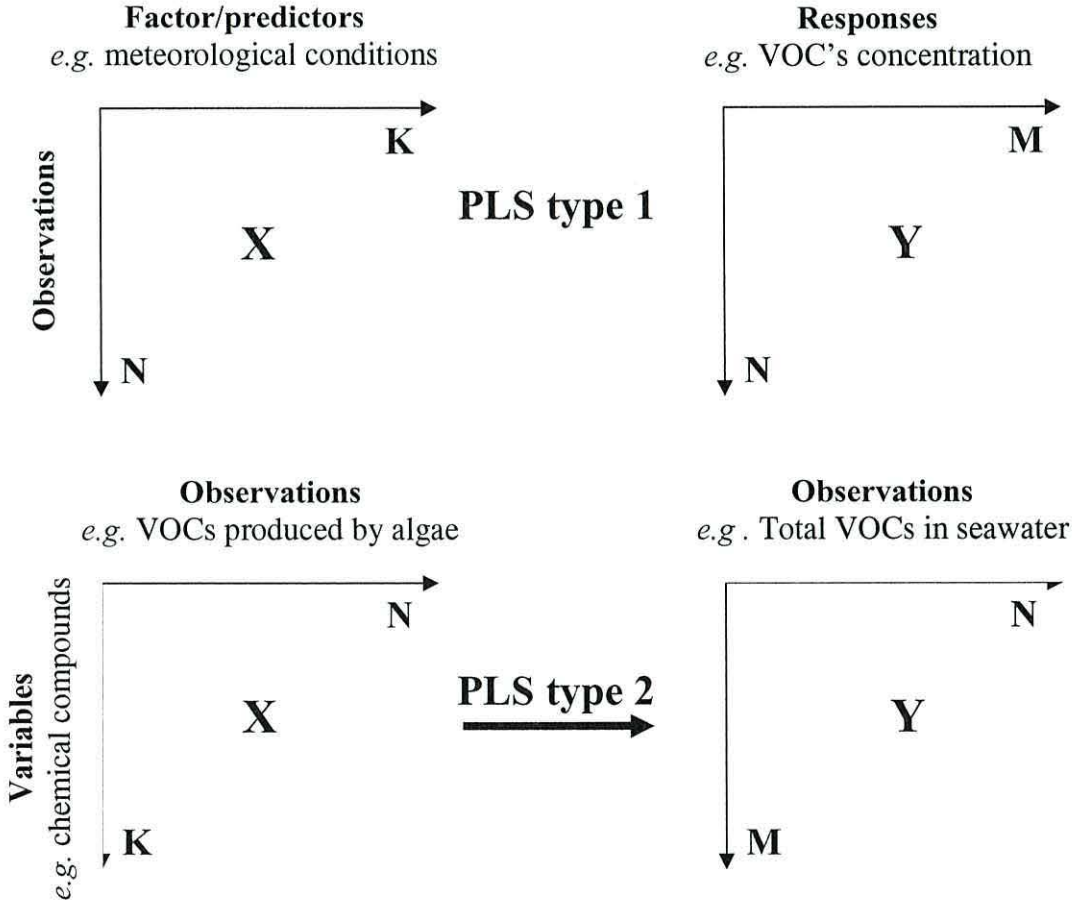


Figure 1.11. Matrices representation for PLS type 1 and 2.

1.7 Aim and objectives

1.7.1 Aim

The main aim of this project is to quantify the halogenated and other VOCs that are produced in the marine environment in a time series, finding the relationships among different factors influencing and contributing their production and release using multivariate data analysis and examine the release of VOCs from different species of common macroalgae, sediments and microalgae in order to find specific signatures.

1.7.2 Objectives

The specifics objectives to achieve the aim of this project were:

- Quantify the halocarbons and others non-halogenated VOCs produced in the Menai Strait.
- Elucidate the relationships of some meteorological and physico-chemical factors with the production and release of VOCs using PCA and PLS modelling.
- Incorporate the analysis of chlorophyll and pigments produced by phytoplankton in order to find relationships between phytoplankton presence (explained as pigments) and subsequent halocarbons production.
- Investigate the main natural sources of VOCs (sediment, microalgae and macroalgae) separately in order to see their individual contribution to the total amount of VOCs produced in seawater employing PLS type 2 modelling.
- To conduct a cruise to the Irish Sea, to find algal blooms and VOC's production in coastal waters and open oceans.

1.8. References

Abrahamsson, K., Choo, K. S., Pedersen, M., Johansson, G. and Snoeijs, P. (2003). Effects of temperature on the production of hydrogen peroxide and volatile halocarbons by brackish-water algae. *Phytochemistry* **64**(3): 725-734.

Amachi, S., Kamagata, Y., Kanagawa, T. and Muramatsu, Y. (2001). Bacteria mediate methylation of iodine in marine and terrestrial environments. *Applied and Environmental Microbiology* **67**(6): 2718-2722.

Anbar, A. D., Yung, Y. L. and Chavez, F. P. (1996). Methyl bromide: Ocean sources, ocean sinks, and climate sensitivity. *Global Biogeochemical Cycles* **10**(1): 175-190.

Andreae, M. O., Atlas, E., Harris, G. W., Helas, G., deKock, A., Koppmann, R., Maenhaut, W., Mano, S., Pollock, W. H., Rudolph, J., Scharffe, D., Schebeske, G. and Welling, M. (1996). Methyl halide emissions from savanna fires in southern Africa. *Journal of Geophysical Research-Atmospheres* **101**(D19): 23603-23613.

Asher, W. E. (1988). Air/sea interface chemistry and air/sea gas exchange. *Applied Geochemistry* **3**: 99.

Aucott, M. L., McCulloch, A., Graedel, T. E., Kleiman, G., Midgley, P. and Li, Y. F. (1999). Anthropogenic emissions of trichloromethane (chloroform, $CHCl_3$) and chlorodifluoromethane (HCFC-22): Reactive Chlorine Emissions Inventory. *Journal of Geophysical Research-Atmospheres* **104**(D7): 8405-8415.

Bey, I., Jacob, D. J., Yantosca, R. M., Logan, J. A., Field, B. D., Fiore, A. M., Li, Q. B., Liu, H. G. Y., Mickley, L. J. and Schultz, M. G. (2001). Global modeling of tropospheric chemistry with assimilated meteorology: Model description and evaluation. *Journal of Geophysical Research-Atmospheres* **106**(D19): 23073-23095.

Bianchi, A. P. and Varney, M. S. (1998). Volatile organic compounds in the surface waters of a British estuary. Part 1. Occurrence, distribution and variation. *Water Research* **32**(2): 352-370.

Blake, N. J., Blake, D. R., Simpson, I. J., Meinardi, S., Swanson, A. L., Lopez, J. P., Katzenstein, A. S., Barletta, B., Shirai, T., Atlas, E., Sachse, G., Avery, M., Vay, S., Fuelberg, H. E., Kiley, C. M., Kita, K. and Rowland, F. S. (2003). NMHCs and halocarbons in Asian continental outflow during the Transport and Chemical

Evolution over the Pacific (TRACE-P) Field Campaign: Comparison with PEM-West B. *Journal of Geophysical Research-Atmospheres* **108**(D20): art. no.-8806.

Blake, N. J., Blake, D. R., Sive, B. C., Chen, T. Y., Rowland, F. S., Collins, J. E., Sachse, G. W. and Anderson, B. E. (1996). Biomass burning emissions and vertical distribution of atmospheric methyl halides and other reduced carbon gases in the South Atlantic region. *Journal of Geophysical Research-Atmospheres* **101**(D19): 24151-24164.

Blake, N. J., Blake, D. R., Wingenter, O. W., Sive, B. C., McKenzie, L. M., Lopez, J. P., Simpson, I. J., Fuelberg, H. E., Sachse, G. W., Anderson, B. E., Gregory, G. L., Carroll, M. A., Albercook, G. M. and Rowland, F. S. (1999). Influence of southern hemispheric biomass burning on midtropospheric distributions of nonmethane hydrocarbons and selected halocarbons over the remote South Pacific. *Journal of Geophysical Research-Atmospheres* **104**(D13): 16213-16232.

Brown, R. H. A., Cape, J. N. and Farmer, J. G. (1999). Chlorinated hydrocarbons in Scots pine needles in northern Britain. *Chemosphere* **38**(4): 795-806.

Brunke, E. G., Labuschagne, C. and Scheel, H. E. (2001). Trace gas variations at Cape Point, South Africa, during May 1997 following a regional biomass burning episode. *Atmospheric Environment* **35**(4): 777-786.

Bu, X. and Warner, M. J. (1995). Solubility of Chlorofluorocarbon-113 in Water and Seawater. *Deep-Sea Research Part I-Oceanographic Research Papers* **42**(7): 1151-1161.

Bullister, J. L. and Wisegarver, D. P. (1998). The solubility of carbon tetrachloride in water and seawater. *Deep-Sea Research Part I-Oceanographic Research Papers* **45**(8): 1285-1302.

Bullister, J. L., Wisegarver, D. P. and Menzia, F. A. (2002). The solubility of sulfur hexafluoride in water and seawater. *Deep-Sea Research Part I-Oceanographic Research Papers* **49**(1): 175-187.

Campos, M., Nightingale, P. D. and Jickells, T. D. (1996). A comparison of methyl iodide emissions from seawater and wet depositional fluxes of iodine over the southern North Sea. *Tellus Series B-Chemical and Physical Meteorology* **48**(1): 106-114.

Carpenter, L. J. and Liss, P. S. (2000). On temperate sources of bromoform and other reactive organic bromine gases. *Journal of Geophysical Research-Atmospheres* **105**(D16): 20539-20547.

Carpenter, L. J., Malin, G., Liss, P. S. and Kupper, F. C. (2000). Novel biogenic iodine-containing trihalomethanes and other short-lived halocarbons in the coastal East Atlantic. *Global Biogeochemical Cycles* **14**(4): 1191-1204.

Chai, M., Arthur, C. L., Pawliszyn, J., Belardi, R. P. and Pratt, K. F. (1993). Determination of Volatile Chlorinated Hydrocarbons in Air and Water with Solid-Phase Microextraction. *Analyst* **118**(12): 1501-1505.

Chester, R. (1990). Dissolved gases in sea water. *Marine Geochemistry*. London, Unwin Hyman Ltd: 233-269.

Cho, D. H., Kong, S. H. and Oh, S. G. (2003). Analysis of trihalomethanes in drinking water using headspace- SPME technique with gas chromatography. *Water Research* **37**(2): 402-408.

Class, T., Kohnle, R. and Ballschmiter, K. (1986). Chemistry of Organic Traces in Air .7. Bromochloromethanes and Bromochloromethanes in Air over the Atlantic-Ocean. *Chemosphere* **15**(4): 429-436.

Cox, R. A., Derwent, R. G., Eggleton, E. J. and Lovelock, J. E. (1976). Photochemical oxidation of halocarbons in the troposphere. *Atmospheric Environment* **10**: 303-308.

Crutzen, P. J. and Bruhl, C. (1993). A Model Study of Atmospheric Temperatures and the Concentrations of Ozone, Hydroxyl, and Some Other Photochemically Active Gases During the Glacial, the Preindustrial Holocene and the Present. *Geophysical Research Letters* **20**(11): 1047-1050.

DeBruyn, W. J. and Saltzman, E. S. (1997). Diffusivity of methyl bromide in water. *Marine Chemistry* **57**(1-2): 55-59.

DeBruyn, W. J. and Saltzman, E. S. (1997). The solubility of methyl bromide in pure water, 35 parts per thousand sodium chloride and seawater. *Marine Chemistry* **56**(1-2): 51-57.

Dewulf, J., Drijvers, D. and Vanlangenhove, H. (1995). Measurement of Henrys Law Constant as Function of Temperature and Salinity for the Low-Temperature Range. *Atmospheric Environment* **29**(3): 323-331.

Dewulf, J. and VanLangenhove, H. (1997). Chlorinated C-1- and C-2-hydrocarbons and monocyclic aromatic hydrocarbons in marine waters: An overview on fate processes, sampling, analysis and measurements. *Water Research* **31**(8): 1825-1838.

Dimmer, C. H., Simmonds, P. G., Nickless, G. and Bassford, M. R. (2001). Biogenic fluxes of halomethanes from Irish peatland ecosystems. *Atmospheric Environment* **35**(2): 321-330.

Doney, S. C., Glover, D. M. and Najjar, R. G. (1996). A new coupled, one-dimensional biological-physical model for the upper ocean: Applications to the JGOFS Bermuda Atlantic time-series study (BATS) site. *Deep-Sea Research Part Ii-Topical Studies in Oceanography* **43**(2-3): 591-624.

Dvortsov, V. L., Geller, M. A., Solomon, S., Schauffler, S. M., Atlas, E. L. and Blake, D. R. (1999). Rethinking reactive halogen budgets in the midlatitude lower stratosphere. *Geophysical Research Letters* **26**(12): 1699-1702.

Eisert, R. and Levsen, K. (1996). Solid-phase microextraction coupled to gas chromatography: A new method for the analysis of organics in water. *Journal of Chromatography A* **733**(1-2): 143-157.

Elliott, S. and Rowland, F. S. (1993). Nucleophilic-Substitution Rates and Solubilities for Methyl Halides in Seawater. *Geophysical Research Letters* **20**(11): 1043-1046.

Erickson, D. J. and Eaton, B. E. (1993). Global Biogeochemical Cycling Estimates with Czcs Satellite Data and General-Circulation Models. *Geophysical Research Letters* **20**(8): 683-686.

Erickson III, D. J., Zepp, R. G. and Atlas, E. (2000). Ozone depletion and the air±sea exchange of greenhouse and chemically reactive trace gases. *Chemosphere - Global Change Science* **2**: 137-149.

Eriksson, L., Johansson, E., Kettaneh-Wold, N. and Wold, S. (1999). *Introduction to multi- and megavariate data analysis using projection methods (PCA and PLS)*, Umetrics AB.

Fahr, A., Nayak, A. K. and Kurylo, M. J. (1995). The Ultraviolet-Absorption Cross-Sections of CH_3I Temperature- Dependent Gas and Liquid-Phase Measurements. *Chemical Physics* **197**(2): 195-203.

Fenical, W. (1981). Natural halogenated organics. *Marine organic chemistry, evolution, composition, interactions and chemistry of organic mater in seawater*. E. K. Duursma and R. Dawson. New York, Elsevier. **31:** 375-393.

Ferek, R. J., Reid, J. S., Hobbs, P. V., Blake, D. R. and Liousse, C. (1998). Emission factors of hydrocarbons, halocarbons, trace gases and particles from biomass burning in Brazil. *Journal of Geophysical Research-Atmospheres* **103**(D24): 32107-32118.

Field, J. A., Verhagen, F. J. M. and deJong, E. (1995). Natural organohalogen production by basidiomycetes. *Trends in Biotechnology* **13**(11): 451-456.

Fleming, J., Albus, H., Neidhart, B. and Wegscheider, W. (1997). Terminology and definitions. *Accreditation and quality assurance* **2**: 51-52.

Fogelqvist, E. and Krysell, M. (1991). Naturally and Anthropogenically Produced Bromoform in the Kattegatt, a Semienclosed Oceanic Basin. *Journal of Atmospheric Chemistry* **13**(4): 315-324.

Gagosian, R. B. and Lee, C. (1981). Processes Controlling the distribution of biogenic organic compounds in seawater. *Marine organic chemistry, evolution, composition, interactions and chemistry of organic mater in seawater*. E. K. Duursma and R. Dawson. New York, Elsevier. **31:** 91-107.

Giese, B., Laturnus, F., Adams, F. C. and Wiencke, C. (1999). Release of volatile iodinated C-1-C-4 hydrocarbons by marine macroalgae from various climate zones. *Environmental Science & Technology* **33**(14): 2432-2439.

Glenn, W. J. (2002). State of the Art on Multivariate Chemometric Methods in Environmental Forensics. *Environmental forensics* **3**: 59-79.

Goodwin, K. D., North, W. J. and Lidstrom, M. E. (1997). Production of bromoform and dibromomethane by Giant Kelp: Factors affecting release and comparison to anthropogenic bromine sources. *Limnology and Oceanography* **42**(8): 1725-1734.

Gossett, J. M. (1987). Measurement of Henrys Law Constants for C1 and C2 Chlorinated Hydrocarbons. *Environmental Science & Technology* **21**(2): 202-208.

Grenfell, J. L., Harrison, R. M., Allen, A. C., Shi, J. C., Penkett, S. A., O'Dowd, C., Smith, M., Hill, M., Robertson, L., Hewitt, C. N., Davison, B., Lewis, A. C., Creasey, D., Heard, D., Hebestreit, K., Alicke, B. and James, J. D. (1999). An analysis of rapid increases in condensation nuclei concentrations at a remote coastal site in western Ireland. *Journal of Geophysical Research-Atmospheres* **104**(D11): 13771-13780.

Gribble, G. W. (1992). Sources of Halogenated Alkanes. *Chemical & Engineering News* **70**(45): 3-3.

Gschwend, P. M., Macfarlane, J. K. and Newman, K. A. (1985). Volatile Halogenated Organic-Compounds Released to Seawater from Temperate Marine Macroalgae. *Science* **227**(4690): 1033-1035.

Hamilton, J. T. G., McRoberts, W. C., Keppler, F., Kalin, R. M. and Harper, D. B. (2003). Chloride methylation by plant pectin: An efficient environmentally significant process. *Science* **301**(5630): 206-209.

Harnisch, J., Frische, M., Borchers, R., Eisenhauer, A. and Jordan, A. (2000). Natural fluorinated organics in fluorite and rocks. *Geophysical Research Letters* **27**(13): 1883-1886.

Hoekstra, E. J., De Leer, E. W. B. and Brinkman, U. A. T. (1998). Natural formation of chloroform and brominated trihalomethanes in soil. *Environmental Science & Technology* **32**(23): 3724-3729.

Hoekstra, E. J., Duyzer, J. H., de Leer, E. W. B. and Brinkman, U. A. T. (2001). Chloroform - concentration gradients in soil air and atmospheric air, and emission fluxes from soil. *Atmospheric Environment* **35**(1): 61-70.

Hoekstra, E. J., Verhagen, F. J. M., Field, J. A., De Leer, E. W. B. and Brinkman, U. A. T. (1998). Natural production of chloroform by fungi. *Phytochemistry* **49**(1): 91-97.

Hoffmann, T., O'Dowd, C. and Seinfeld, J. H. (2001). Iodine oxide homogeneous nucleation: An explanation for coastal new particle production. *Geophysical Research Letters* **28**(10): 1949-1952.

Huhn, O., Roether, W., Beining, P. and Rose, H. (2001). Validity limits of carbon tetrachloride as an ocean tracer. *Deep-Sea Research Part I-Oceanographic Research Papers* **48**(9): 2025-2049.

Hunter-Smith, R. J., Balls, P. W. and Liss, P. S. (1983). Henry's Law constants and their air-sea exchange of various low molecular weight halocarbon gases. *Tellus Series B-Chemical and Physical Meteorology* **35B**(5): 170-176.

IPCC, C. C. T. S. B. (2001). *Contribution of Working Group I to the Third Assessment Report of the Intergovernmental Panel on Climate Change*. Cambridge, Intergovernmental Panel on Climate Change, pp881.

Jeffrey, S. W., Mantoura, R. F. C. and Wright, S. W. (1997). *Phytoplankton pigments in oceanography: guidelines to modern methods*. Paris, Unesco, pp651.

Jones, E. P. (1980). Gas Exchange. *Air-Sea interaction (instrument and methods)*. F. Dobson, L. Hasse and R. Davis. New York, Plenum Press.: 433-445.

Jordan, A., Harnisch, J., Borchers, R., Le Guern, F. N. and Shinohara, H. (2000). Volcanogenic halocarbons. *Environmental Science & Technology* **34**(6): 1122-1124.

Keene, W. C., Khalil, M. A. K., Erickson, D. J., McCulloch, A., Graedel, T. E., Lobert, J. M., Aucott, M. L., Gong, S. L., Harper, D. B., Kleiman, G., Midgley, P., Moore, R. M., Seuzaret, C., Sturges, W. T., Benkovitz, C. M., Koropalov, V., Barrie, L. A. and Li, Y. F. (1999). Composite global emissions of reactive chlorine from

anthropogenic and natural sources: Reactive Chlorine Emissions Inventory. *Journal of Geophysical Research-Atmospheres* **104**(D7): 8429-8440.

Keppler, F., Borchers, R., Elsner, P., Fahimi, I., Pracht, J. and Scholer, H. F. (2003). Formation of volatile iodinated alkanes in soil: results from laboratory studies. *Chemosphere* **52**(2): 477-483.

Keppler, F., Eiden, R., Niedan, V., Pracht, J. and Scholer, H. F. (2001). Halocarbons produced by natural oxidation processes during degradation of organic matter (vol 403, pg 298, 2000). *Nature* **409**(6818): 382-+.

Khalil, M. A. K., Moore, R. M., Harper, D. B., Lobert, J. M., Erickson, D. J., Koropalov, V., Sturges, W. T. and Keene, W. C. (1999). Natural emissions of chlorine-containing gases: Reactive Chlorine Emissions Inventory. *Journal of Geophysical Research-Atmospheres* **104**(D7): 8333-8346.

Kleefeld, S., Hoffer, A., Krivacsy, Z. and Jennings, S. G. (2002). Importance of organic and black carbon in atmospheric aerosols at Mace Head, on the West Coast of Ireland (53 degrees 19 ' N, 9 degrees 54 ' W). *Atmospheric Environment* **36**(28): 4479-4490.

Kloster, S. (2006). DMS cycle in the marine ocean-atmosphere system - a global model study. *Biogeosciences* **3**(1): 29-51.

Koziel, J., Jia, M. Y., Khaled, A., Noah, J. and Pawliszyn, J. (1999). Field air analysis with SPME device. *Analytica Chimica Acta* **400**: 153-162.

Kozlov, S. N., Orkin, V. L., Huie, R. E. and Kurylo, M. J. (2003). OH reactivity and UV spectra of propane, n-propyl bromide, and isopropyl bromide. *Journal of Physical Chemistry A* **107**(9): 1333-1338.

Kraus, E. B. (1972). The state of matter near the interface. *Ocean-atmosphere interaction*. P. A. Sheppard. Oxford. **Oxford:** 41-67.

Krysell, M. (1991). Bromoform in the Nansen Basin in the Arctic-Ocean. *Marine Chemistry* **33**(1-2): 187-197.

Kuran, P. and Sojak, L. (1996). Environmental analysis of volatile organic compounds in water and sediment by gas chromatography. *Journal of Chromatography A* **733**(1-2): 119-141.

Kurylo, M. J. and Rodriguez, J. M. (1998, 1999). Short-lived ozone-related compounds. Eds: G. C. A. Ennis, Switzerland: World Meteorological Organization., WMO Scientific Assessment of Ozone Depletion,

Laturnus, F. (2001). Marine macroalgae in polar regions as natural sources for volatile organohalogens. *Environmental Science and Pollution Research* **8**(2): 103-108.

Laturnus, F., Haselmann, K. F., Borch, T. and Gron, C. (2002). Terrestrial natural sources of trichloromethane (chloroform, $CHCl_3$) - An overview. *Biogeochemistry* **60**(2): 121-139.

Liss, P. S. and Merlivat, L. (1986). The role of air-sea exchange in geochemical cycling. *Air-sea gas exchange rates: introduction and synthesis*. P. Buat-Menard, Dordrecht: D. Reidel: 113-127.

Liss, P. S., Watson, A. J., Liddicoat, M. I., Malin, G., Nightingale, P. D., Turner, S. M. and Upstill-Goddard, R. C. (1994). Chapter 12: Trace gases and air-sea exchanges. *Understanding the North Sea system*. H. Charnock, K. R. Dyer, J. M. Huthnance, P. S. Liss, J. H. Simpson and P. B. Tett. London, Chapman & Hall for The Royal Society: 153-163.

Lobert, J. M., Butler, J. H., Montzka, S. A., Geller, L. S., Myers, R. C. and Elkins, J. W. (1995). A Net Sink for Atmospheric CH_3Br in the East Pacific-Ocean. *Science* **267**(5200): 1002-1005.

Lobert, J. M., Keene, W. C., Logan, J. A. and Yevich, R. (1999). Global chlorine emissions from biomass burning: Reactive Chlorine Emissions Inventory. *Journal of Geophysical Research-Atmospheres* **104**(D7): 8373-8389.

Louis, F., Gonzalez, C. A., Huie, R. E. and Kurylo, M. J. (2001). An ab initio study of the kinetics of the reactions of halomethanes with the hydroxyl radical. 3. Kinetic parameters predictions for the potential halon replacements CH_2FBr, $CHFBr_2$, $CHFClBr$, $CHCl_2Br$, and $CHClBr_2$. *Journal of Physical Chemistry A* **105**(9): 1599-1604.

Manley, S. L. and delaCuesta, J. L. (1997). Methyl iodide production from marine phytoplankton cultures. *Limnology and Oceanography* **42**(1): 142-147.

McCulloch, A., Aucott, M. L., Graedel, T. E., Kleiman, G., Midgley, P. M. and Li, Y. F. (1999). Industrial emissions of trichloroethene, tetrachloroethene, and dichloromethane: Reactive Chlorine Emissions Inventory. *Journal of Geophysical Research-Atmospheres* **104**(D7): 8417-8427.

McGivern, W. S., Francisco, J. S. and North, S. W. (2002). Investigation of the atmospheric oxidation pathways of bromoform: Initiation via OH/Cl reactions. *Journal of Physical Chemistry A* **106**(26): 6395-6400.

McInnes, L. M., Quinn, P. K., Covert, D. S. and Anderson, T. L. (1996). Gravimetric analysis, ionic composition, and associated water mass of the marine aerosol. *Atmospheric Environment* **30**(6): 869-884.

Mellouki, A., Talukdar, R. K., Schmoltner, A. M., Gierczak, T., Mills, M. J., Solomon, S. and Ravishankara, A. R. (1992). Atmospheric Lifetimes and Ozone Depletion Potentials of Methyl- Bromide (CH_3Br) and Dibromomethane (CH_2Br_2). *Geophysical Research Letters* **19**(20): 2059-2062.

Miller, L. G., Kalin, R. M., McCauley, S. E., Hamilton, J. T. G., Harper, D. B., Millet, D. B., Oremland, R. S. and Goldstein, A. H. (2001). Large carbon isotope fractionation associated with oxidation of methyl halides by methylotrophic bacteria. *Proceedings of the National Academy of Sciences of the United States of America* **98**(10): 5833-5837.

Monks, P. S. (2000). A review of the observations and origins of the spring ozone maximum. *Atmospheric Environment* **34**(21): 3545-3561.

Moore, R. M., Geen, C. E. and Tait, V. K. (1995). Determination of Henry Law Constants for a Suite of Naturally- Occurring Halogenated Methanes in Seawater. *Chemosphere* **30**(6): 1183-1191.

Moore, R. M., Groszko, W. and Niven, S. J. (1996). Ocean-atmosphere exchange of methyl chloride: Results from NW Atlantic and Pacific Ocean studies. *Journal of Geophysical Research-Oceans* **101**(C12): 28529-28538.

Mudge, S. M. (2002). Aspects of Hydrocarbon Fingerprints Using PLS-New Data From Prince William Sound. *Environmental forensics* **3**: 323-329.

Murphy, B. L. and Morrison, R. D. (2002). *Introduction to environmental forensics*. San Diego, Academic Press, pp560.

Nielsen, J. E. and Douglass, A. R. (2001). Simulation of bromoform's contribution to stratospheric bromine. *Journal of Geophysical Research-Atmospheres* **106**(D8): 8089-8100.

O'Dowd, C. D., Facchini, M. A., Cavalli, F., Ceburnis, D., Mircea, M., Decesari, S., Fuzzi, S., Jun Yoon, Y. and Putaud, J.-P. (2004). Biogenically driven organic contribution to marine aerosol. *Nature* **431**(7009): 676-680.

O'Dowd, C. D. and Seinfeld, J. H. (2001). Mid-latitude North-Atlantic aerosol characteristics in clean and polluted air. *Atmospheric Research* **58**(3): 167-185.

Orkin, V. L., Khamaganov, V. G., Guschin, A. G., Huie, R. E. and Kurylo, M. J. (1997). Atmospheric fate of chlorobromomethane: Rate constant for the reaction with OH,

UV spectrum, and water solubility. *Journal of Physical Chemistry A* **101**(2): 174-178.

Page, B. D. and Lacroix, G. (1993). Application of Solid-Phase Microextraction to the Headspace Gas-Chromatographic Analysis of Halogenated Volatiles in Selected Foods. *Journal of Chromatography* **648**(1): 199-211.

Palmer, P. I., Jacob, D. J., Mickley, L. J., Blake, D. R., Sachse, G. W., Fuelberg, H. E. and Kiley, C. M. (2003). Eastern Asian emissions of anthropogenic halocarbons deduced from aircraft concentration data. *Journal of Geophysical Research-Atmospheres* **108**(D24): art. no.-4753.

Penkett, S. A., Jones, B. M. R., Rycroft, M. J. and Simmons, D. A. (1985). An Interhemispheric Comparison of the Concentrations of Bromine Compounds in the Atmosphere. *Nature* **318**(6046): 550-553.

Penuelas, J. and Llusia, J. (2003). BVOCs: plant defense against climate warming? *Trends in Plant Science* **8**(3): 105-109.

Platt, U. and Honninger, G. (2003). The role of halogen species in the troposphere. *Chemosphere* **52**(2): 325-338.

Prather, M. J. and Watson, R. T. (1990). Stratospheric Ozone Depletion and Future Levels of Atmospheric Chlorine and Bromine. *Nature* **344**(6268): 729-734.

Prilepsky, E. B., Povarov, V. G., Bredelev, N. V. and Isidorov, V. A. (1998). Formation of halocarbons in the methane-alkaline halide crystal system under UV radiation. *Russian Chemical Bulletin* **47**(10): 1910-1913.

Prinn, R. G., Weiss, R. F., Miller, B. R., Huang, J., Alyea, F. N., Cunnold, D. M., Fraser, P. J., Hartley, D. E. and Simmonds, P. G. (1995). Atmospheric Trends and Lifetime of CH_3CCl_3 and Global OH Concentrations. *Science* **269**(5221): 187-192.

Quack, B. and Wallace, D. W. R. (2003). Air-sea flux of bromoform: Controls, rates, and implications. *Global Biogeochemical Cycles* **17**(1): art. no.-1023.

Ramacher, B., Rudolph, J. and Koppmann, R. (1999). Hydrocarbon measurements during tropospheric ozone depletion events: Evidence for halogen atom chemistry. *Journal of Geophysical Research-Atmospheres* **104**(D3): 3633-3653.

Roberts, A. L., Sanborn, P. N. and Gschwend, P. M. (1992). Nucleophilic-Substitution Reactions of Dihalomethanes with Hydrogen-Sulfide Species. *Environmental Science & Technology* **26**(11): 2263-2274.

Rudolph, J., Khedim, A., Koppmann, R. and Bonsang, B. (1995). Field-Study of the Emissions of Methyl-Chloride and Other Halocarbons from Biomass Burning in Western Africa. *Journal of Atmospheric Chemistry* **22**(1-2): 67-80.

Rudolph, J., von Czapiewski, K. and Koppmann, R. (2000). Emissions of methyl chloroform (CH_3CCl_3) from biomass burning and the tropospheric methyl chloroform budget. *Geophysical Research Letters* **27**(13): 1887-1890.

Saini, H. S., Attieh, J. M. and Hanson, A. D. (1995). Biosynthesis of Halomethanes and Methanethiol by Higher-Plants Via a Novel Methyltransferase Reaction. *Plant Cell and Environment* **18**(9): 1027-1033.

Saxena, D., Aouad, S., Attieh, J. and Saini, H. S. (1998). Biochemical characterization of chloromethane emission from the wood-rotting fungus Phellinus pomaceus. *Applied and Environmental Microbiology* **64**(8): 2831-2835.

Scarratt, M. G. and Moore, R. M. (1998). Production of methyl bromide and methyl chloride in laboratory cultures of marine phytoplankton II. *Marine Chemistry* **59**(3-4): 311-320.

Scharlin, P. and Battino, R. (1995). Solubility of CCl_2F_2, $CClF_3$, CF_4, and CH_4 in Water and Seawater at 288.15-303.15-K and 101.325-Kpa. *Journal of Chemical and Engineering Data* **40**(1): 167-169.

Schwandner, F. M., Seward, T. M., Gize, A. P., Hall, P. A. and Dietrich, V. J. (2004). Diffuse emission of organic trace gases from the flank and crater of a quiescent active volcano (Vulcano, Aeolian Islands, Italy). *Journal of Geophysical Research-Atmospheres* **109**(D4): art. no.-D04301.

Schwarzenbach, R. P., Gschwend, P. M. and Imboden, D. M. (1993). *Environmental organic chemistry*. New York, Wiley Intersciences, pp681.

Simmonds, P. G., Alyea, F. N., Cardelino, C. A., Crawford, A. J., Cunnold, D. M., Lane, B. C., Lovelock, J. E., Prinn, R. G. and Rasmussen, R. A. (1983). The Atmospheric Lifetime Experiment .6. Results for Carbon- Tetrachloride Based on 3 Years Data. *Journal of Geophysical Research-Oceans and Atmospheres* **88**(NC13): 8427-8441.

Simmonds, P. G., Cunnold, D. M., Alyea, F. N., Cardelino, C. A., Crawford, A. J., Prinn, R. G., Fraser, P. J., Rasmussen, R. A. and Rosen, R. D. (1988). Carbon-Tetrachloride Lifetimes and Emissions Determined from Daily Global Measurements During 1978-1985. *Journal of Atmospheric Chemistry* **7**(1): 35-58.

Smith, A. E. and Bridges, D. C. (1996). Potential movement of methyl bromide through golf course greens. *Communications in Soil Science and Plant Analysis* **27**(9-10): 2381-2395.

Solomon, S., Garcia, R. R. and Ravishankara, A. R. (1994). On the Role of Iodine in Ozone Depletion. *Journal of Geophysical Research-Atmospheres* **99**(D10): 20491-20499.

Sturges, W. T., Cota, G. F. and Buckley, P. T. (1992). Bromoform Emission from Arctic Ice Algae. *Nature* **358**(6388): 660-662.

Tanhua, T., Fogelqvist, E. and Basturk, O. (1996). Reduction of volatile halocarbons in anoxic seawater, results from a study in the Black Sea. *Marine Chemistry* **54**(1-2): 159-170.

Thunis, P. and Cuvelier, C. (2000). Impact of biogenic emissions on ozone formation in the Mediterranean area - a BEMA modelling study. *Atmospheric Environment* **34**(3): 467-481.

Tokarczyk, R., Goodwin, K. D. and Saltzman, E. S. (2001). Methyl bromide loss rate constants in the North Pacific Ocean. *Geophysical Research Letters* **28**(23): 4429-4432.

Tokarczyk, R., Goodwin, K. D. and Saltzman, E. S. (2003). Methyl chloride and methyl bromide degradation in the Southern Ocean. *Geophysical Research Letters* **30**(15): art. no.-1808.

Tokarczyk, R. and Saltzman, E. S. (2001). Methyl bromide loss rates in surface waters of the North Atlantic Ocean, Caribbean Sea, and eastern Pacific Ocean (8 degrees-45 degrees N). *Journal of Geophysical Research-Atmospheres* **106**(D9): 9843-9851.

Tokarczyk, R., Saltzman, E. S., Moore, R. M. and Yvon-Lewis, S. A. (2003). Biological degradation of methyl chloride in coastal seawater. *Global Biogeochemical Cycles* **17**(2): art. no.-1057.

Wallace, D. W. R., Beining, P. and Putzka, A. (1994). Carbon-Tetrachloride and Chlorofluorocarbons in the South- Atlantic Ocean, 19-Degrees-S. *Journal of Geophysical Research-Oceans* **99**(C4): 7803-7819.

WMO (2002). World Meteorological Organization (WMO), Scientific Assessment Of Ozone Depletion 2002, Report 47, WMO Global Ozone Research and Monitoring Project. Geneva.

Wold, S., Albano, C., Dunn, W. J., Edlund, U., Esbensen, K., Geladi, P., Hellberg, S., Johansson, E., Lindberg, W. and Sjostrom, M. (1984). *Multivariate data analysis in chemistry*, Dordrecht, Holland D. Reidel Publishing Company,

Wright, S. W., Jeffrey, S. W., Mantoura, R. F. C., Llewellyn, C. A., Bjornland, T., Repeta, D. and Welschmeyer, N. (1991). Improved HPLC Method for the Analysis of Chlorophylls and Carotenoids from Marine-Phytoplankton. *Marine Ecology-Progress Series* **77**(2-3): 183-196.

Yamamoto, H., Yokouchi, Y., Otsuki, A. and Itoh, H. (2001). Depth profiles of volatile halogenated hydrocarbons in seawater in the Bay of Bengal. *Chemosphere* **45**(3): 371-377.

Yunker, M. B., Macdonald, R. W., Veltkamp, D. J. and Cretney, W. J. (1995). Terrestrial and marine biomarkers in a seasonally ice-covered Artic estuary-intregration of multivariate and biomarker approaches. *Marine Chemistry* **49**: 1-50.

Yvon, S. A. and Butler, J. H. (1996). An improved estimate of the oceanic lifetime of atmospheric CH_3Br. *Geophysical Research Letters* **23**(1): 53-56.

YvonLewis, S. A. and Butler, J. H. (1997). The potential effect of oceanic biological degradation on the lifetime of atmospheric CH_3Br. *Geophysical Research Letters* **24**(10): 1227-1230.

Zepp, R. G. and Ritmiller, L. F. (1995). Photoreactions Providing Sinks and Sources of Halocarbons in Aquatic Environments. *Aquatic Chemistry*. Washington, AMER CHEMICAL SOC. **244:** 253-278.

Zhang, Z. Y., Saini, R. D., Kurylo, M. J. and Huie, R. E. (1992). A Temperature-Dependent Kinetic-Study of the Reaction of the Hydroxyl Radical with CH_3Br. *Geophysical Research Letters* **19**(24): 2413-2416.

CHAPTER 2. MATERIALS AND METHODS

2.1 Sample collection and extraction for VOCs analysis

2.1.1 VOCs in the Menai Strait

Surface seawater samples were collected in the Menai Strait (Latitude 53°13.521 N, Longitude 04°09.549 W), see Figure 2.1. The samples were collected using a 4.85 L amber glass bottle. It was gently filled by immersion with surface seawater and sealed to avoid gas leaking during the transportation. Other volumes of sample were utilized (10 and 100 mL) but due to low sensitivities, larger volumes of analysis were employed (e.g. 4.5 L).

Samples were carried to the laboratory and extracted immediately. The volume extracted was 4.5 L with a head space volume of ~350 mL. The seawater was purged with extra pure nitrogen (~150 mL min^{-1}) for 1 hour at ambient temperature under continuous stirring to homogenize the sample and release the VOCs dissolved in the seawater. The nitrogen passing through the seawater was filtered through an organic trap (ELGA) to minimize the possible volatile organic content in this gas. The system utilized is shown in Figure 2.2. The same volume of seawater (filtered 0.1 μm, sterilized with UV light and degassed for two days with nitrogen) was used for blank analysis. To test the production of any compound product of column or fibre bleeding chromatograms without sample were run as well. The seawater was spiked with 20 μL of the internal standard (1778 pg L^{-1}) and the VOCs purged were trapped on a SPME fibre for an hour, then the fibre was retracted ready for desorption and analysis.

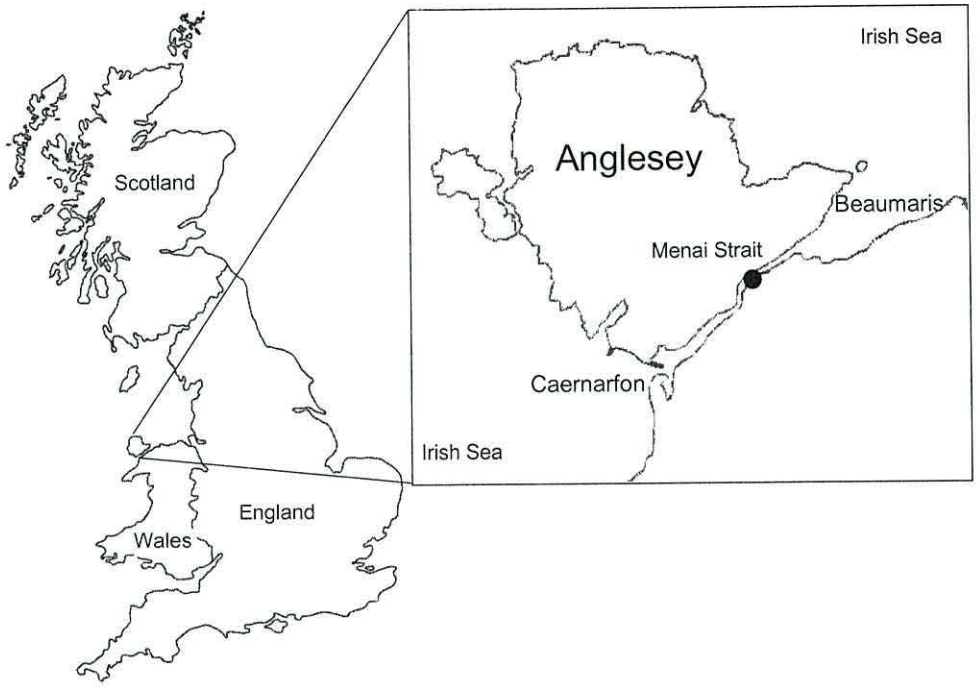


Figure 2.1. Map showing the location of the Menai Strait and the sampling point (•).

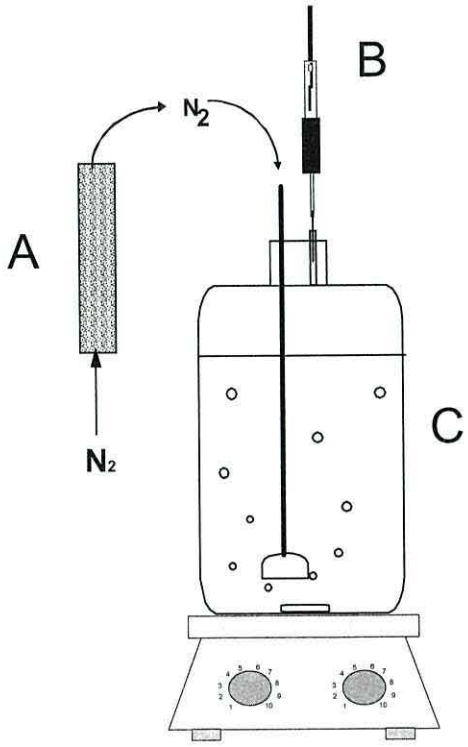


Figure 2.2. Diagram showing the purging and concentration system employed for VOCs analysis in seawater. A) Organic filter, B) SPME fibre and C) Amber bottle of 4.85 L (4.5 L of seawater and 0.35 L of head-space) with continuous stirring.

2.1.2 VOCs in the Irish Sea and Liverpool Bay

Surface seawater samples were collected across Liverpool Bay and River Mersey between 25 and 31 March 2006 at eighteen stations (Figure 2.3). Water samples were collected from the RV Prince Madog using a polished stainless steel container and transferred very slowly to avoid sample disturbance. Sampling was performed with the ship's prow towards the dominant wind and with the engine off in order to avoid sampling the gases coming from the ship and stirring from the ship's propeller. The water was transferred to a 4.85 L amber glass bottle; 4.5 L of water were added leaving a head space volume of approximately 350 mL. The purging procedure was the same as described in section 2.1.1 and the system employed is shown in Figure 2.2. The seawater was spiked with an internal standard (4-bromofluorobenzene 1778 pg L^{-1}, Supelco) prior to purging and VOCs were trapped on a SPME fibre for an hour. The fibre was retracted and transferred to the GC-MS for analysis. All the analyses were conducted immediately after purging on board the ship.

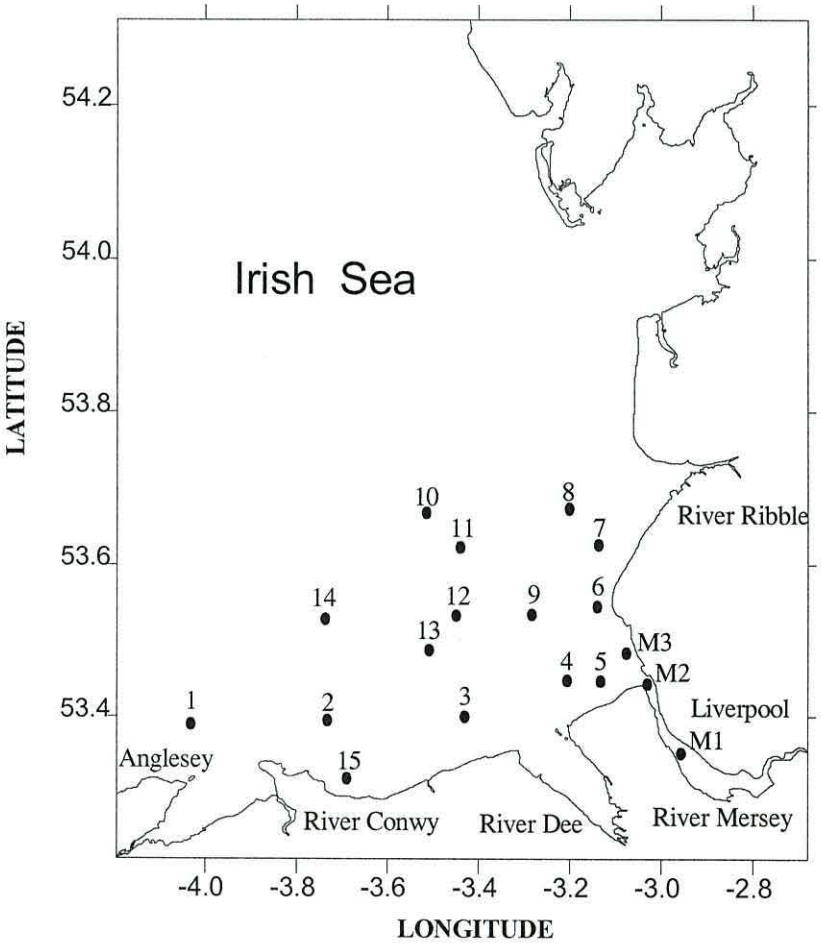


Figure 2.3. Map of the sampling locations.

2.1.3 VOCs in sediments

The samples were collected from a range of sediment types in and around the Menai Strait, North Wales, UK. VOCs produced in marine sediment samples were sampled *in situ* at low tide. This area is characterized by having a large tidal range (~8 m on springs) enabling *in situ* sampling without the need to perform complex underwater sampling or taking the samples into the laboratory.

Sampling was performed using a stainless-steel funnel coupled to a small vacuum pump and a SPME fibre (Figure 2.5). The vacuum pump was a modified computer keyboard cleaner; a variable resistor was mounted between the two AA batteries and the motor so that the flow rate at atmospheric pressure could be adjusted. A flow rate of 100 ml min^{-1} was chosen and maintained for all measurements.

This fibre was mounted in a Supelco SPME manual holder and the entire assembly was fitted in a Quick-fit still head with PTFE tape ensuring a gas tight seal. The active portion of the fibre was positioned in the narrow part of a Pasteur pipette so all vapours had to pass close by allowing adsorption. These details can be seen in Figure 2.5c. Prior to sampling, the fibre was conditioned for an hour at 230°C in the split / splitless injector of a gas chromatograph, transported to the sampling site in a sealed bag filled with nitrogen and exposed to the sediment derived VOCs for an hour.

500 μL of the internal standard (200 ng L^{-1} 4-bromofluorobenzene from Supelco, dissolved in methanol previously degassed with N_2 and sonicated) was dispersed onto the sediment surface immediately before the extraction commenced. The rim of the funnel was pushed 2 cm below the sediment surface to obtain a good seal and also to avoid sampling the surrounding air. After adsorption, the fibre was sealed with a capillary glass to reduce the potential for losses and placed in a cool box. Sealing the syringe with a capillary glass after the VOCs extraction reduces the potential for losses. Sample could be kept at -20°C for 24 hours before analysis: no significant losses in the number of compounds detected and their concentrations were observed. The redox potential was measured after VOC sampling with a WTW meter and probe. Sub-samples of the sediment (~3cm deep) were taken after VOCs sampling to determine the percentage of mud, total organic carbon (TOC) and moisture. For sample point positioning a Garmin GPS model MAP76CS was utilized.

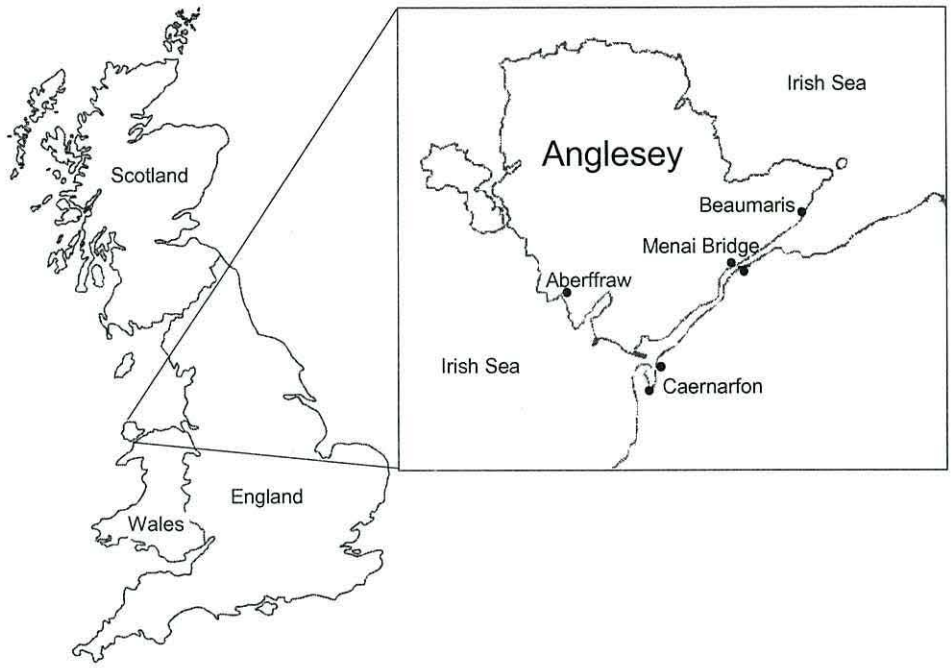
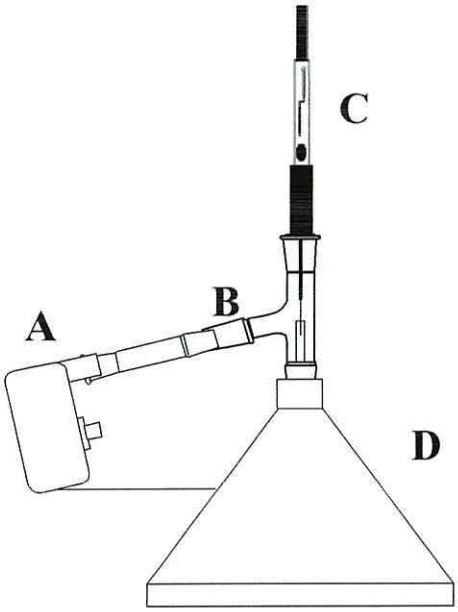


Figure 2.4. Map showing the stations sampled in the Menai Strait and surrounding areas (•).

1)



2)

3)

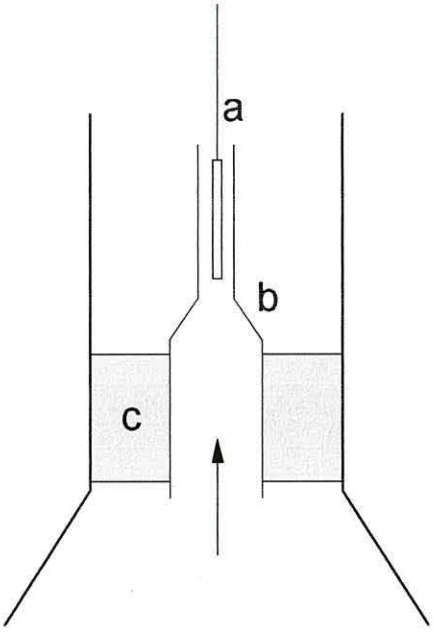


Figure 2.5. 1) Diagram of the system employed to collect the samples. a) Vacuum pump with a flow controller set at ~100 ml min^{-1}. b) Glass connectors. c) SPME fibre and manual holder. d) Stainless-steel funnel: internal volume: 3.8 L, height: 23 cm, internal diameter: 24.5 cm. 2) Picture of the system employed for sampling VOCs in sediments *in situ*. 3) Detail of the connection between the still head and the steel funnel. a) SPME fibre b) cut down Pasteur pipette c) PTFE tape coated rubber bung.

2.1.4 VOCs in macroalgae

Different types of fresh brown (Phaeophyta: *Ascophyllum nodosum*, *Fucus vesiculosus* (FV), *Fucus serratus* (FS), *Laminaria digitata* (LD)), red (Rhodophyta: *Palmaria palmata* (PP) and *Grifithsia flocculosa* (GF)) and green macroalgae (Chlorophyta: *Ulva lactuca* (UL), *Enteromorpha sp* (EN)) were collected on different days at low tide in the Menai Strait (Latitude 53°13.521 N, Longitude 04°09.549 W). These algae chosen were the most abundant in the strait and are common to shores around the UK and Northern Europe. Figure 2.6 shows schematically where the algae were collected from according to their position in the intertidal zone.

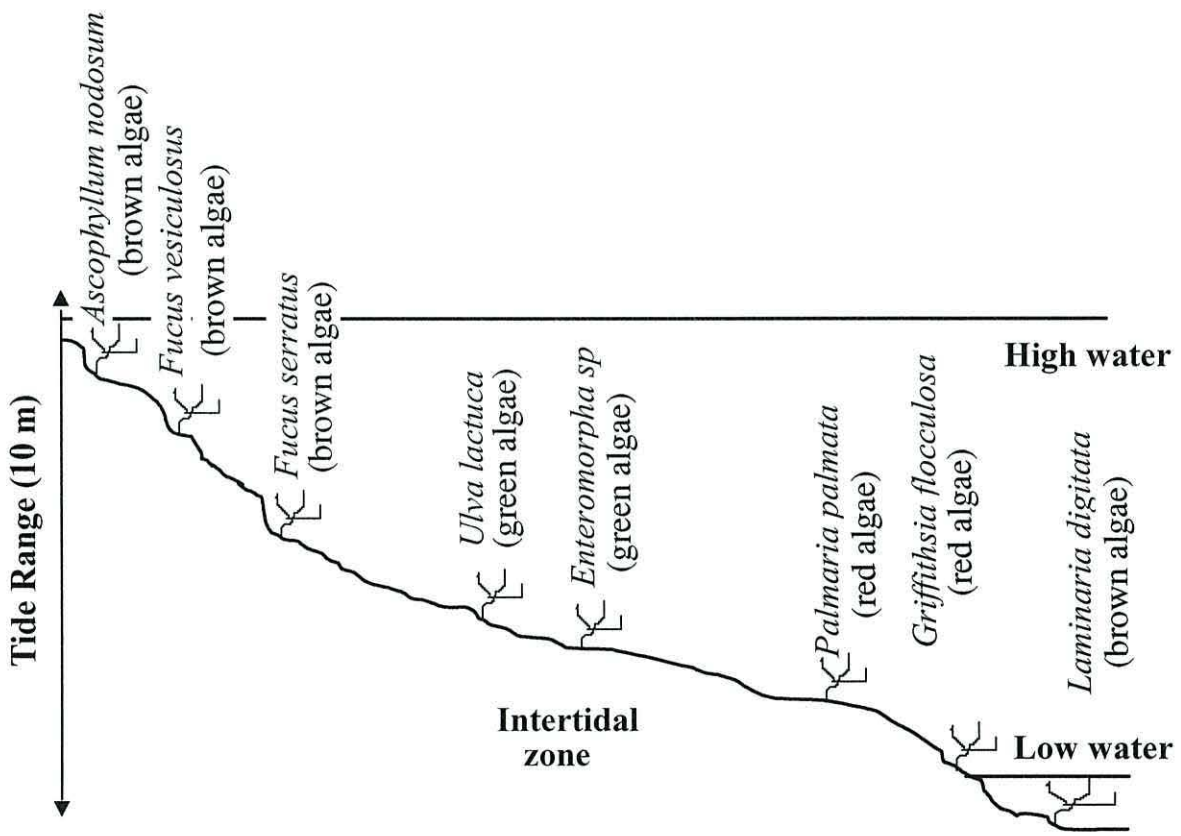


Figure 2.6. Intertidal profile showing the relative position of the collected macroalgae.

2.1.4.1 Temporal evolution of VOCs from macroalgae.

As a source of photosynthetic active radiation (PAR), a set of Sylvania Grolux® F20W/GRO (Germany) lamps were employed. A Biospherical Instrument Inc. QS2-100 irradiance meter was used to measure photon fluxes. The photon irradiance was measured placing the sensor at 10 cm of the lamps (50 μmol photons m^{-2} s^{-1}) and inside the bottles with seawater (68 μmol photons m^{-2} s^{-1}).

Prior to the algae collection, a series of glass bottles filled with 4.5 L of filtered seawater (sand filter, 30 μm, 10 μm, 5 μm, 0.2 μm and sterilized with a UV lamp) were left overnight (6-8 hours) bubbling with filtered air to saturate the water with oxygen. Algae were collected immediately after low tide and at dawn (to avoid desiccation). They were transported immediately to the laboratory with seawater and washed with filtered seawater to remove the sand and other particles. Grazers and other marine organisms were removed by hand and undamaged algae were selected for the experiments. Algae were roughly weighed to use the same amount for each experiment and placed into a set of bottles under illumination for 3, 6, 9, 12 hours, fully filled with seawater and sealed with rubber stoppers covered with a thick film of Teflon, leaving no head space. Another experiment was run in parallel under dark condition for 12 hours; the algae were placed into the bottle and covered with aluminium foil and placed in a box at the same temperature as the test algae. Two blanks were run, one with seawater immediately after bubbling at the start of the experiment and the other after 12 hours exposure to the light source but without algae; this was to determine the photochemical production of VOCs in the seawater despite the filtration and sterilization process.

The temperature of the seawater was measured before and after the incubation with values ranging between 16-20°C. The temperature did not increase by more than 2 degrees throughout the experiments. All algae were removed from the bottle before purging the seawater for VOCs. The algae were subsequently oven dried at 50°C for two days and weighed.

Figure 2.7. Incubation of *Laminaria*. From left to right the bottles for 3 hrs, blank at 0 min, 6 hours, 9 hours, blank at 12 hrs, 12 hours and dark condition. Note: Picture was taken before fully filling the bottles with seawater.

2.1.4.2. Desiccation induced VOC production from macroalgae

To determine which VOCs are produced by algae at low tide when they are exposed to the atmosphere and subsequently re-hydrated, the following experiment was performed. The same procedure of collection and algae pre-treatment described above was followed for this experiment. Only algae which are normally exposed to desiccation at low tides were used. Red algae were excluded since they usually remain underwater most of the time. One species was collected per day. After cleaning, the algae were hung at room temperature (16 to 18 °C) for up to six hours. The first sample was not exposed to desiccation; it was immediately placed into filtered seawater as above and the VOC content analyzed one hour later. The other samples were exposed to the air for 2, 4 and 6 hours before placing in seawater for one hour. A blank with treated seawater was run in parallel to determine the abiotic production of VOCs in the water prior to the start of the experiment.

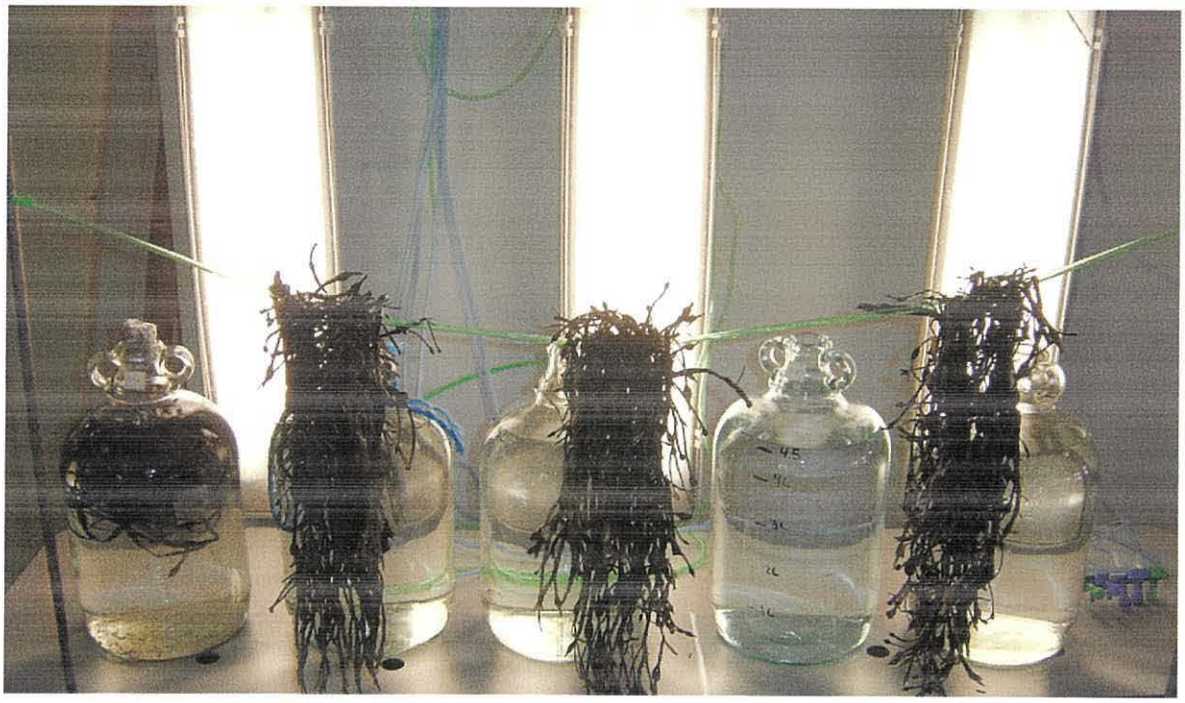


Figure 2.8. Desiccation of *Ascophyllum nodosum* illustrating the experiment carried out to study the effect of the desiccation on the VOCs production. Note: After inserting the algaes the bottles were fully filled with seawater.

2.2 Solid phase micro-extraction (SPME) extraction

VOCs contained in the samples (seawater, sediment and algae) were trapped by a SPME fibre. Solid-phase microextraction (SPME) was developed by Pawliszyn and co-workers (Chai *et al.*, 1993). It is a technique of extraction that combines sampling and concentration in one step. It requires no solvent and provides good results for a wide range of analyte concentrations. This technique has been used to analyze different compounds in water. The references on the use in halocarbons analyses has been done generally in drinkable water (Eisert and Levsen, 1996) air samples (Koziel *et al.*, 1999) and food (Page and Lacroix, 1993), but the analysis of halocarbons or other VOCs in seawater have yet to be reported.

A Jade valve kit for SPME for Fisons series 8000 GC from Alltech was used as an injector device for the fibre's syringe. A SPME fibre of 2cm-50/30 μm DVB/carboxen/PDMS for manual sampling was employed. Before the sample extraction, the fibre was conditioned for 1 hour at 230 ℃ according to the manufacturer instruction in order to remove compounds adsorbed on the fibre and to stabilize the phase. Conditioning was carried out in a split/splitless port (split open) with helium (99.99% pure). The compounds adsorbed on the fibre were immediately desorbed into the injector for 5 minutes at 230 ℃ with the split/splitless valve closed for thermal desorption of the extracted compounds. Figure 2.9 shows the process of using SPME in VOCs analysis.

The fibre selection was based on the criteria that the compounds to be detected and quantified were going to be found at trace levels and characterized by having different polarities. The fibre used to concentrate the VOCs was the most suitable in terms of sensitivity and selectivity due to its major surface and area of absorption (length of 2 cm) and the presence of different phases make it very versatile and able to analyse compounds with different polarities. Table 2.1 shows some of the fibre available and their common uses.

The desorption time was fixed at 1 hour to give the system enough time to reach the equilibrium of absorption due to the amount of sample employed. The time necessary for reaching the absorption equilibria from aqueous solutions are, in general ≥ 1 h. However, there is no need to achieve complete equilibrium concentrations if only the exposure time of the fibre is kept exactly constant (Eisert and Levsen, 1996). In order to determine the optimum time of purging an experiment was developed (using the system described in figure 2.2) spiking treated seawater with VOCs standards whose final concentration was

100 ng L^{-1} and then purged for 30, 60, 90 and 120 minutes. Figure 2.10 shows that 1 hour was enough time to reach the equilibrium of adsorption for the volume employed (4.5L) for the VOCs investigated.

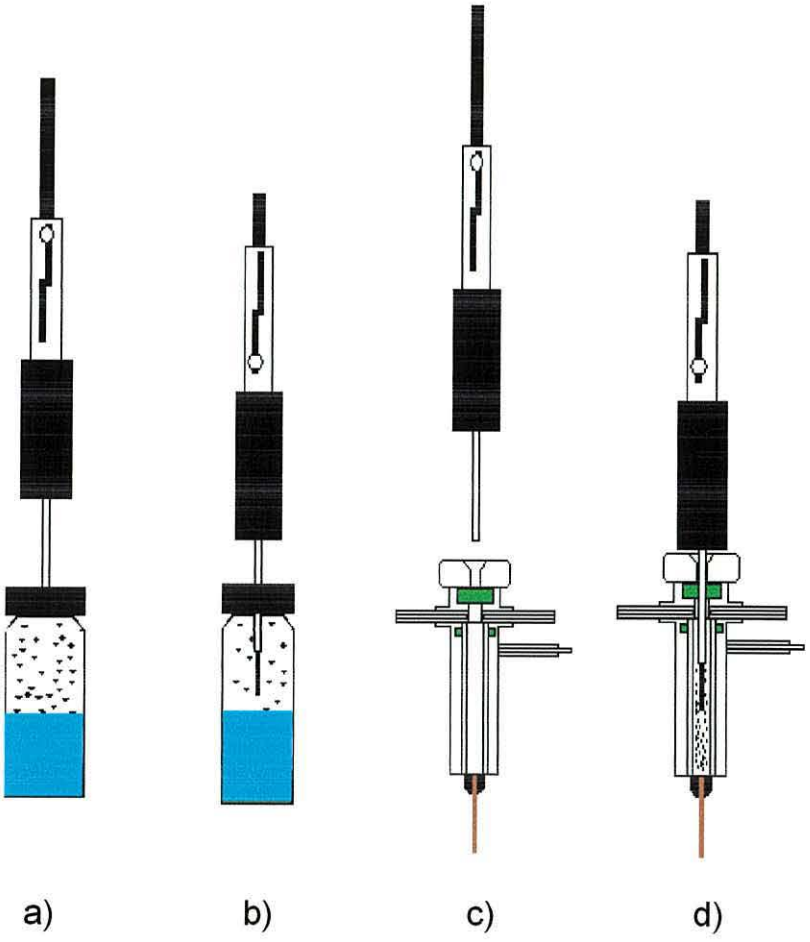


Figure 2.9. Absorption and desorption process using SPME. A) SPME device is placed in the sample's head-space. B) The fibre is released and the VOCS absorbed on it. C) The fibre is retrieved and ready to be injected into a GC injector. D) The fibre is injected and the compounds desorbed into the GC column for further analysis.

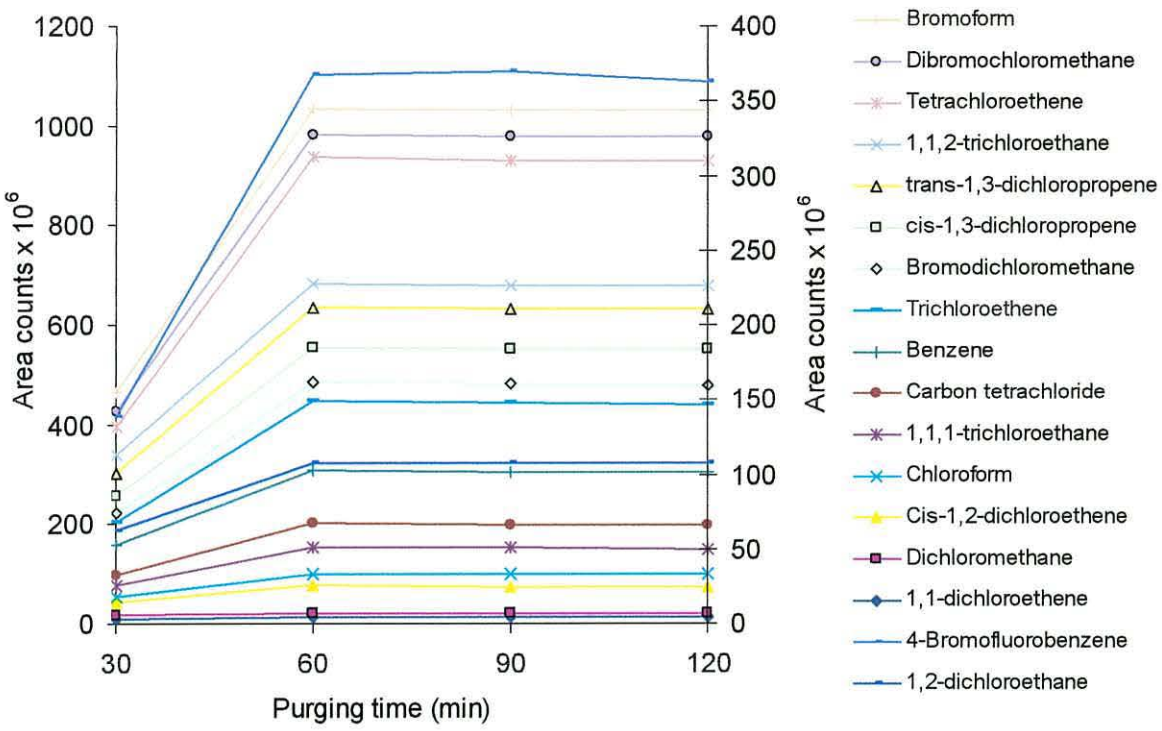


Figure 2.10. Purging time versus area counts showing that 1 hour is enough time to reach the equilibrium for the investigated VOCs (for an initial concentration of 100 ng L^{-1}).

Table 2.1. Fibre selection guide according to VOCs molecular weight and polarities provided by Supelco®.

Fibre type	Common uses
75 μm/85 μm Carboxen/ polydimethylsiloxane	Gases and low molecular weight compounds (MW 30-225)
100 μm polydimethylsiloxane	Volatiles (MW 60-275)
65 μm polydimethylsiloxane /divinylbenzene	Volatiles, amines and nitro-aromatic compounds (MW 50-300)
85 μm polyacrylate	Polar semi-volatiles (MW 80-300)
7 μm Polydimethylsiloxane	Non-polar high molecular weight compounds (MW 125-600)
30 μm Polydimethylsiloxane	Non-polar semi-volatiles (MW 80-500)
65 μm/70 μm Carbowax/ divinylbenzene polydimethylsiloxane	Alcohols and polar compounds (MW 40-275)
50 μm/30 μm divinylbenzene/ Carboxen on polydimethylsiloxane on a stableflex fibre	Flavour compounds: volatiles and semivolatiles C_3-C_{20} (MW 40-275)
50 μm/30 μm divinylbenzene/ Carboxen on polydimethylsiloxane on a 2 cm stableflex fibre	Trace compound analysis (MW 40-275)

2.2.1 SPME theoretical considerations

The work of (Zeng and Noblet, 2002) clearly states the theoretical background necessary to understand how SPME works with complex environmental samples. They consider an analyte partitioning among a truly dissolved phase, a solid-phase comprised of suspended solids, a colloidal phase containing dissolved organic matter (DOM), and an air phase. Mass balance requires that the total amount of the analyte in the system is equal to the sum of the amounts in the individual phases. The total amount, N_0, of the analyte in the system before SPME can be expressed as

$$N_0 = N_s^0 + N_{dom}^0 + N_w^0 + N_a^0$$

Where N_s^0, N_{dom}^0, N_w^0 and N_a^0 are the amounts of the analyte in the solid, DOM, aqueous (truly dissolved), and air phases, respectively. After SPME is complete, is possible to use the following formula

$$N_0 = N_s + N_{dom} + N_w + N_a + N_f$$

Where N_s, N_{dom}, N_w, N_a *and* N_f are the amounts of the analyte in the solid, DOM, aqueous and air phases, and the SPME fibre, respectively. It is commonplace in environmental chemistry to normalize contaminant in solids to the organic carbon (OC) fraction of this phase. Also, DOM is most often expressed as dissolved organic carbon (DOM) because the carbon fraction is typically what is measured. Therefore, is defined that $N_s^0=C_{oc}^0\, m_{oc}$, $N_{dom}^0=C_{doc}^0\, m_{doc}$, $N_w^0=C_w^0 V_w$, $N_a^0=C_a^0 V_a$, $N_s=C_{oc}\, m_{oc}$, $N_{dom}=C_{doc}\, m_{doc}$, $N_w= C_w V_w$, $N_a= C_a V_a$, and $Nf = C_f V_f$, where C_{oc}^0, C_{doc}^0, C_w^0 and C_a^0 are the analyte concentrations in the solid (OC normalized), DOM (DOC normalized), aqueous and air phases, before SPME; and C_{oc}, C_{doc}, C_w and C_a and C_f are the analyte concentration in the solid (OC normalized), DOM (DOC normalized), aqueous and air phases, and the SPME fibre (normalized to the polymer phase) after SPME, respectively; m_{oc} and m_{doc} are the mass of OC in the solid phase and DOC in the DOM phase, respectively; V_w, V_a and V_f are the volumes of the aqueous and air phases, and the sorbing fraction of the SPME fibre respectively.

When the system is at thermodynamic equilibrium and since partitioning processes have been verified experimentally as the dominant mechanism for extraction of hydrophobic organic compounds with nonpolar SPME fiber coatings, the usual partition coefficients can be used to describe the analyte distribution in the system:

$$K_{oc} = C_{oc}^0/C_w^0 = C_{oc}/C_w;\ K_{doc} = C_{doc}^0/C_w^0 = C_{doc}/C_w;\ K_f = C_f/C_w;\ K'_H = K_H/RT = C_a^0/C_v^0 = C_a^0/C_w.$$

Where K_{oc}, K_{doc} and K_f are the equilibrium partition coefficients of the analyte (solid-aqueous, DOM-aqueous, and SPME fibre-aqueous). Also, K_H and K'_H are the Henry's law constant and the dimensionless Henry's Law constant, respectively, R is the universal gas constant, and T is the absolute temperature.

In SPME experiments, the parameter actually measured is the amount of the analyte sorbed on the SPME fiber (N_f). Therefore, to determine the concentrations of analyte in the sample, it is necessary to derive a relationship between N_f and C_w^0. Combining equations results in.

$$N_f = [K_f V_f(V_w + \theta + K'_H V_a) / K_f V_f + V_w + \theta + K'_H V_a]\ Cw^0$$

Where $\theta = K_{oc}\ m_{oc} + K_{doc}\ m_{doc}$, a matrix sorption term reflecting the effects on SPME from suspended solids and DOM. As shown later, θ is the key parameter for understanding how SPME experiments may be affected by various sample parameters.

The next equation can be used to calculate the initial dissolved phase concentrations of analytes in the sample.

$$N_f = [K_f V_f / K_f V_f + V_w + \theta +] N_0$$

The next equation can be used to calculate the total concentration of analyte in a complex sample. Another useful relationship can be derived the last equation. If the amounts of sorbing phases in the system are insignificant (*i.e.*, $m_{oc} \approx 0$ and $m_{doc} \approx 0$), then θ approaches zero and if N'_f is defined as the amount of the analyte in the SPME fiber with insignificant amounts of sorbing represented by the following equation.

$$N'_f = [K_f V_f / K_f V_f + V_w] N_0$$

This is the most basic equation in SPME and has been successfully used for analysis of volatile organic chemicals in the samples matrixes. Combining the last two equations result.

$$N_f / N'_f = 1 - (\theta / K_f V_f + V_w + \theta)$$

The equation above can be used to calculate the amount of an analyte sorbed on the SPME fiber in a complex matrix relative to the amount sorbed in a relatively "clean" sample or pure water standard of the same volume. It suggests that the presence of sorbing phases in a sample will lower the apparent recovery of the analyte, which is of course an artifact due to a lack of consideration of the partitioning behaviour of the analyte within the system. The efficiency of SPME is the same for both cases, the lower amount of analyte extracted in the complex sample is due to a lower dissolved phase concentration in the presence of sorptive phases.

The matrix term θ can be generalized to include any number of heterogeneous solid and DOM phases. In generalised form θ can be expressed as:

$$\theta = \sum_{i=1}^{n} K_{oc}{}^{i} m_{oc}{}^{i} + \sum_{j=1}^{n'} K_{doc}{}^{j} m_{doc}{}^{j}$$

Where n and n' are the total numbers of solid and DOM phases, respectively. The unique aspect of the equations derived thus far is that they provide a complete description of the partitioning of organic chemicals between the various phases of any heterogeneous environmental sample during an SPME extraction. Moreover, the governing equations are parameterised in terms of system qualities frequently and easily measured or estimated by environmental scientists. Such parameterization allows for a rapid interpretation of how changes in analyte, sample, and fiber properties will affect the performance of SPME in sample analysis.

2.3 Gas chromatographic system and conditions

The VOCs adsorbed onto the fibre were analyzed on a Fisons MD800 Gas Chromatograph coupled to a mass spectrometry detector (GC-MS). A fused silica capillary column AT-502.2 (Alltech 60m x 0.32 mm i.d. and film thickness 1.8 μm) was used for the separation of all halocarbons and other VOCs. The chromatographic conditions were: helium as a carrier gas (~4.3 ml min^{-1}), at a pressure of 140 KPa; temperature programme: isothermal at 40℃ held for 5 min, 4℃ min^{-1} to 60℃ held for 3 minutes, 4℃ min^{-1} to 80℃ and held for 2 min, 4℃ min^{-1} to 150℃ and isothermal at 150℃ for 10min. The injector temperature was kept in 230℃ throughout analysis. The mass spectrometer conditions were: electron impact ionisation (70 eV), source temperature at 200℃ and interface temperature at 160℃. The same conditions were maintained for all VOCs analysis with seawater, sediment and algae.

2.3.1 Identification and quantification

Identification of VOCs and halocarbons was preformed in a scan mode (47–270 *m/z*). Quantification was performed spiking a known amount of internal standard (1,778 pg L^{-1}, 4-bromofluorobenzene, Supelco) before the extraction commenced. External calibration was also used for quantification through calibration curves of halocarbons standard (JMHW VOC Mix A, 16 analytes 1000 μg mL^{-1}, Supelco) see Figure 2.11. Single ion monitoring (SIM) was used to identify and quantify the halocarbons of interest; the fragments chosen for each compound as *m/z* are listed in Table 2.2. The targets compounds were equally divided through two SIM programs and care was taken to have the same dwell time and inter-channel delay among the fragments

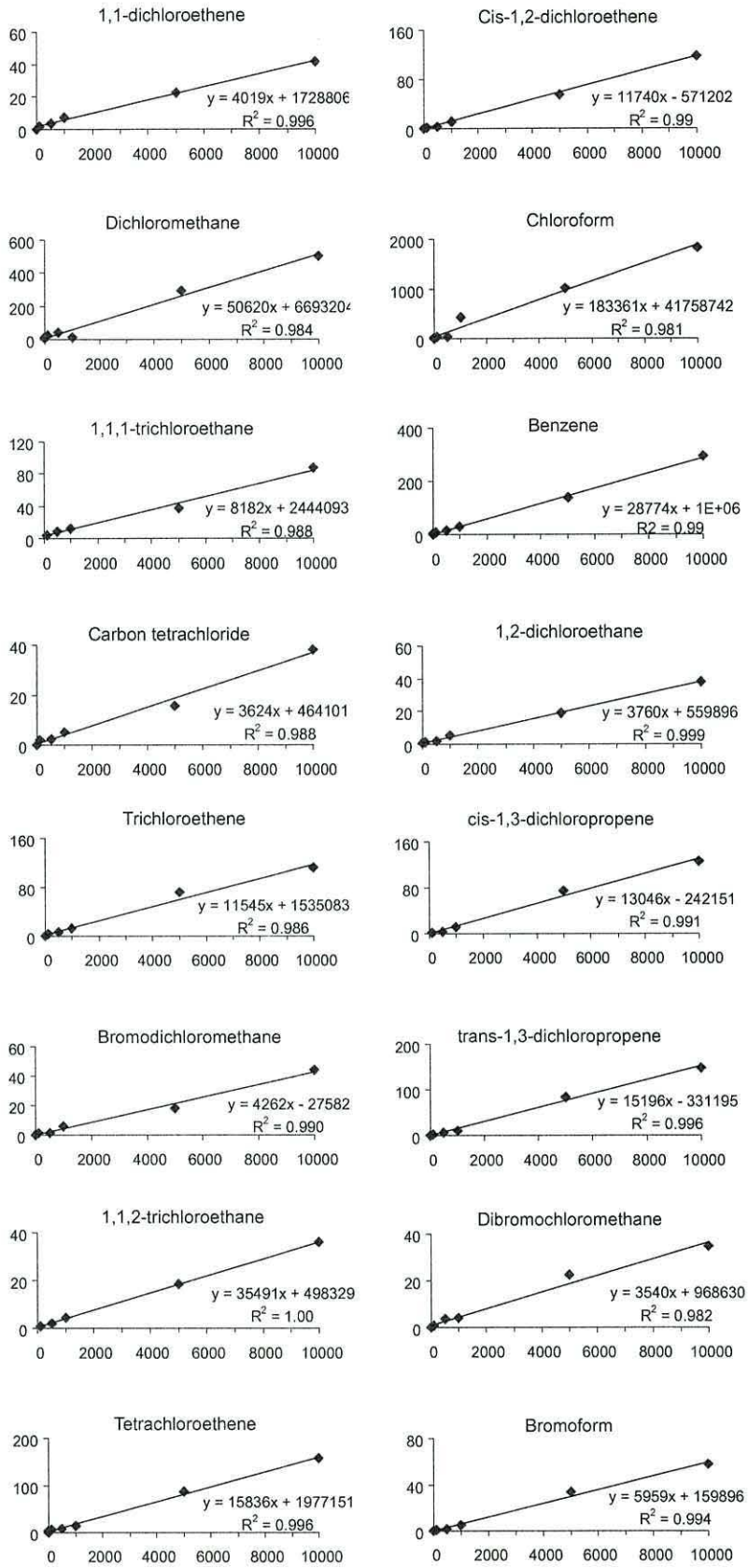


Figure 2.11. Calibration curves for standards employed for quantification purposes. Area counts (by millions) against concentrations (pg L^{-1}).

Table 2.2. Properties of the standard solution with the internal standard (I.S.). Showing, retention time (RT), quantification masses (*m/z*, used to detect and quantify with SIM mode), boiling point (Bp) and molecular weight (MW). The numbers of the compounds are referred to the order of elution in the chromatogram shown in Figure 2.10.

N°	Compound	RT [min]	*m/z*	Bp [° C]	MW [g mol^{-1}]
1	1,1-dichloroethene	3.83	61	37	96
2	Dichloromethane	6.67	49	40	84
3	Cis-1,2-dichloroethene	12.43	61	60	96
4	Chloroform	13.16	83	61	118
5	1,1,1-trichloroethane	15.24	97	74	132
6	Carbon tetrachloride	16.50	117	77	152
7	1,2-dichloroethane	17.29	62	84	98
8	Benzene	17.50	78	80	78
9	Trichloroethene	20.47	95	87	130
10	Bromodichloromethane	22.67	83	90	162
11	cis-1,3-dichloropropene	23.47	75	104	110
12	trans-1,3-dichloropropene	28.30	75	112	110
13	1,1,2-trichloroethane	29.02	97	114	132
14	Tetrachloroethene	30.50	166	121	164
15	Dibromochloromethane	31.43	127	119	206
16	Bromoform	38.71	173	150	250
I.S.	4-Bromofluorobenzene	39.74	174	152	174

2.3.2 Standard preparation and analysis

2.3.2.1 Standard solution

An ampoule containing a range of compounds to be used as a standard solution (JMHW VOC Mix A, 16 analytes 1000 μg mL^{-1}, SUPELCO) was transferred to a 2 mL amber vial and preserved at -20℃. To prepare the stock solution, 2 μL of this standard solution were transferred to a 20 mL vial filled with methanol giving a final concentration of 100 μg L^{-1}. The aliquots were taken with SGE syringes. When external calibration was used, 10 μL of the stock solution was spiked into 4.5 L of seawater (filtered 0.1μm, sterilized with UV light and degassed for two days with nitrogen) with a final concentration of 222 pg L^{-1}.

The internal standard (I.S.) 1-bromofluorobezene (1000 μg mL^{-1} purchased from Supelco) was transferred to a 2 mL amber vial and stored at -20℃. A stock solution was prepared using a SGE syringe taking 8 μL of the original solution and transferred to a 20 mL volumetric flask and filled with methanol with a final concentration of 400 μg L^{-1}. The stock solution was transferred to a 20 mL vial with screw cap and silicone liner faced with PTFE and stored at -20℃ in the freezer. 20 μL of the stock solution containing the internal standard was spiked into the seawater samples before using SPME fibre. The final concentration in the sample was brought to 1778 pg L^{-1}. Figure 2.12 shows a chromatogram including the 16 analytes and the internal standard.

An additional standard was prepared with different halocarbons and other VOCs, not included in the Supelco standard. Fifteen pure chemicals from different suppliers were spiked (1 μL each) in a vial with 20 mL of methanol. The final concentration of each one was calculated by using their densities (see Table 2.2). Then 10 μL of these stock solutions were spiked in treated seawater to amplify the range of quantifiable halocarbons with a final concentration between 86 to 332 pg L^{-1}.

Stock solutions were prepared with methanol (HPLC grade, Rathburn Scotland) degassed for 20 minutes in an ultrasonic bath at 30 ℃ and then transferred immediately to a Pyrex bottle.

Table 2.3. Properties of the standards used from pure chemical for identification.

Compound	Formula	Bp [°C]	Density [g L^{-1}]	MW [g mol^{-1}]	*m/z*
2-chloropropane	$CH_3CHClCH_3$	35	0.86	43	**43**,63
1-bromoethane	CH_3CH_2Br	39	1.46	73	**108, 29**, 27,110
1-bromopropane	$CH_2BrCH_2CH_3$	71	1.35	67.5	**43,** 41,122
2-chlorobutane	$CH_3CHClCH_2CH_3$	68	0.87	43.5	**57**,56,41
Iodoethane	CH_3CH_2I	72	1.93	96.5	**156,127**
1-chlorobutane	$CH_2ClCHCH_2CH_3$	78.5	0.89	44.5	**56**,41
2-iodopropane	CH_3CHICH_3	88	1.7	85	**43,** 41, 170
Chloroiodomethane	CH_2ClI	108	2.42	121	**176,127**
1-iodobutane	$CH_2ICH_2CH_2CH_3$	130	1.61	80.5	**57,** 41,**184**
2,3-dibromopropene	$C_3H_4Br_2$	142	1.93	96.5	**39,** 121, 200
Diiodomethane	CH_2I_2	182	3.32	166	**268,141**
Toluene	C_6H_5-CH_3	110	0.87	92	**91**
Hexane	C_6H_{14}	69	0.66	86	**57**
Pentane	C_5H_{12}	36	0.63	72	**43**
DMS	CH_3CH_2S	37	0.84	62	**62**

2.3.3 Limit of detection (LoD)

The detection limit of an individual analytical procedure is the lowest amount of analyte in a sample which can be detected but not necessarily as an exact value (Fleming *et al.*, 1997). The limit of detection was determined by multiple analyses of the blanks and determining their standard deviation (SD). The standard deviation is multiplied by three (probability of 99.7) ensuring that the signal is different from the blank. Then this value is extrapolated into the calibration curve. The results were calculated using the following relation:

$$LoD = 3 \times SD_{blank}/Slope$$

Where, LoD=is the analyte mass or concentration in the detection limit, 3 is a constant to get 99% of confidence, SD=is the standard deviation obtained through the blank injected at least 3 times and the slope correspond to the slope obtained for the calibration curve. The calculated limits of detection ranged from 25 up to 49 pg L^{-1}.

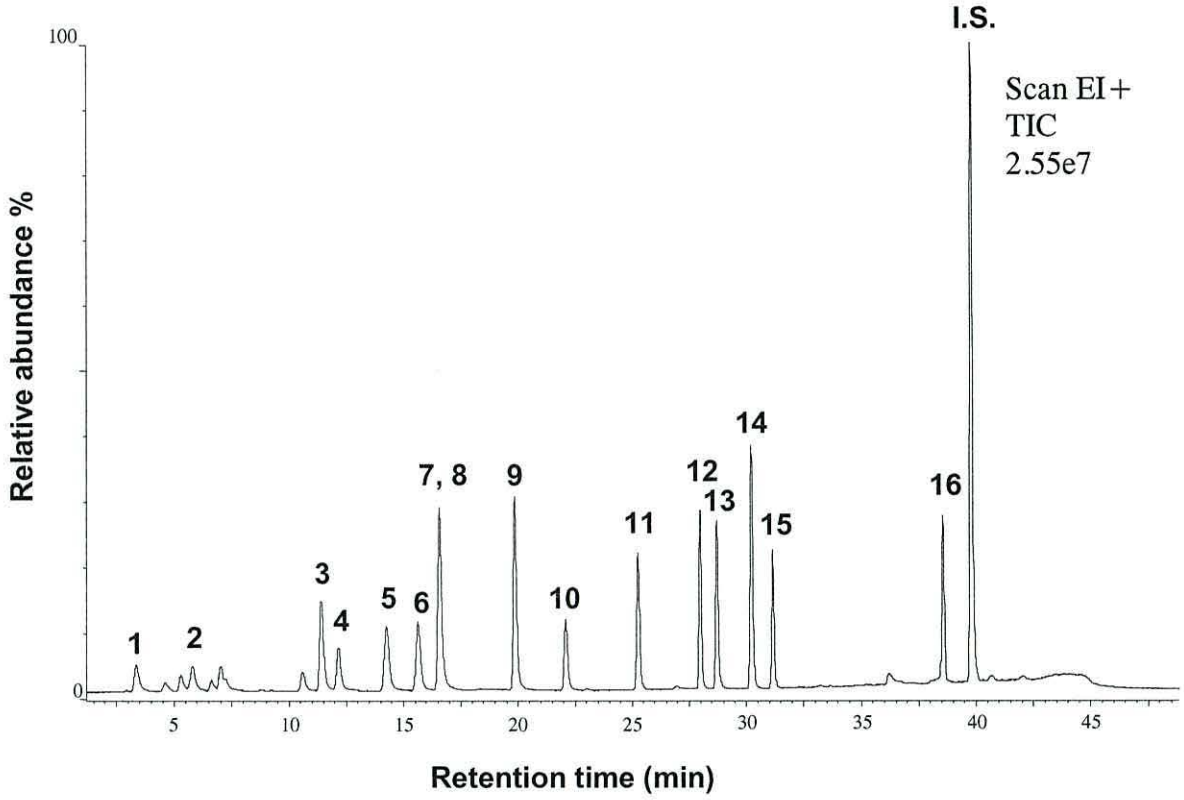


Figure 2.12. Total ion chromatogram obtained from injection of the standard solution. Where: 1) 1,1-dichloroethene 2) dichloromethane 3) cis-1,2-dichloroethene 4) chloroform 5) 1,1,1-trichloroethane 6) carbon tetrachloride 7) 1,2-dichloroethane 8) benzene 9) trichloroethene 10) bromodichloromethane 11) cis-1,3-dichloropropene 12) trans-1,3-dichloropropene 13) 1,1,2-dichloroethane 14) tetrachloroethene 15) dibromochloromethane 16) bromoform and I.S.) 4-bromofluorobenzene.

2.4 Pigments sampling and analysis

2.4.1 Field samples collection for pigments analysis

2.4.1.1 Samples taken in the Menai Strait

A total of 73 water samples were taken in Menai Strait during the period of October 2004 to July 2005 in the same place where the samples for VOCs were collected (see Figure 2.1). Surface water samples were collected using a 5L plastic carboy and transported to the laboratory immediately. Samples were filtered through a Whatman 47 mm GF/F filter using a water-pumped vacuum system equipped with a Sartorious (Germany) apparatus for filtering. The filters were folded and wrapped using aluminium foil, labelled and kept in the freezer at -20°C prior to analysis. The storage period was not longer than one month. Some samples and standards prepared a month before were injected to test degradability during storage. No discernible changes occurred while storing the samples for a month time in a fridge at -20°C. The volumes filtered varied between 2 and 5 litres, due to the high amount of suspended particles, especially during algal blooms.

2.4.1.2 Samples taken in the Irish Sea and Liverpool Bay

Seawater sub-samples were also taken for photosynthetic pigment analysis by HPLC (See Figure 2.3). Waters were filtered on board through a Whatman 47 mm GF/F filter using a vacuum pump. The filters were folded and wrapped using aluminium foil, labelled and kept frozen at -20°C for up to 10 days. From prior analysis, no discernible changes were detected while storing the samples and standards at this temperature for one month. The volumes filtered varied between 2 and 5 litres, due to the high amount of suspended particles, especially near to river mouths.

2.4.2 Sample extraction

After sample collection, all the samples were extracted in batches. The filters were unwrapped, and cut in thin slices and extracted in 5 mL of 90:10 acetone/water for 24 hours in the freezer at - 20°C. After this period, the filters were sonicated for 5 minutes and centrifuged at 5500 rpm using a Hermle Z230-A centrifuge for 10 to 15 minutes. Then, 1

mL of the surface's extract was transferred using a Pasteur pipette (VWR international) to a 2 mL vial (Chromacol, Ltd). 100 μL were analysed by HPLC using the Joint Global Ocean Flux Study (JGOFS) method.

2.4.2.1 Pigments Standards from algal cultures

Due to the unavailability of all the existent pigments commercially and in order to know their retention time and maximal wavelength of absorption, a 100 ml of pure microalgae cultures of *Rhinomona*, *Skeletonema costatum*, *Pavlova lutheri* and *Tetraselmis chui* were filtered using a Whatman 47 mm GF/F filter. These were extracted in 90:10 acetone/water and followed the same procedure as described above. Wavelengths (λmax) were used for the identification, and compared with ones reported by Jeffrey *et al.* (1997).

2.4.2.2 Pigments Standards from Pure chemicals

The following standards were employed to determine the concentration of pigments present in the seawater samples: *β,β*-carotene, fucoxanthin, 19'-hexanoyloxyfucoxanthin, alloxanthin, chlorophyll *b*, phaeophytin *a* (DHI Water and Environment, Denmark) and Chlorophyll *a* (Sigma). Calibrations curves were created by diluting the standards with 90% acetone. The pigments were identified in a range of 200-700 nm and the peak areas quantified at 436 nm. The standards prepared at different concentration were injected into a HPLC. Due to the fact that it is impossible to get pure standards for all the existent pigments, different pigment found were matched according to chemical properties with a standard purchased in order to quantify them.

2.4.2.3 Equipment

A HPLC (High Performance Liquid Chromatography) was employed to analyze the pigments present in the seawater. The machine employed was a ThermoSeparation Products comprising a solvent pump (Spectra System P4000), autosampler (AS3000), diode array detector (UV 3000HR), interface (SN4000) and a column Spheroclone 5μ ODS(2) 250x4.6 mm (Phenomenex) with a matched guard column.

The software Chromquest 4.1 (Thermo Electro Corporation) was used to identify and quantify the pigments.

Solvents employed were HPLC grade (Rathburn, Scotland). The solvent program utilized for the analysis reported by Wright *et al.* (1991) is shown in Table 2.4.

Table 2.4. HPLC solvent mixture program. Where **A**: 80:20 methanol:ammonium acetate 0.5M, **B**: 90:10 acetonitrile:distilled water, **C**: Ethyl acetate.

Time	**Solvents**			**Flow**
(min)	**% A**	**%B**	**%C**	**(mL min^{-1})**
0	100			1
2.0		100		1
2.6		90	10	1
13.6		65	35	1
18.0		31	69	1
23.0		31	69	1
25.0		100		1
26.0	100			1
34.0	100			1

2.5 Physico-chemical and meteorological data collection

2.5.1 Physico-chemical data

The physico-chemical data including temperature, salinity, conductivity and depth were obtained from a CTD placed in the Menai Strait. Salinity and density were calculated using UNESCO algorithms. Conductivity and turbidity are calculated variables and are subject to errors caused by bio-fouling of the sensors especially in spring and summer. The CTD is placed 100 meters from the sampling point.

2.5.2 Meteorological data

The meteorological parameters, such as wind speed, wind direction, air temperature, humidity, barometric pressure, solar irradiation and rain fall were obtained from the meteorological station mounted on the roof of the Westbury Mount building of the School of Ocean Sciences at a height of 28 m above sea level.

2.5.2.1 Irradiation data

The irradiation data was obtained from a meteorological station in Snowdonia 500 metres above sea-level. (Grid reference SH638551). This station is the nearest meteorological station to the Menai Strait, but due to its location in the mountains this site is sometimes cloudy while the Strait might be in sunshine. The data utilized was the direct irradiation obtained from the sensor pointing skywards (CM6B). The sensor at each weather station measures the total power of the sunshine in kilowatts per square metre. The instruments employed are illustrated in the next Figure 2.13.

During the last period of sampling an irradiation sensor was acquired in the School of Ocean Sciences. The instrument was placed on the roof of one of the departments, giving values in Lux.

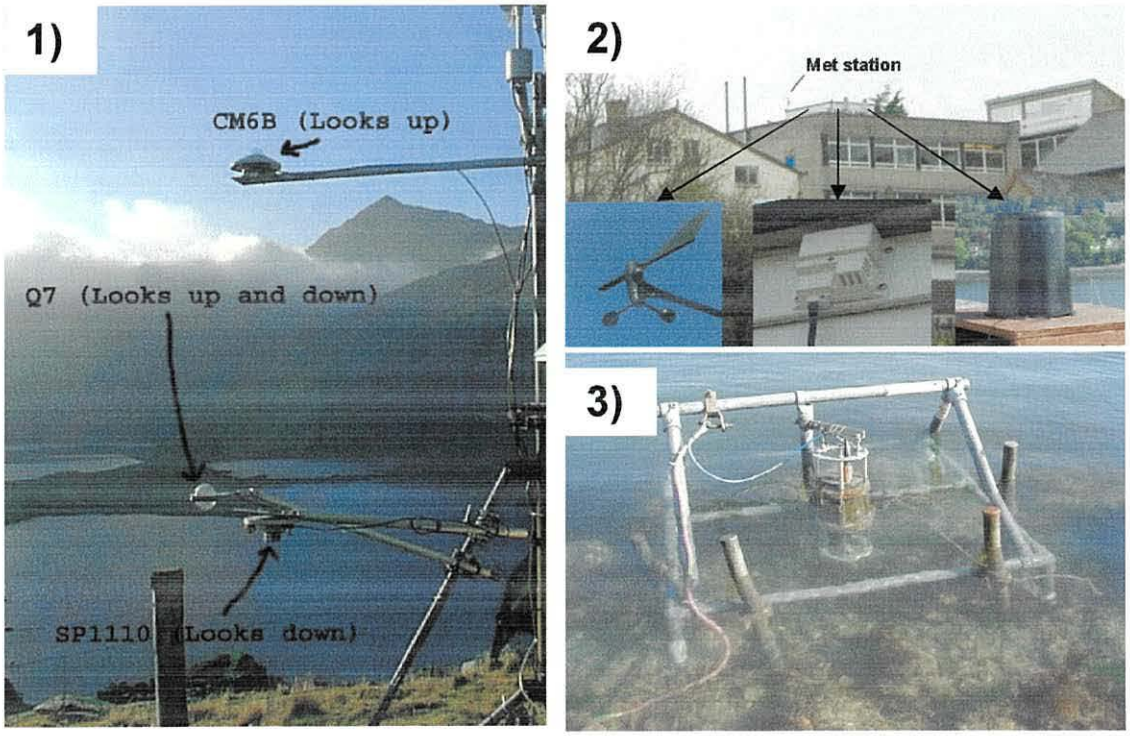


Figure 2.13. Instruments for meteorological and physico-chemical parameters acquisition. 1) Irradiation sensor placed in Snowdonia. 2) Meteorological station including from left to right, the anemometer, the temperature censor and the rain gauge meter. 3) CTD instrument.

2.6 Other analyses with sediment samples

2.6.1 Grain size analysis

Approximately 100 g of wet sediment were sieved through a 63 μm sieve. The fraction collected was filtered through a N°1 Whatman filter paper, dried at 90°C and weighed. The fraction remaining in the sieve was oven dried at 90°C for 14 hours. The dry fraction was sieved through 2, 1, 0.5, 0.25, 0.125, 0.063mm mesh filters for 10 minutes using a rotatory shaker. The fractions were weighed as an accumulative weight. The mud content was estimated from the amount of particles filtrated plus the amount of particles collected in the pan after passing through the last 63μm sieve.

2.6.2 Total organic carbon (TOC) and moisture content

About 20 g of sediment were oven dried (Heraeus D-6450 Instrument Hanau) at 80°C for 20 hours and weighed to determine the moisture content. After drying, the samples were placed into a muffle furnace (CWF 1100 Carbolite) at 400°C for 22 hours, re- weighed and the losses used to determine the TOC content.

2.7 Multivariate statistical analysis

The software SIMPA-P version 10.0.2.0 from Umetrics AB was used to perform the PCA and PLS analyses.

2.7.1 PCA analysis

PCA analysis was performed to see the relationships among the variables studied. Previous to data analysis, the VOC data was standardized using proportion to avoid the concentration effect in the samples. This was achieved by summing all the concentrations of the components in a sample. Then this value divides each single component in the sample, obtaining a proportion for each component in the sample.

2.7.2 PLS analysis

PLS was used to model and see how some factors affect the production and release of VOCs in the Menai Strait. The VOC data was also used as a proportion and logarithmically transformed when needed.

2.8. References

Chai, M., Arthur, C. L., Pawliszyn, J., Belardi, R. P. and Pratt, K. F. (1993). Determination of volatile chlorinated hydrocarbons in air and water with solid-phase microextraction. *Analyst* **118**(12): 1501-1505.

Eisert, R. and Levsen, K. (1996). Solid-phase microextraction coupled to gas chromatography: A new method for the analysis of organics in water. *Journal of Chromatography A* **733**(1-2): 143-157.

Fleming, J., Albus, H., Neidhart, B. and Wegscheider, W. (1997). Terminology and definitions. *Accreditation and quality assurance* **2**: 51-52.

Jeffrey, S. W., Mantoura, R. F. C. and Wright, S. W. (1997). *Phytoplankton pigments in oceanography: guidelines to modern methods*. Paris, Unesco, pp651.

Koziel, J., Jia, M. Y., Khaled, A., Noah, J. and Pawliszyn, J. (1999). Field air analysis with SPME device. *Analytica Chimica Acta* **400**: 153-162.

Page, B. D. and Lacroix, G. (1993). Application of Solid-Phase Microextraction to the Headspace Gas-Chromatographic Analysis of Halogenated Volatiles in Selected Foods. *Journal of Chromatography* **648**(1): 199-211.

Wright, S. W., Jeffrey, S. W., Mantoura, R. F. C., Llewellyn, C. A., Bjornland, T., Repeta, D. and Welschmeyer, N. (1991). Improved HPLC Method for the Analysis of Chlorophylls and Carotenoids from Marine-Phytoplankton. *Marine Ecology-Progress Series* **77**(2-3): 183-196.

Zeng, E. Y. and Noblet, J. A. (2002). Theoretical considerations on the use of solid-phase microextraction with complex environmental samples. *Environmental Science & Technology* **36**(15): 3385-3392.

CHAPTER 3. TIME SERIES SAMPLING IN THE MENAI STRAIT

3.1 Introduction

Coastal waters are considered an important source of Volatile Organic Compounds (VOCs) due to the presence of macroalgae and phytoplankton (Ballschmiter, 2003). The global production of halocarbons by marine algae is not the major source on a global scale (Scarratt and Moore, 1998; Haselmann *et al.*, 2000), but may be important at the local scale due to the occurrence of high biomass in coastal regions (Baker *et al.*, 1999; Laturnus *et al.*, 2000; Laturnus, 2001). Combined emissions of macro and microalgae contribute substantial amounts of bromine to the global cycle, perhaps in the same order of magnitude as anthropogenic sources (Goodwin *et al.*, 1997). Marine phytoplankton, comprised by photosynthetic bacteria and microalgae, are a natural source of halocarbons and other studies have demonstrated iodinated (Manley and delaCuesta, 1997), brominated (Cota and Sturges, 1997) and chlorinated (Scarratt and Moore, 1996; Scarratt and Moore, 1998; Scarratt and Moore, 1999) compounds are produced by phytoplankton. Several spatial studies have been conducted in order to determine the halocarbon and other VOC concentrations in seawater and fluxes to the atmosphere. However, there are few systematic studies of the temporal fluctuations of VOCs in the marine environment and how external factors drive their production and release. Bianchi and Varney (1998) conducted one of the first surveys studying the incidence and variation of several VOCs in British waters. Their findings showed that the distribution of biogenic VOCs was significantly influenced by the seasons and can be characterised by biogenic as well as anthropogenic sources.

The Menai Strait is a narrow (minimum width 200 m, maximum width 2000m) stretch of shallow tidal water (maximum depth 28 m) about 23 km long. The differential tides at the ends of the Strait lead to strong currents that flow in both directions. The principal sources of water within this region are the relatively high salinity water from the Irish Sea and a small fresh water component from the river Conwy and some waters which have been circulating in Liverpool Bay (Morris, 1974). It has regular periods of algal blooms with a range of photosynthetic pigments. The annual phytoplankton cycle is comprised by a mixed diatom bloom in the late March or April followed by blooms of diatoms and *Phaeocystis* in May and June (Blight *et al.*, 1995). Some later blooms with low biomass occur in August and October. Unpublished results in the Menai Strait

revealed that during the spring bloom, *Skeletonema sp* dominates during April with about the 64% of the total phytoplankton population, while *Phaeocystis sp* dominates during May with about 84% of the community. During the spring bloom there is a succession of species which may produce and release different suites of VOCs.

Pigments in seawater are known to provide an indicator of the productivity in the oceans and seawater in general (Jeffrey *et al.*, 1997). Different species of phytoplankton produce different suites of pigments. For instance, it is possible to determine the community structure in the water and, to an extent, its physiological status and grazing pressure. Chlorophyll *a* (Chl *a*) is the main pigment in most algae and plants and it is usually used as an indicator for phytoplankton presence, which are one of the main producers of halocarbons in the oceans (Tokarczyk and Moore, 1994).

This chapter reports the results of a time series sampling in the Menai Strait. The main aim was to identify the temporal trend in VOC concentrations and secondly to identify any relationships between the VOCs and some external physico-chemical, meteorological and biological parameters.

3.2 Results and discussions

3.2.1 Sampling variability

In order to determine the degree of intra-sample variability, three samples were collected simultaneously and stored as details in Chapter 2 before analysis. The concentrations in those that were stored for 2 to 4 hours decreased at 5 – 30% per hour. However, samples that were purged simultaneously and the SPME fibre stored in the freezer in a sealed N_2 purged bag in the freezer prior analysis, had little or no change in concentrations. The variability of these samples expressed as relative standard deviation (RSD) for 64 compounds ranged from 4 to 20 RSD% with a median value of 12 RSD%. This variability might be due to analytical limitations or differences in the purging efficiency. However, considering that most of the VOCs analyzed are at very trace levels, tiny differences in concentrations from one sample to another can lead to variable results.

3.2.2 VOCs in the Menai Strait water

Sixty four different compounds were detected and quantified in the Menai Strait during a year sampling. Table 3.1 shows the compounds detected and summarises the data from the samples analyzed including mean, standard deviation, minimum and maximum concentration. The compounds detected can be classified as follow:

3.2.2.1 Halogenated compounds

Halocarbons were the compounds most widely detected; twenty different compounds were detected. The halocarbons were classified according to their composition as chlorinated (<LoD to 75.59 ng L^{-1}), brominated (<LoD to 906.96 ng L^{-1}), iodinated (<LoD to 58.50 ng L^{-1}) and mixed halogen (<LoD to 42.91 ng L^{-1}).

Chlorinated halocarbons were measured with two carbons (1,1-dichloroethene, 2-chloropropane, *cis*-1,2-dichloroethene and tetrachloroethene) and with three carbons (2-chloropropane, *cis*-1,3-dichloropropene and *trans*-1,3-dichloropropene). In the literature it is common to find reports of halocarbons with one or two carbons; three carbons are rarely reported as compounds produced from biological sources. In addition, no chemical industries contribute halocarbons to the Menai Strait, although it is not possible to discard potential anthropogenic source of these compounds. Ship-borne analyses performed in Liverpool Bay waters (see Chapter 6) showed that these chlorinated compounds originated in the River Mersey and were most likely to be anthropogenic in origin. Bianchi and Varney (1998) reported the presence of chlorinated compounds in a British Estuary and attribute dichloromethane, 1,1,1-trichloroethane, trichloroethene and tetrachloroethene to anthropogenic sources as they are chemicals that have been used for over 30 years in Britain.

Brominated compounds were not widely found, however, bromoform was present in high concentrations and was several times more concentrated than the other halocarbons measured. The sources of bromoform are largely biogenic (Krysell, 1991) and can be produced naturally in algal belts along the coast (Fogelqvist and Krysell, 1986). The concentrations of bromoform were similar to those reported in coastal sites by other authors (Fogelqvist and Krysell, 1986; Nightingale *et al.*, 1995; Christof *et al.*, 2002). The three carbon compound, 1-bromopropane, was detected at very low concentrations and might have a novel biological source although it has been reported as a replacement for

high-end chlorofluorocarbon (HCFC) solvents (Whitten *et al.*, 2003). Burkholder *et al.* (2002) found that this compound is not an ozone depletor and its atmospheric lifetime is only a few hours.

Five iodinated compounds were found in the Menai Strait; these compounds are generally degraded quickly in the upper water column (Carpenter *et al.*, 2000), and as a consequence of this, they are rarely reported. The iodinated compounds are seldom classed as anthropogenic pollutants in seawater and are mainly biological in origin. The concentrations of iodomethane measured in the Strait were similar to that reported by Fogelqvist *et al.* (1996) who suggested an algal source.

The mixed halogen compounds quantified were bromodichloromethane, chloroiodomethane and dibromochloromethane. The concentrations of bromodichloromethane and chloroiodomethane were close to those reported elsewhere in coastal seawater (Nightingale *et al.*, 1995; Connan *et al.*, 1997; Christof *et al.*, 2002) although the concentration of dibromochloromethane was very low in comparison to those reported by Nightingale *et al.* (1995) and Christof *et al.* (2002).

3.2.2.2 BTEXs and mono-aromatic compounds

Thirteen aromatics compounds were measured in the Menai Strait including methyl substituted benzene compounds (BTEXs). Their concentrations ranged between <LoD to 4,282 ng L^{-1}. These values were high compared to findings reported elsewhere. For instance, Gschwend *et al.* (1982) and Mantoura *et al.* (1982) have reported a maximum concentration of 500 ng L^{-1} in coastal waters ostensibly free from anthropogenic inputs. Marti *et al.* (2001) reported aromatic hydrocarbons in surface seawater in a range of 23 to 68 pg L^{-1}, values very low in comparison with the findings in this study. The amounts found in each place depend intimately on the inputs to the area and the uses of the water. The Menai Strait is used for recreation during the summer and a lot of activities involve the use of diesel or petrol powered-engines and so it is not surprising to find products derived from fuels like benzenes, alkylbenzenes and PAHs. In addition, oily films were occasionally seen during the sampling. Production and release of toluene, presumably produced by biological processes in marine sediments, were detected in the seawater (see Chapter 5).

3.2.2.3 Sulphur containing compounds

Some phytoplankton in the oceans produce dimethylsulphoniopropionate (DMSP), which may be a cellular osmoregulatory compound. Its formation is physiologically dependent upon environmental factors such as light, temperature, salinity, and nutrient availability, but the primary release mechanism is through cellular lysis. Once in the water column, DMSP is converted to DMS by a lyase that is primarily produced by heterotrophic bacteria (Kiene and Bates, 1990). Some grazers/protozoa and a few algae have also been shown to contain this lyase (Wolfe and Steinke, 1996), and a few phytoplankton species directly emit DMS to the water column. A portion of DMS is photo-oxidized to DMSO in the water column (Brimblecombe and Shooter, 1986), and a portion is lost to the atmosphere.

Only two sulphur VOCs were quantified in the Menai Strait seawater; dimethyl sulphide (0.078 to 70.98 ng L^{-1}) and dimethyl disulphide (<LoD to 159.94 ng L^{-1}). Sharma *et al.* (2003) in the Strait of Georgia detected summer concentrations of DMS ranging from 12.4 to 868 ng L^{-1}, high values compared with those found in the Menai Strait. Bianchi and Varney (1998) reported concentrations of dimethylsulphide (DMS_2) in seawater from a British estuary of 1,190 ng L^{-1}.

Reports suggest that organosulphides are found in higher concentration in spring time rather than summer or autumn (Sharma *et al.*, 2003) and probably their seasonally production by phytoplankton can be an explanation why the concentrations in the Menai Strait are minor than reported for other authors. However, in the review of Buckley and Mudge (2004) pointed out that the differences between the amounts reported of DMS in ocean, might be that DMS and all its components vary widely from one location to other and therefore it is not practical to compare results from different places.

Greater numbers of sulphur containing compounds were detected in sediments (see chapter 5) but only two were detected in seawater. This difference in number might be due DMS and DMS_2 were more concentrated than the others in seawater and also these compounds have diverse sources apart from bacterial production in sediments such as phytoplankton and macroalgae.

3.2.2.4 Non-methane hydrocarbons (NMHC) and terpenes

It is well known that the marine phytoplankton, zooplankton, bacteria and marine algae exude or excrete alkanes and alkenes (Broadgate *et al.*, 2004). The alkane concentrations in the Strait ranged from <LoD to 1,787 ng L^{-1}, probably produced by algal blooms which predominate during the spring and summer. These concentrations were higher than the values reported by Marti *et al.* (2001) with a range of n-alkanes from 50 to 63 ng L^{-1} in a similar system. However, anthropogenic inputs from oil may need to be considered as local sources in the Strait.

Terpenes such as limonene and α-pinene were also detected. They were present during all sampling and may be related to terrestrial sources as they have few associations to phytoplankton production (Bianchi and Varney, 1998).

3.2.2.5 Oxygenated compounds

Oxygenated compounds were not the most abundant compounds in the Strait; only two aldehydes (hexanal and decanal) and 2,4-dimethylfuran were detected. Bianchi and Varney (1998) have reported that aldehydes from C_{10} to C_{16} are probably from biogenic origin potentially through the oxidation of fatty acids.

Furans are emitted to the atmosphere from the combustion of fossil fuels, refuse and biomass burning. They are also known to be products of the photo-oxidation of hydrocarbons and toluene (Shepson *et al.*, 1984; Dumdei *et al.*, 1988). Results obtained during this investigation with pure algal cultures and seawater have shown the presence of 2,4-dimethylfuran suggesting it can be produced biologically. This compound has been reported as an aroma in food (Ramarathnam *et al.*, 1993; Diosady and Ramarathnam, 1994) and also as a by-product of wood combustion (McDonald *et al.*, 2000). The atmospheric lifetime for 2,4-dimethylfuran is 1.2 min (Kind *et al.*, 1996). The positional isomer 2,5-dimethylfuran has been reported in the literature as a microbial VOC (Claeson *et al.*, 2002).

Figure 1 shows the spectrum of the 2,4-dimethylfuran demonstrating that is not the congener 2,5-dimethylfuran commonly reported. In this figure is possible see that the fragments 39, 41 and 67 are the main differences between them.

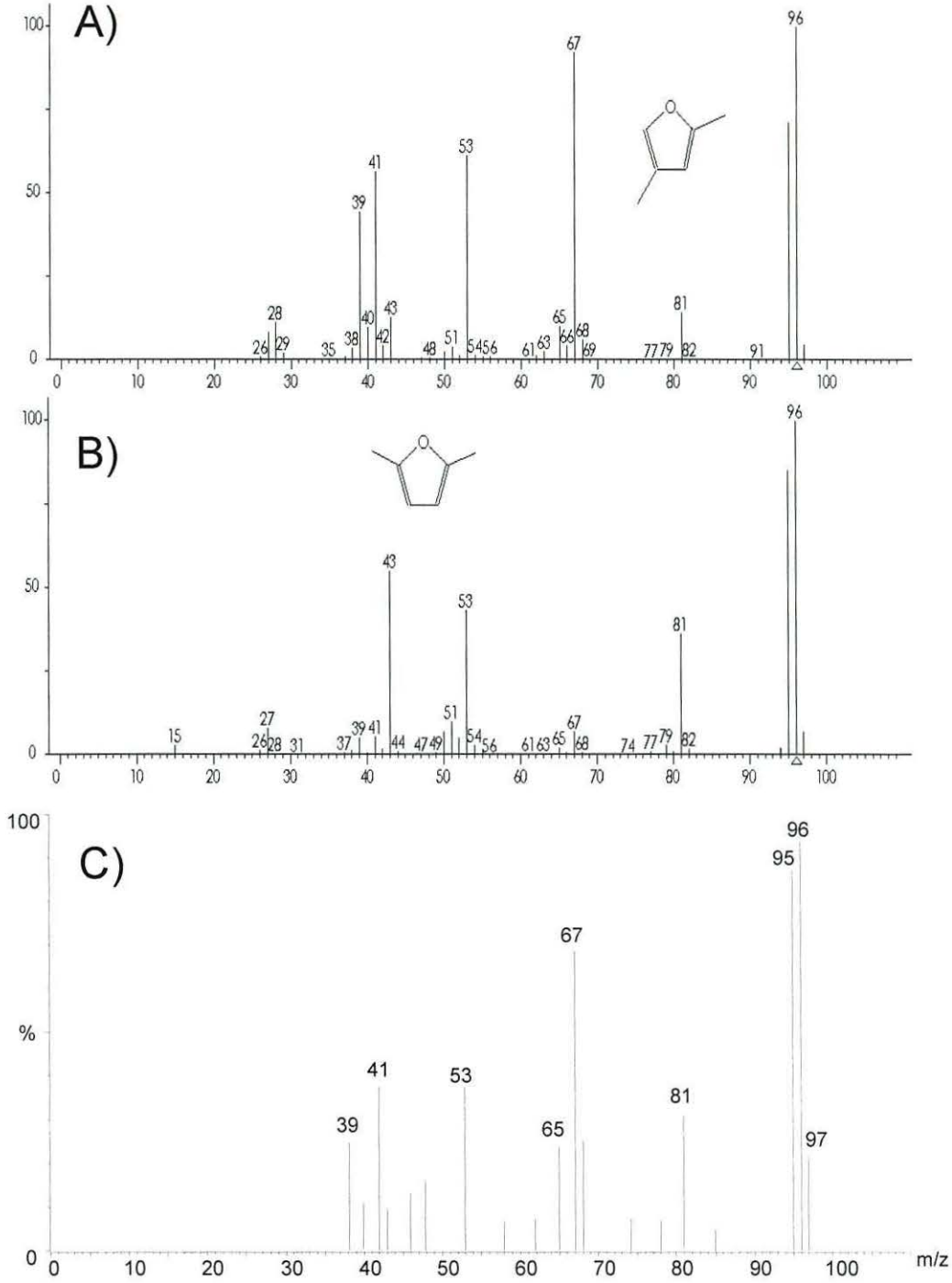


Figure 3.1. Mass spectra for A) 2,4-dimethylfuran, B) 2,5-dimethylfuran and C) seawater sample collected in the Menai Strait (scan mode from 38-270 *m/z*).

Table 3.1. The VOCs quantified in Menai Strait seawater with their respective chromatographic retention time (RT), the fragment utilized for single ion monitoring (*m/z*), standard deviation, mean concentrations and ranges. n=79. (<LoD = Below the limit of detection).

Compounds	RT (min)	*m/z*	Median (pg L^{-1})	Mean (pg L^{-1})	S.D. (pg L^{-1})	Range (pg L^{-1}) Min	Range (pg L^{-1}) Max
Chlorinated							
1,1-dichloroethene	3.83	61	69	75	56	<LoD	323
2-chloropropane	4.11	43	3,641	5,389	5,036	24	26,117
Dichloromethane	6.67	49	4,424	5,640	5,372	532	38,337
2-chlorobutane	11.4	57	1,278	1,945	2,311	34	16,160
Cis-1,2-dichloroethene	12.43	61	138	305	499	<LoD	2,444
Chloroform	13.16	83	14,969	16,925	12,279	550	61,921
1,1,1-trichloroethane	15.24	97	94	123	103	<LoD	765
1-chlorobutane	15.42	56	5,055	8,663	11,181	86	75,592
Carbon tetrachloride	16.50	117	399	523	435	60	2,487
1,2-dichloroethane	17.29	62	189	230	203	<LoD	1,123
Trichloroethene	20.47	95	284	347	264	<LoD	1,702
Cis-1,3-dichloropropene	23.47	75	44	61	47	<LoD	286
Trans-1,3-dichloropropene	28.30	75	47	64	67	<LoD	416
1,1,2-trichloroethane	29.02	97	172	587	2,664	<LoD	23,578
Tetrachloroethene	30.50	166	569	2,177	3,783	20	17,194
Iodinated							
Iodomethane	5.9	142	620	949	1,394	<LoD	11,351
Iodoethane	13.18	156	881	1,482	1,357	54	4,864
2-iodopropane	18.49	43	922	2,524	6,849	53	58,502
1-iodobutane	31.95	184	2,364	2,615	2,096	46	7,901
Diiodomethane	41.78	268	241	727	1,453	<LoD	8,872
Brominated							
1-bromoethane	5.75	108	51	108	57	<LoD	504
1-bromopropane	9.65	43	733	6,613	26,996	78	236,719
Dibromomethane	22.83	174	202	945	2,491	<LoD	19,044
1-bromopentane	32.80	71	4,609	8,459	11,022	<LoD	64,364
2,3-dibromopropene	37.05	39	3,963	10,444	35,414	<LoD	312,131
Bromoform	38.80	173	4,080	54,143	137,170	751	906,965
Mixed halogenated							
Bromodichloromethane	22.67	83	151	829	3,105	<LoD	26,455
Chloroiodomethane	25.43	176	100	161	182	<LoD	1,000
Dibromochloromethane	31.43	127	1,565	3,603	7,163	87	42,913
Sulphur containing compounds							
Dimethyl sulphide	5.34	62	5,197	10,974	14,275	78	70,987
Dimethyl disulphide	26.4	94	2,229	6,300	18,586	<LoD	159,939

Compounds	RT (min)	*m/z*	Median (pg L^{-1})	Mean (pg L^{-1})	S.D. (pg L^{-1})	Range (pg L^{-1}) Min	Range (pg L^{-1}) Max
Mono-aromatics hydrocarbons							
Benzene	17.50	78	11,224	17,331	38,833	890	336,843
Toluene	27.27	91	90,084	141,357	198,890	<LoD	1,108,561
Ethylbenzene	34.82	91	24,091	106,800	498,812	78	4,282,984
m-Xylene	35.20	91	62,830	131,372	231,714	319	1,428,336
p-Xylene	37.20	91	25,680	64,193	159,611	1165	1,268,039
n-propylbenzene	40.79	91	9,260	41,106	143,683	459	1,067,764
1,3,5-trimethylbenzene	41.29	105	22,183	21,921	80,400	<LoD	676,670
1,2,4-trimethylbenzene	41.58	105	6,788	77,811	289,870	<LoD	2,424,439
1-ethyl-2-methylbenzene	42.89	105	4,593	17,760	63,202	<LoD	526,246
1-ethyl-3-methylbenzene	47.51	105	4,287	20,668	94,103	38	796,971
1,2,3-trimethylbenzene	43.64	105	22,570	77,376	303,149	<LoD	2,571,543
sec-butylbenzene	47.71	105	1,655	7,243	30,607	<LoD	261,123
aromatic unknown	48.05	105	704	2,249	5,189	78	35,763
aromatic unknown	49.44	105	1,101	3,264	6,757	35	36,165
Oxygenated and others							
2,4-dimethylfuran	21.28	96	257	860	4,870	36	43,546
Alkyne unknown	34.70	93	2,506	17,716	49,056	22	371,418
Limonene	38.46	93	5,076	12,807	27,077	147	207,299
α-pinene	45.13	93	61,307	84,704	67,423	865	271,879
Decanal	42.30	43	9,894	39,480	178,720	171	1,539,594
Hexanal	30.21	43	5,391	10,351	15,462	<LoD	95,215
NMHC							
Nonane (C_9)	34.40	57	4,817	9,498	11,256	323	56,450
C10 Branched a	35.38	57	389	2,971	8,098	<LoD	45,795
C10 Branched b	35.56	57	370	2,479	6,909	<LoD	44,416
C10 Branched c	36.58	43	961	7,942	18,377	<LoD	100,590
C10 Branched d	37.19	43	7,532	13,840	34,041	<LoD	269,745
C10 Branched e	37.34	43	5,551	13,121	31,788	<LoD	206,953
C10 Branched f	39.34	43	4,993	10,709	16,961	<LoD	98,649
Decane (C_{10})	40.00	57	23,953	39,330	48,742	342	310,480
C11 branched a	41.14	57	3,633	17,004	47,939	<LoD	323,425
C11 branched b	43.97	57	6,428	51,482	2,24,496	257	1,787,916
C11 branched c	44.35	57	3,590	14,674	43,086	418	331,378
C11 branched d	44.81	57	3,606	9,959	16,802	<LoD	100,693
Undecane (C_{11})	47.28	57	27,607	38,376	35,353	<LoD	172,987

3.2.3 Temporal trends of VOCs in Menai Strait water.

Trends varied among the VOCs studied: halogenated compounds such as dichloromethane, chloroform and tetrachloroethene (Fig. 3.2a, b and e) tended to increase in concentration during the algal bloom period in May and June. However, no clear correlations were found with chlorophyll *a* (R= 0.14, -0.13 and 0.37 respectively) this might be due to these compounds are produced by different sources such as marine sediments, macroalgae, *etc*. No tendencies were observed for the other chlorinated compounds shown (Fig. 3.2c, d, f) suggesting that they have not got a clear seasonal correlation with natural occurring sources and are likely to be related to anthropogenic sources. Bromoform and dibromomethane (Fig. 3.2g and h) behaved similarly (R= 0.92) and they may have the same sources probably from macroalgae. 1-bromopentane (Fig. 3.2i) concentrations increased from March onwards. Iodomethane and diiodomethane (Fig. 3.2k and l) had maximal concentrations during the algal bloom and can be probably related to phytoplanktonic sources. Iodoethane (Fig. 3.2j) increased during the spring-summer period as solar irradiation increased (R= 0.54) suggesting a possible photochemical production of this compound as well biological. Mixed halogens (Fig. 3.2m to o) did not have a clear pattern; they had maximal values in a beginning of spring but decreased through to the summer. DMS and DMS_2 (Fig. 3.2p and q) concentrations increased during the spring bloom. Oxygenated compounds (Fig. 3.2r to t) had relatively constant concentration through the year. Limonene (Fig. 3.2u) did not vary significantly and had maximal concentration in April. NMHCs (Fig. 3.2v to x) behaved similarly across the sampling period. Toluene and ethylbenzene (Fig. 3.2y and zz) concentrations increased during the spring-summer period. Benzene (Fig 3.2 z) did not have a clear pattern through the year.

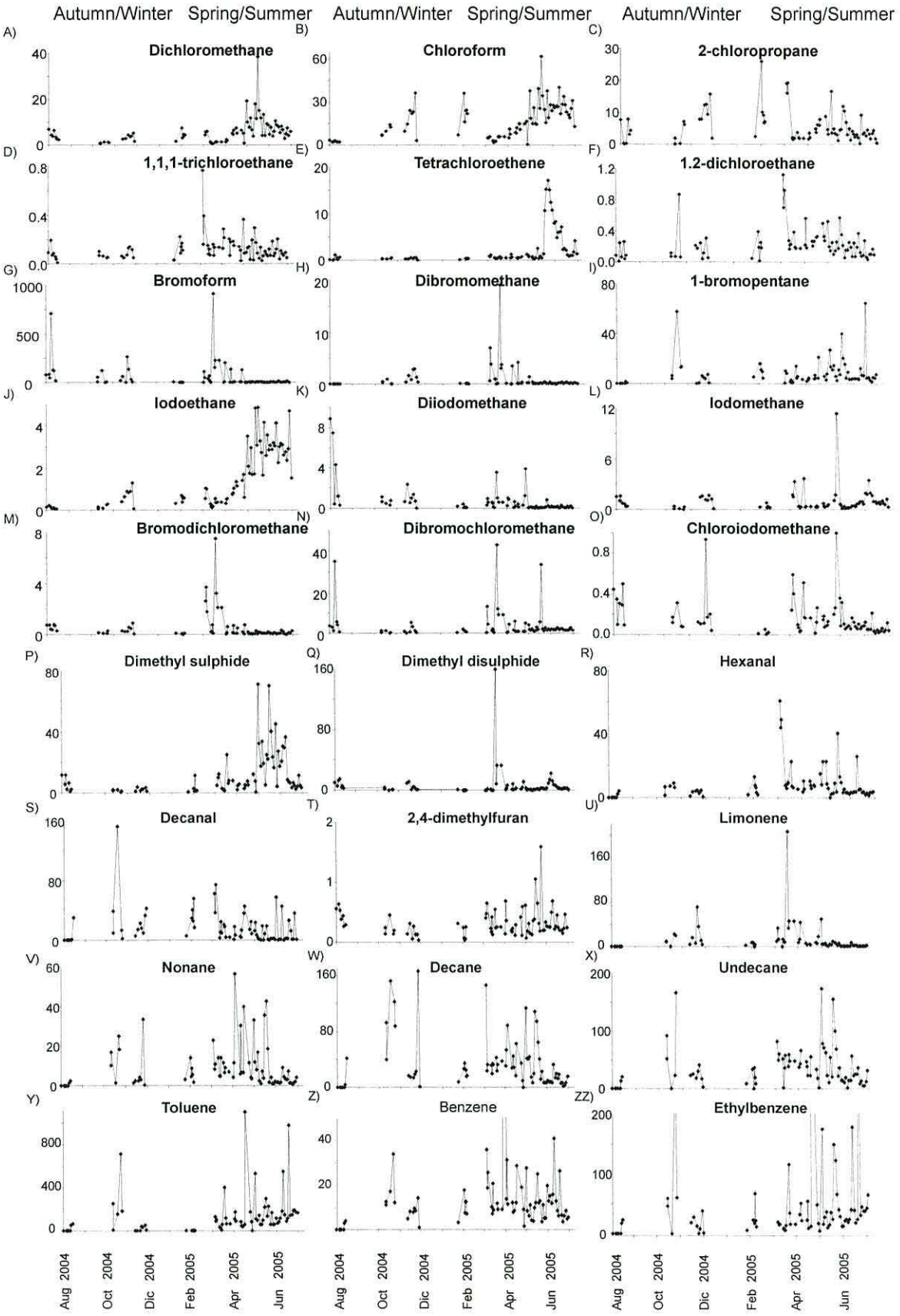


Figure 3.2. Trends through the sampling year for selected VOCs showing the periods of autumn/winter and spring/summer. Concentrations are given in ng L^{-1}.

3.2.4 Statistical analysis.

PCA was used to identify relationships between the individual compounds with factors such as phytoplankton presence (expressed as pigments), meteorological and physico-chemical data. PCA and PLS type 1 analysis were performed with the VOC concentrations, pigments, meteorological and physicochemical values. VOC data were normalised to their proportions and the remaining data were used without further modification.

PCA analysis (Figure 3.3a, b) showed a clear division between the periods autumn/winter and spring/summer. The former was characterized by the major presence of hydrocarbons (NMHC) and BTEXs and the latter by halogenated and sulphur containing compounds. The three different groups of factors that may influence the production and release of VOCs in the strait are discussed as follows:

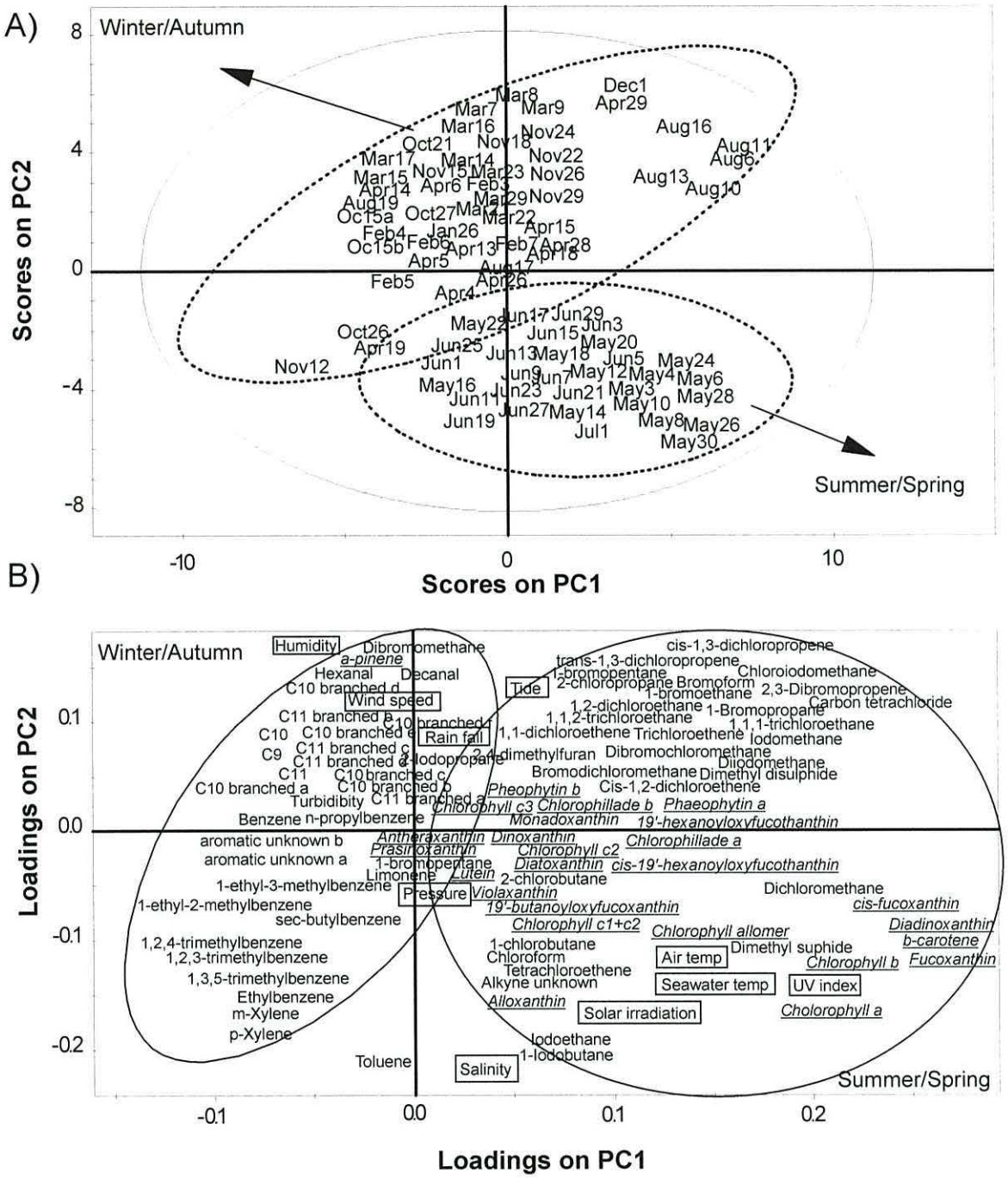


Figure 3.3. PCA analysis for the time series survey. A) Scores plot and B) Loadings plot. Both show that VOCs trends are governed by physico-chemical, meteorological factors (framed) and pigments (underlined and italics) characteristics.

3.2.4.1 Pigments as indicator of phytoplankton

Although it is improbable that chl *a* is directly involved in the marine production of halocarbons, it has been suggested that it could be used as an indicator for the biogenic production of these compounds (Schall *et al.*, 1997). Total pigment concentrations increased during the algal bloom period: the concentration of chl *a* increased during March with two main peaks in May and June. Similar trends were observed for chlorophyll allomer, chlorophyll *b*, *β*-carotene, *cis*-fucoxanthin and fucoxanthin (see Figure 3.4).

Pigments such as phaeophorbide *a*, *b* and phaeophytin *a, b* can be used as indicators of zooplankton grazing (Vernet and Lorenzen, 1987). Phaeophytin *b* was the main grazer indicator found in these samples. It was detected from April to July and the main peaks coincided with those of Chl *a*. This indicates that in maximal periods of phytoplankton growth, it was actively being consumed which might have implications for the VOCs produced during this period. It has been proposed that phytoplankton release VOCs as a defence mechanism and to avoid grazing (Young *et al.*, 1981). Zooplankton was observed in the samples during April and May. Table 3.2 shows the common marine phytopigments and their occurrences in the marine environment.

PCA (Figure 3.3b) shows the VOCs that co-vary with chl *a* and other pigments, (especially during the algal bloom in May and June in the Menai Strait) are iodoethane, 1-iodobutane, 1-chlorobutane, 2-chlorobutane, dichloromethane, chloroform, tetrachloroethene, DMS and toluene. Liss *et al.* (1994) found a correlation between iodinated compounds and chl *a* concentration. Co-variance between halocarbons might indicate the same sources or formation mechanisms; good correlation has been found among brominated compounds by Yokouchi *et al.* (1997) and Schall *et al.* (1997) suggesting the same biogenic origin and mechanism of formation. DMS is produced by marine phytoplankton (Shenoy *et al.*, 2006). Toluene may be produced principally in sediments by biological sources such as bacteria and not associated to direct production from phytoplankton (see chapter 5). Tetrachloroethene also has natural sources such as macroalgae (Abrahamsson *et al.*, 1995). However, little is known about the correlation of pigments and halocarbons presence. Abrahamsson *et al.* (2004) found that only the photosynthetic pigment 19'-hexanoyloxyfucoxanthin could explain the distribution and production of halocarbons. Pearson's correlation for chl *a* and the VOCs listed above (except toluene) were R= 0.57, 0.65, 0.75, 0.71, 0.60, 0.43, 0.38 and 0.43 respectively. These results suggest that chl *a* is a moderate predictor of the production of VOCs in

seawater. However, is important to consider that several factors affect the amounts and distribution of these compounds since they are released into the seawater, affecting the direct relationship between production and detection due to processes of degradation and losses to the atmosphere.

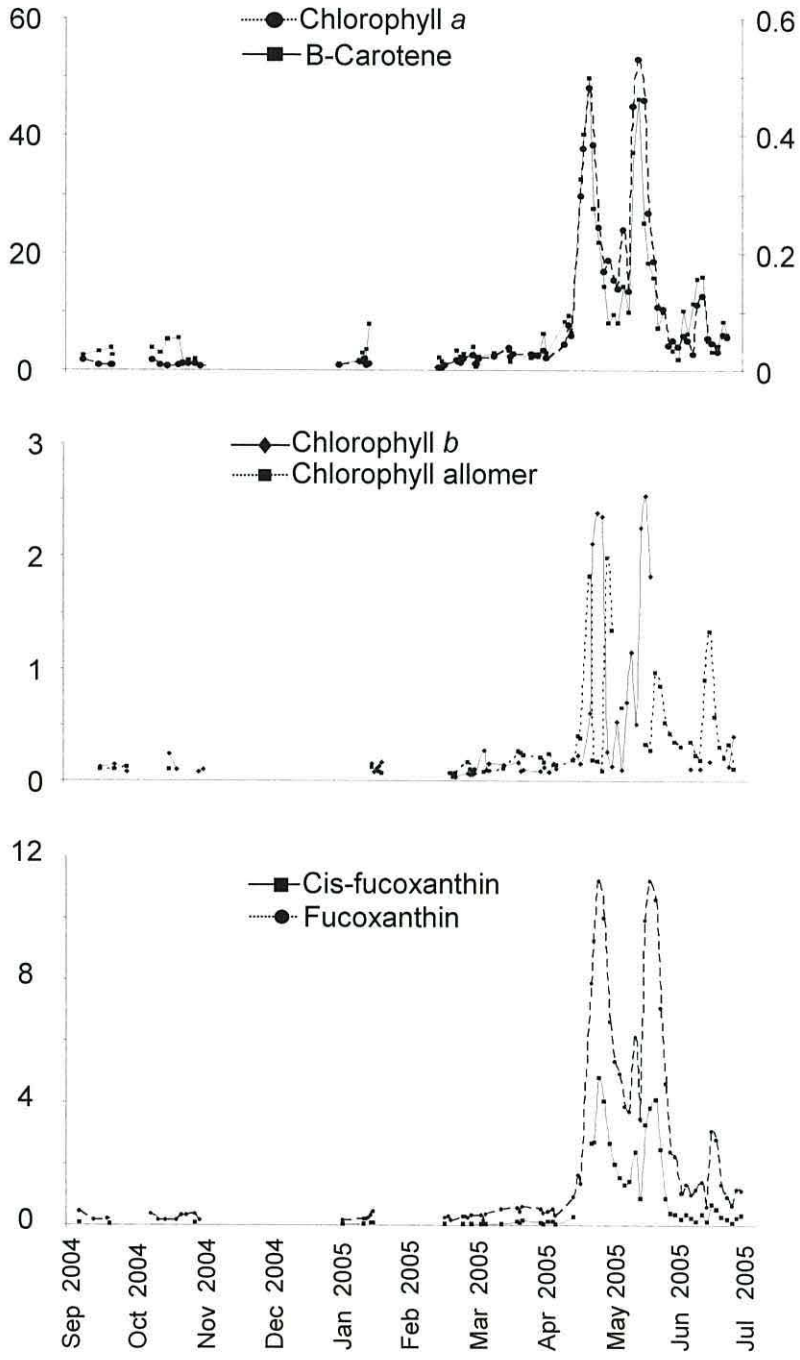


Figure 3.4. Distribution of selected pigments (μg L^{-1}) measured through the sampling period. Chl *a* is plotted against the left axis.

Table 3.2. Marine photopigments and their occurrences in the marine environment.

Pigment	Occurrence
Chlorophillade *a* and *b*	Senescent tissue, zooplankton faecal pellets, damaged centric diatoms
Chlorophyll *c3*	Some prymnesiophytes, some diatoms, chrysophytes
Chlorophyll *c2* and *c1+c2*	Chromophyte algae, brown seaweeds
Peridinin	Photosynthetic dinoflagellates (major pigment)
19'-butanoyloxyfucoxanthin	Major pigment in some prymnesiophytes (eg Phaeocystis), marine chrysophytes (eg Pelagococcus) and 3 dinoflagellates. Trace pigment in other prymnesiophytes (eg Emiliana)
Fucoxanthin	Major pigment in diatoms, prymnesiophytes, brown seaweeds, raphidophytes, some dinoflagellates with endosymbionts
19'-hexanoyloxyfucothanthin	Major or minor pigment in several prymnesiophytes, some dinoflagellates.
cis-fucoxanthin	Fucoxanthin isomer
cis-19'-hexanoyloxyfucothanthin	19'-hexanoyloxyfucothanthin isomer
Prasinoxanthin	Major pigment in some prasinophytes (e.g. some Micromonadophyceae)
Violaxanthin	Major pigment in higher plants, green algae, eustigmatophytes, brown seaweeds.
Dinoxanthin	Major pigment in dinoflagellates, except those containing endosymbionts of other algal classes
Diadinoxanthin	Major pigment in diatoms, prymnesiophytes, some chrysophytes and dinoflagellates.
Antheraxanthin	Green algae, higher plants (minor pigment)
Alloxanthin	Cryptomonads
Monadoxanthin	Major pigment in cryptomonads
Diatoxanthin	Minor or trace pigment in diatoms, prymnesiophytes, some chrysophytes and dinoflagellates.
Lutein	Major pigment in red seaweeds, green algae, higuer plants
Zeaxanthin	Major or minor in prochlorophytes, cyanobacteria (coccoid), green algae, most chrysophytes, raphidophytes
Canthaxanthin	Minor or trace pigment in some green and blue green algae, diatoms, prymnesiophytes, eustigmatophytes
Chlorophyll b	Higher plants, green algaes, symbiotic prochlorophytes
Chlorophyll allomer	Prochlorococcus marinus (class Prochlorophyceae)
Cholorophyll *a*	All photosynthetic algae and higher plants
Lycopene	Minor pigment in prasinophytes, trace pigment in cyanophytes
Pheophytin *b*	Terrestrial plant detritus
Pheophytin a	Plant and algal detritus
β-carotene	Major pigment in higher plants, green algae; minor or trace pigment in chromophyte algae

3.2.4.2 Physico-chemical and meteorological data

Physicochemical as well the meteorological data acquisition were described in Chapter 2. The results for the whole period of sampling are presented as a daily average for each sampling day. Variation of physico-chemical and meteorological data through the sampling period is shown in Figure 3.5. PLS type 1 modelling was used to identify which of the physico-chemical and meteorological data had the greatest effect on the VOCs signatures (Figure 3.6). This method was employed when the two matrices contained different variables; in this case, physico-chemical and meteorological data are used to predict the VOCs proportions. Unsurprisingly, the model showed that climatic conditions during the year trigger the production of certain VOCs in the seawater; for example, solar irradiation was directly related to photochemical and biological production of VOCs in seawater (Wennberg, 1999). Some iodinated compounds, DMS and mixed halogen compounds were produced in greater proportions during spring/summer conditions with higher solar irradiation, air temperature, seawater temperature and salinity. Conversely, some chlorinated compounds and NMHC were induced by autumn/winter conditions such as higher wind speed, humidity and rain fall. Although, as data was normalised, it may just mean that the other compounds were present in minor proportions or absent rather than there was more production of them. This period is characterized by lower phytoplankton numbers leading to two main sources of natural VOCs, macroalgae and sediments. Estimations of the influences of both factors, meteorological and physico-chemical on the VOCs production using PLS analysis, indicated that the seawater physico-chemical properties (*e.g.* water temperature) have more influence than the meteorological factors (*e.g.* wind speed). Figure 3.7 shows the importance of the main variables studied, values obtained from the PLS analysis are significant if the value is greater than one.

The physico-chemical and meteorological parameters can influence the VOC concentrations in a variety of ways. For instance, the fluxes toward the atmosphere or the distribution in the surface layer may be governed by wind speed (Liss *et al.*, 1994). Tidal height has an important effect in coastal waters; when the tide is high, macroalgae and sediments are covered and VOCs from these sources are directly released into the water. At low tide, when the algae and sediments are exposed and the fluxes of VOCs are direct to the atmosphere. In Figure 3.6, is possible to see that high tide correlates with some brominated compounds (*e.g.* bromoform) which are known to be produced by marine

macroalgae (Itoh *et al.*, 1997). Table 3.3 summarises the expected effect on the VOCs production and release of physico-chemical and meteorological factors in seawater.

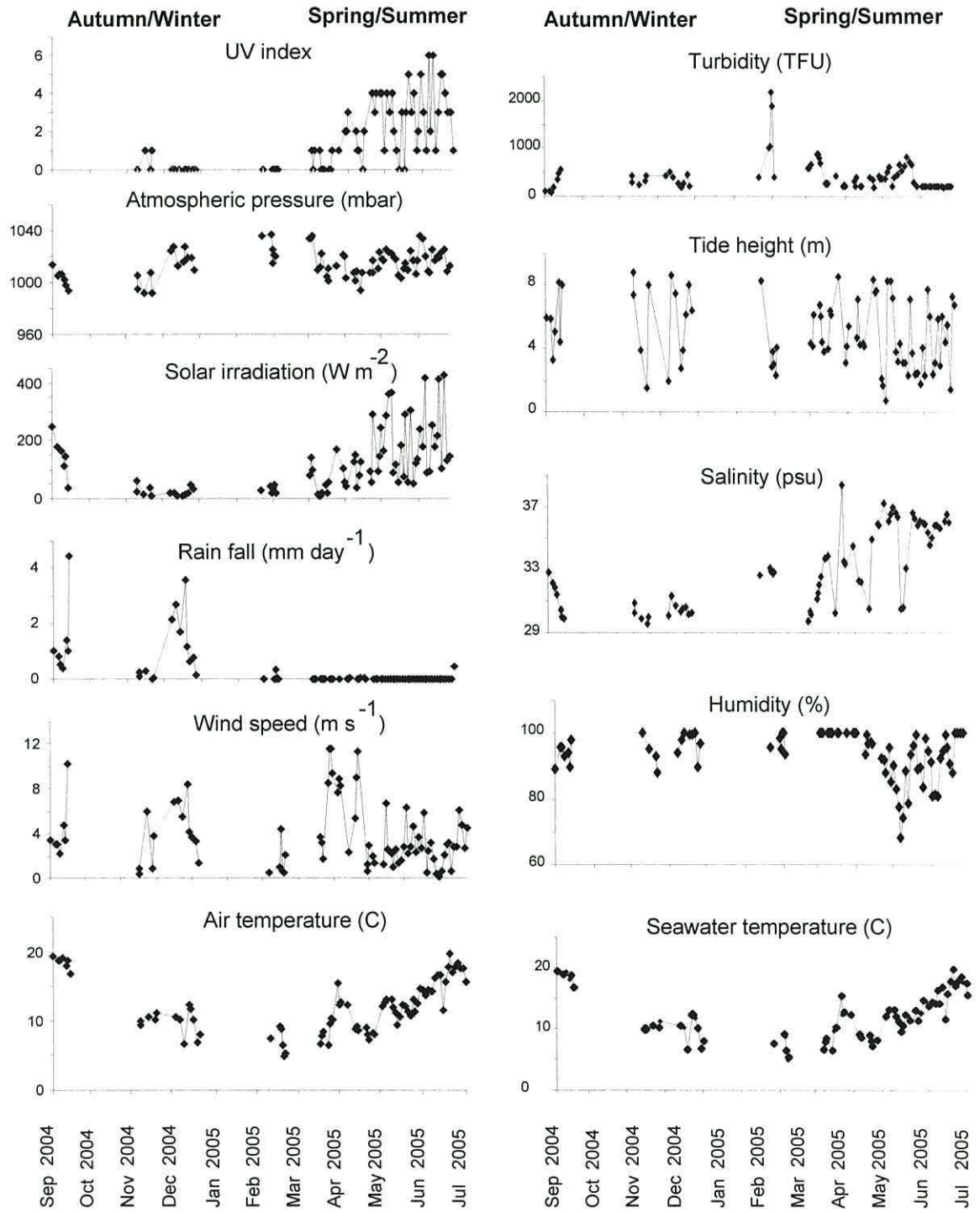


Figure 3.5. Physico-chemical and meteorological parameters for the time series analyses showing the variations through the winter/autumn and summer/spring periods.

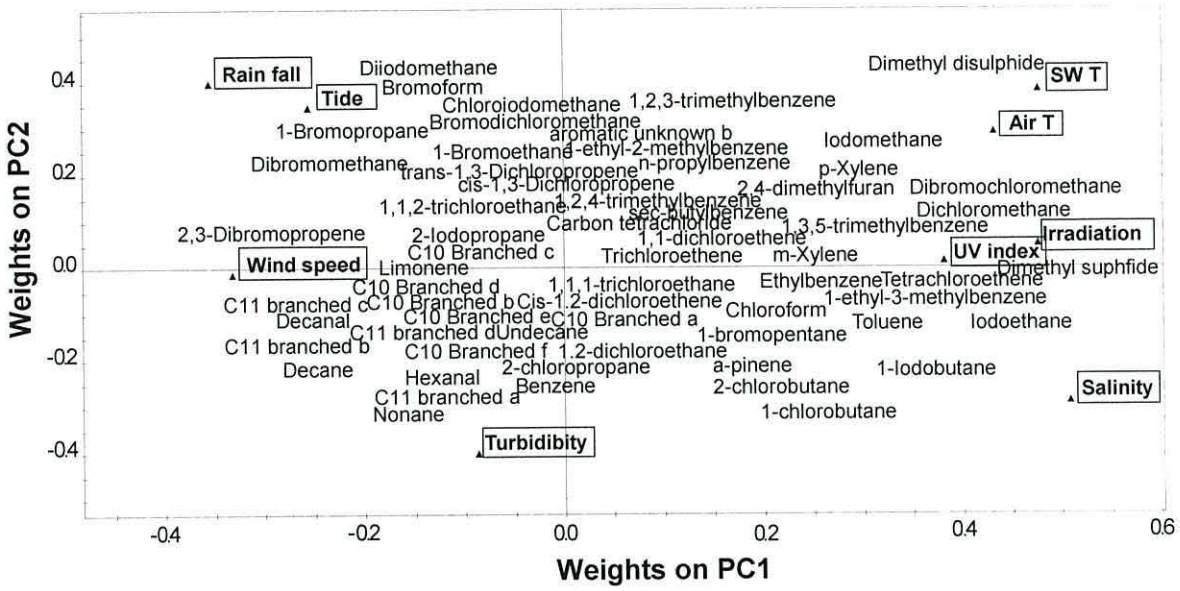


Figure 3.6. PLS type 1 analysis using physico-chemical and meteorological factors (framed) to predict the types of VOCs obtained under different conditions.

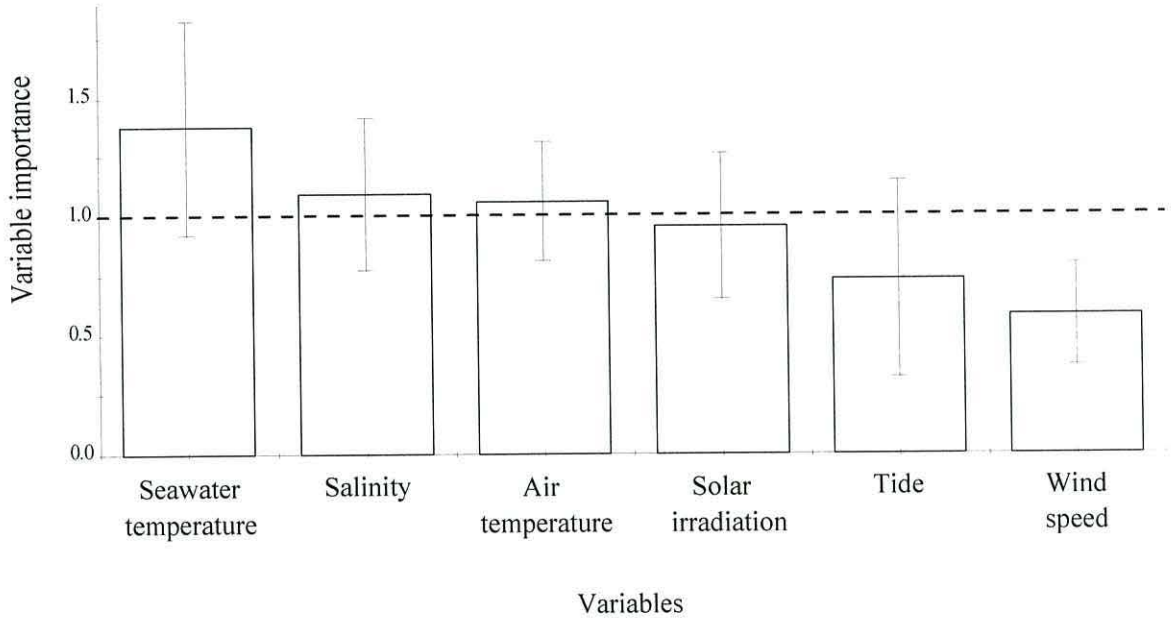


Figure 3.7. Variable importance factor derived from a PLS 1 model showing the importance of physico-chemical and meteorological factors on the production of VOCs.

Table 3.3. Studied external parameters and the expected effects on the production and release of VOCs in seawater.

Parameter	Expected effects on the VOCs production and release
Wind speed	High wind speed affects the transfer velocity of VOCs from the surface seawater to the atmosphere.
Rain fall	Affects the salinity and may change the pH of the water, and also may contribute with wet deposition and atmospheric transport of VOCs.
Irradiation	Affects the presence of photosynthetic organisms which are involved in the VOCs production and also influence the photochemical reaction of generation and depletion of VOCs and their lifetimes.
Seawater temperature	Affects the equilibriums (Henry's constant), mobility, diffusivity, solubility, production, degradation and also the seawater/atmosphere transferences.
Air temperature	Affects the seawater temperature as well some atmospheric reactions.
UV index	It may affect the production of some VOCs by bioorganisms as well some photochemical reactions.
Salinity	It affects the solubility and diffusivity of the gases dissolved in seawater (Henry's constant) but the effects are considered insignificant compared with seawater temperature.
Turbidity	It may affect the solubility and also the adsorption/desorption processes by particles in seawater.
Pressure	It affects the equilibriums and distribution of VOCs in seawater/atmosphere interface.
Tide	It may not have a direct affect in the production and release of VOCs, but might affect the macroalgae as stress due to the exposition and dryness.

3.2.4.3 PLS type 2 modelling

A PLS type 2 analysis was conducted to determine how much of the variance (Q^2) of VOCs in the seawater can be predicted by models derived from individual VOC sources. Data were normalized to proportions and due to were not normally distributed a logarithmic transformation was done. The signatures studied were as follows:

Macroalgae signatures. Several experiments were performed to identify the VOCs produced by the most abundant macroalgae in the Strait (see Chapter 4). A combined signature from brown, red and green algae was used and the results are shown in Figure 3.8. The predictable variance (Q^2) varies through the year with a minimum value of 8% in February and a maximum value of 36% in June. Individual contributions (Figure 3.9) showed that brown algae were a better predictor than other macroalgae, principally due to their abundance in the Strait.

Sediment signatures. The results of VOCs present in gases drawn from intertidal sediments are presented in Chapter 5. The proportion of the variance in the seawater VOC data that can be predicted from this source tended to increase through the year with maximal values in May and June (21 and 22% respectively); its importance declines during July (Figure 3.8). The VOCs may be evolved from the bacterial metabolism of depositing organic matter formed during the algal bloom or from benthic algal blooms.

Microalgae signatures. Cultures of the major spring bloom species (*Skeletonema sp*) were used to obtain signatures and predict the variability of VOCs in the seawater. Unfortunately the spring blooming alga, *Phaeocystis sp*, was not available for culture during this study.

The culture of *Skeletonema sp* used was taken from the algal culture room in the School of Ocean Sciences. From previous experiment was demonstrated that the culture of this microalgae under laboratory conditions reaches its maximal population within 30 days. Six samples were taken representing the different growing phases of the culture. The compounds detected were not quantified, and the areas were used as proportions in order to get the necessary signatures from this type of algae. The analysis of the VOCs was the same one described on Chapter 2. Compounds which presented the most significant signatures at different growing phases are shown in Figure 3.10.

PLS indicated that *Skeletonema sp* predicted the greatest amount of variance in April (45%) coinciding with its maximum abundance during this month. Outside of this bloom time, a considerably smaller amount of variance (~10%) could be predicted from this source (Figure 3.8) due to the presence of this macroalgae out of the algal bloom is low. *Phaeocystis* is one of the main microalgae present during the spring bloom and is expected that it should give an important contribution and for instance a good explanation of the variance during May when its population reaches maximum values.

The total explained variance that could be predicted from the individual signatures was greater during the spring/summer period with values ranging from 55 up to 78%. The autumn/winter was poorly explained, with values not greater than 46%. However, it is important to consider that there are other sources that need to be considered such as other marine organisms (*e.g.* zooplankton) and anthropogenic sources. In addition, even isolating the source and obtaining the signatures, the experiments are performed almost at constant or ideal conditions and in the field the same sources (*e.g.* macroalgae) are under a very changeable environment with variable meteorological and physico-chemical conditions which may have different and variable implications on the production of VOCs.

It is important to consider that not all the compounds detected in seawater were present in the individual sources, and for instance the explanation of the variance using PLS type 2 analysis was done for the compounds that were in common for the individual sources and those detected in seawater. Nevertheless, the signatures obtained explained well the variance of the VOCs concentration through out the year.

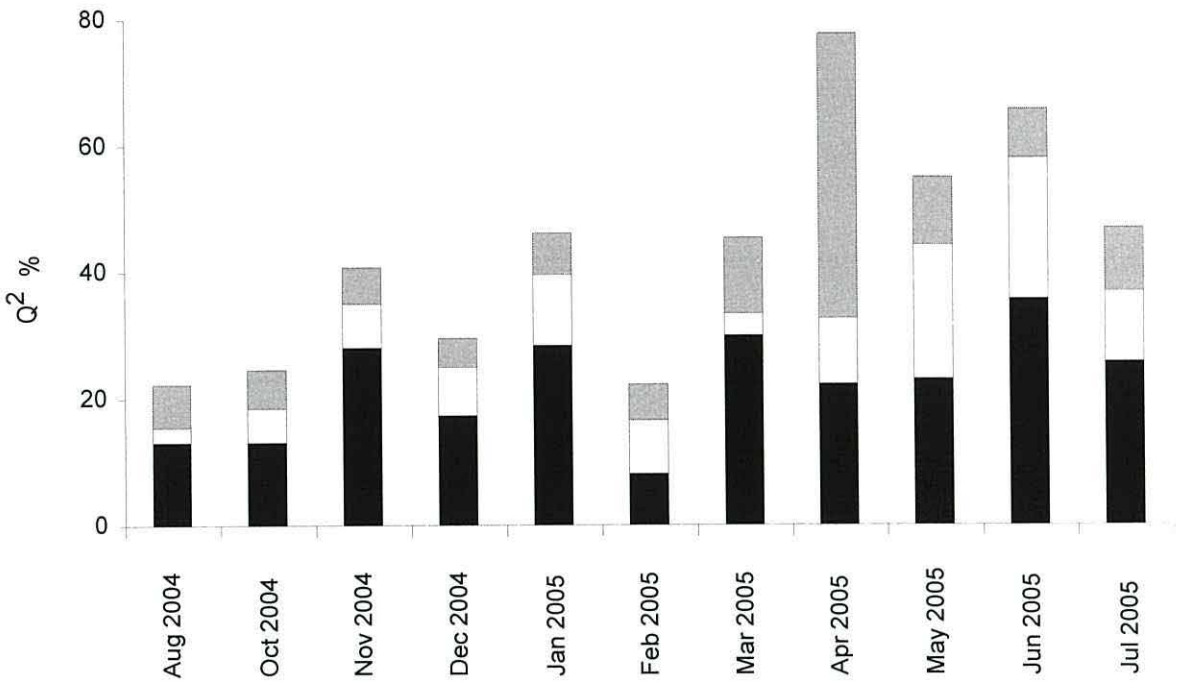


Figure 3.8. Percentage of the variance through the sampling period that can be predicted (Q^2) using signatures from sediments, macroalgae and microalgae (*Skeletonema*) using PLS type 2 analysis. The black bars represent macroalgae, white bars sediments, grey bars microalgae (*Skeletonema*). No samples were taken during September.

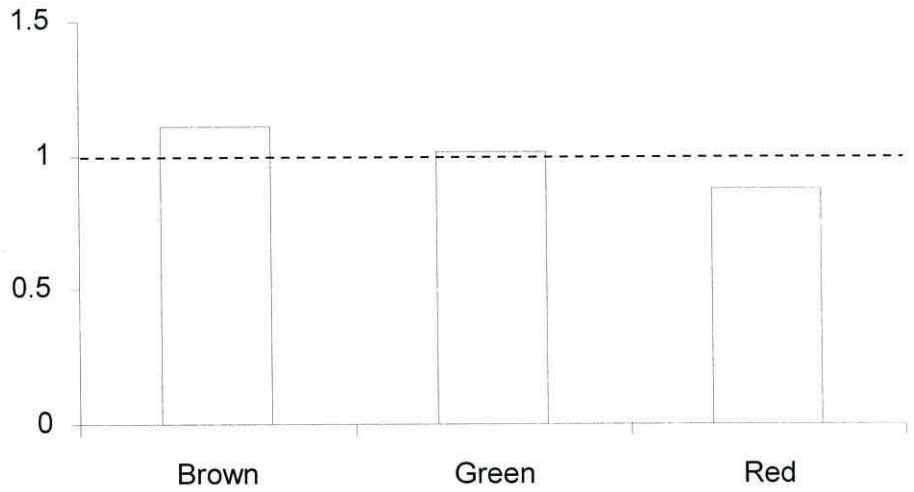
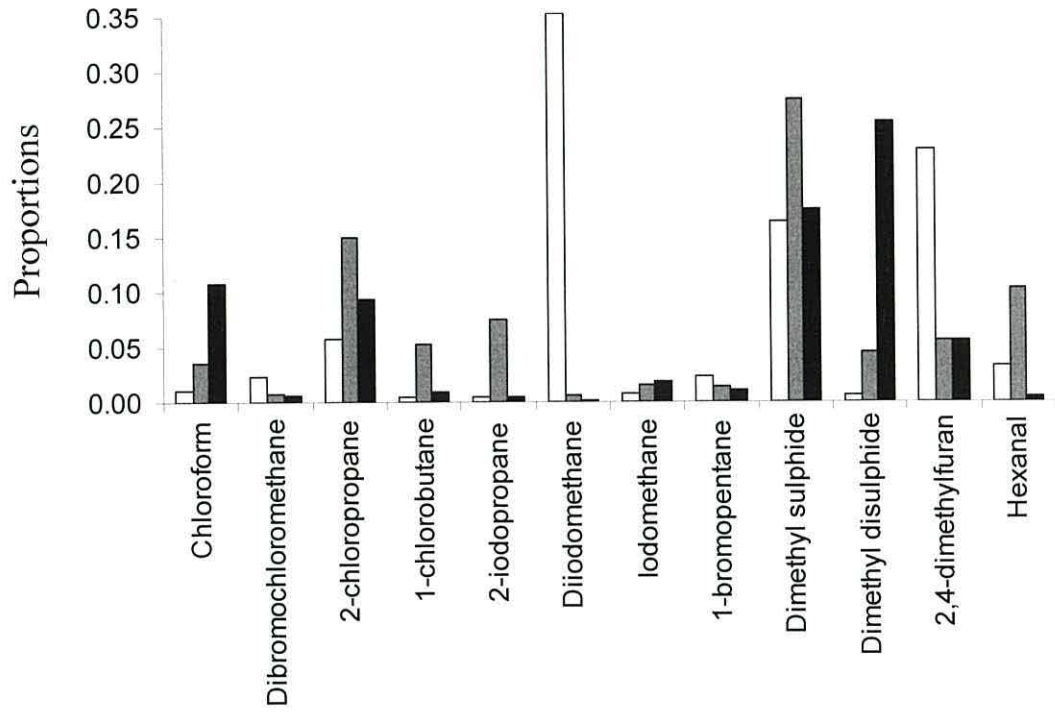


Figure 3.9. Variable importance derived from the PLS 2 model showing the values obtained for brown, green and red macroalgae.



3.10. Main signatures obtained from Skeletonema costatum at different growing phases expressed as proportions. Lag phase (white bars), log phase (grey bars) and stationary phase (black bars). The samples considered where taken at the 3, 15 and 28 days after started the culture.

3.2.5 Diurnal sampling

A day and night survey was conducted to determine the micro-temporal variability of the concentrations of VOCs in surface seawater. Two experiments were conducted: the first consisted of taking thirteen samples every 2 hours for 24 hours. The second consisted of taking samples at midday and midnight for four consecutive days.

The first survey shows (Figure 3.11a and b) that tidal height correlated with the fluctuations in concentration of dichloromethane, bromoform, iodoethane and DMS. This correlation was observed with most of the VOCs studied. An explanation for this is that waters in the Strait arising from the Irish Sea have different properties. Waters on the flood tide (from Caernarfon) are low in nutrients and organic matter whereas waters on the ebb tide (from Beaumaris Bay) are more productive (Saurel, C. *et al*, in preparation).

Furthermore, macroalgae and sediments at high tide are covered with seawater and sampling at low or high tides has implications in the type and amount of VOCs observed in the water column and finally in surface waters. PCA (Figure 3.12) indicates that iodocarbons are present in major proportion at the time when irradiation is maximal suggesting potential photochemical production. The opposite was observed for brominated compounds which were observed in higher proportion at high tide and during the night. This indicates that the VOCs in seawater are highly influenced by factors that vary daily.

The second survey was performed to exclude the tidal effect between samples in the same day. The sum of the VOCs by group showed that halogenated and NHMC are inversely correlated with seawater temperature (R = -0.81 and -0.89 respectively). An increment in the water temperature during the sampling was observed, which may have led to a reduction in the solubility of the VOCs and a reduction in the concentrations observed in the water column. Figure 3.13 shows the concentration and the distribution of the different VOC groups: physico-chemical and meteorological parameters are presented in Table 3.4. Higher concentrations of total VOCs were observed during the day rather than night, especially for iodinated compounds. Sulphur containing and oxygenated compounds did not have a clear pattern during the sampling.

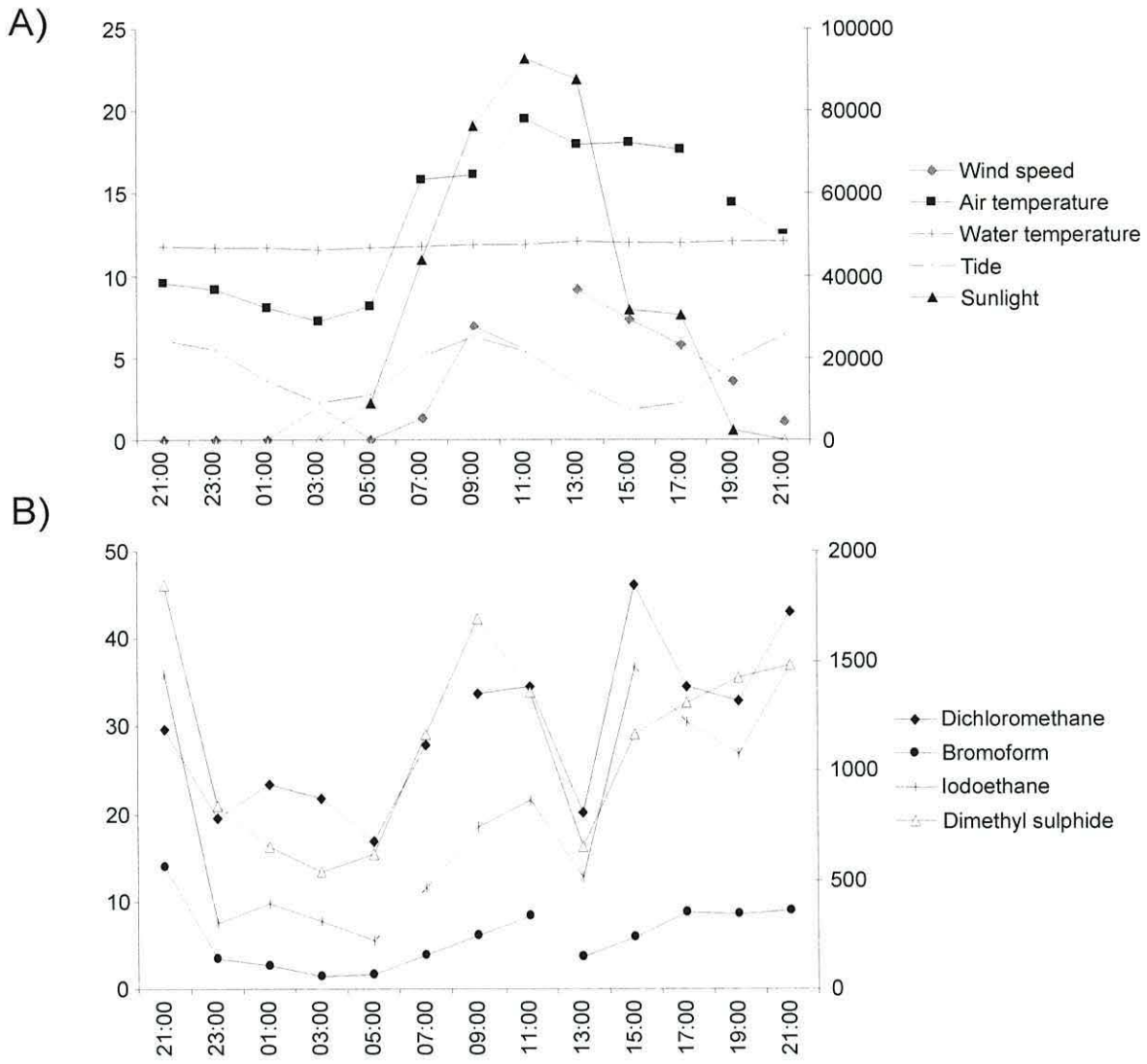


Figure 3.11. A) Selected meteorological and physico-chemical data for the day/night sampling. Wind speed (m s^{-1}), air and water temperature (°C), sunlight (Lux, plotted on the right axis). B) Selected VOC seawater concentrations in pg L^{-1} (DMS is plotted on the right axis).

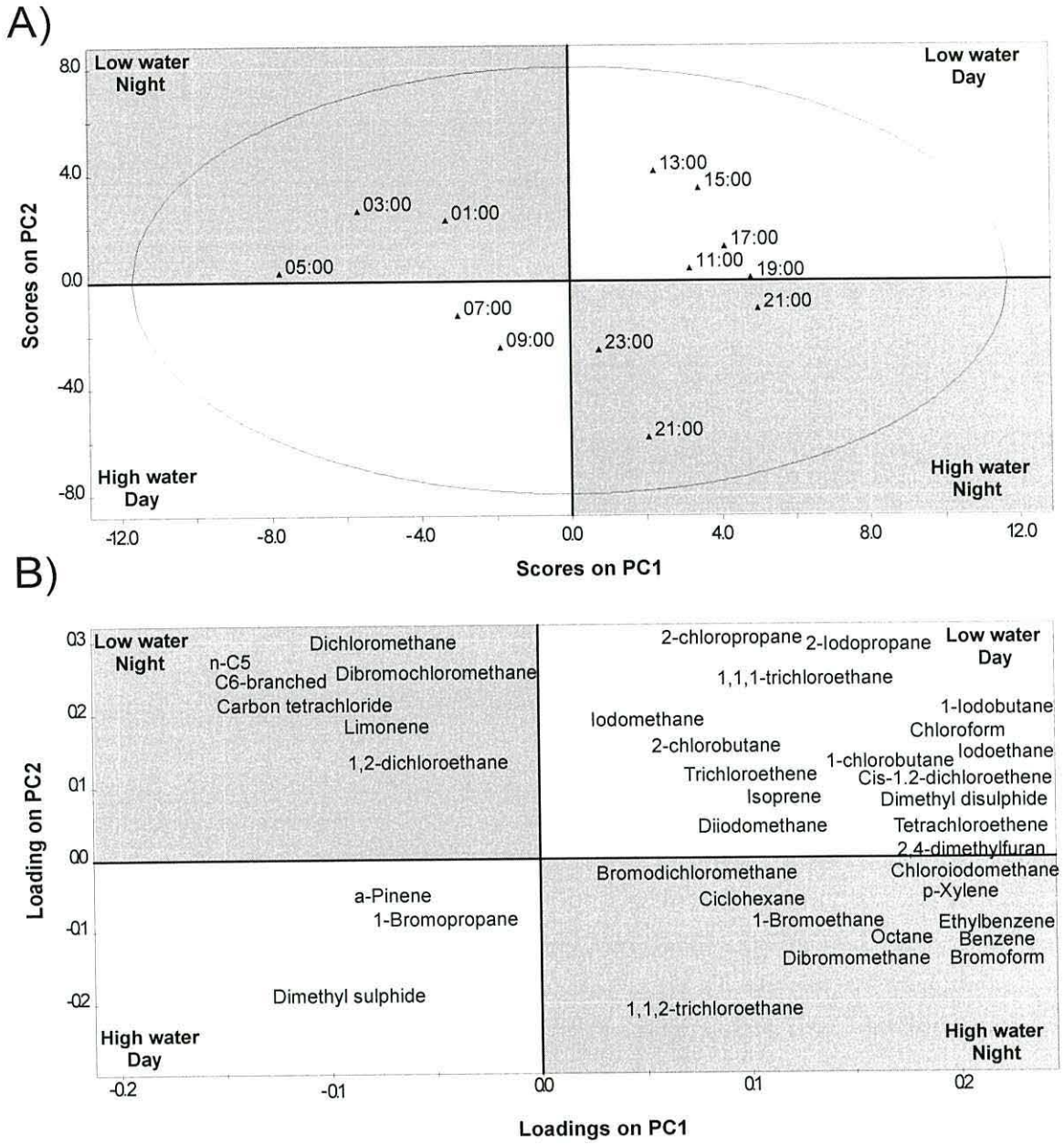


Figure 3.12. PCA for the 24 hours survey. A) Scores plot. B) Loadings plot. Both indicate that the VOCs are distributed according to the tide and the day / night pattern.

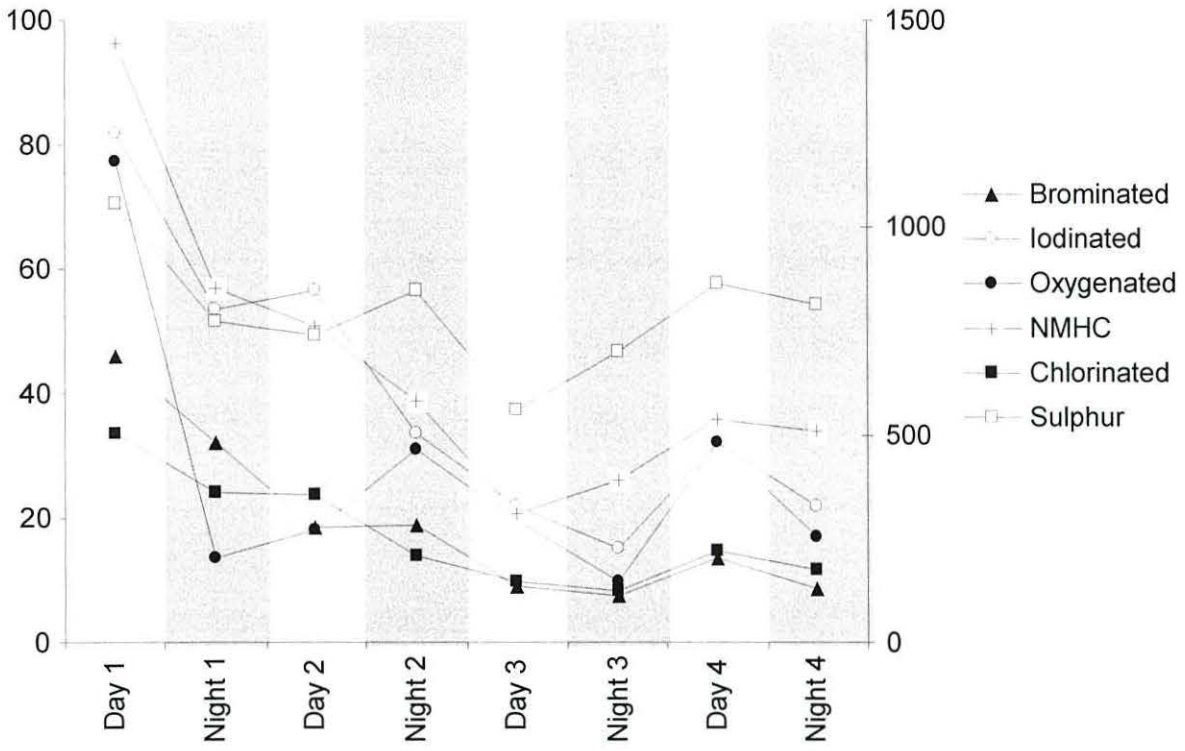


Figure 3.13. VOCs totals (ng L^{-1}) quantified during the day and night survey over four days; the coincident physicochemical and meteorological conditions can be seen in Table 3.4. Sulphur, NMHC and chlorinated compounds are plotted on the right axis.

3.2.6 Fluxes to the atmosphere.

Seawater samples and air samples were taken at midday and midnight for four consecutive days and the VOCs content in both matrixes were quantified. The parameters that are known to affect the water/air distribution such as wind speed were recorded (see Table 3.4). The air samples were taken with a funnel device described in Chapter 2. The sampling device was placed 10 cm above the sea level for one hour to absorb VOCs released from water.

Results for selected VOCs are shown in Table 3.4. Patterns are not clear, however, wind speed seems to play an important role on the diffusion of VOCs to the atmosphere. Day 3 was characterized by having practically the same wind speed during the day and night. As a result of this, similar fluxes for all selected VOCs were measured. Lowest values of fluxes were observed during night 2 and 4 when wind speed was nil. Bromoform, dichloromethane and chloroform correlated to the state of the tide.

Table 3.4. Fluxes (water/air) for selected VOCs in the Menai Strait in ng m^{-2} day^{-1} and physico-chemical and meteorological data for the sampling period.

Compounds	Fluxes [ξ]							
	Day1	Night1	Day2	Night2	Day3	Night3	Day4	Night4
Dichloromethane [a]	269.5	-166.7	244.6	-0.2	-5.4	-15.0	-41.3	-0.3
Chloroform [b]	1332.7	-715.5	1149.3	-2.4	-133.1	-93.9	-263.2	-1.4
1,1,1-trichloroethane [c]	-198.9	163.8	-256.8	0.9	100.7	105.4	110.1	0.9
Carbon tetrachloride [d]	-2464.6	2059.9	-3204.8	11.2	1251.7	1309.7	1365.7	11.2
1,2-dichloroethane [e]	-13.3	16.4	-27.6	0.1	10.8	12.0	10.6	0.1
Bromodichloromethane [f]	-3.9	3.8	-3.5	0.0	3.0	2.9	2.5	0.0
Tetrachloroethene [g]	-266.2	235.1	-363.8	1.3	142.1	150.8	154.6	1.3
Bromoform [h]	42.7	-6.2	12.7	-0.1	-6.2	-1.1	-7.0	0.0
Iodomethane [i]	-447.7	375.4	-585.6	2.0	228.2	239.1	249.1	2.0
Dibromomethane [j]	2.8	2.5	-3.5	0.0	1.9	2.3	1.1	0.0
Dimethyl sulphide [k]	-350.3	295.2	-458.2	1.6	179.8	187.8	194.8	1.6
Physico-chemical and meteorological data								
Wind speed (m s^{-1})	21.4	10.7	15.2	0.0	7.7	7.3	9.2	0.0
Air temperature (°C)	13.8	9.9	15.0	9.0	24.8	11.9	14.9	7.6
Sunlight (Lux)	121,000	0	110,000	0	111,000	0	96,900	0
Tide (m)	4.5	4.3	3.6	3.6	3.0	3.3	3.0	3.3
Water temperature (°C)	10.1	10.2	10.3	10.5	11.0	11.0	11.3	11.5

[ξ] Fluxes were calculated with the relationship proposed by Liss *et al.* (1994) ($F=K_{(T)w}(\Delta C)$). Henry's constant measured at 10°C in seawater were obtained from a, d, g Gossett (1987); b, f, h, i, j Moore *et al.* (1995); c, e Dewulf *et al.* (1995) and k Wong and Wang (1997). Transfer velocity was obtained using the relationship proposed by Liss and Merlivat (1986).

The results showed a wide variety of VOCs in surface waters in the Menai Strait. The VOC origins may be summarised by Table 3.5 which gives some examples of the most representative compounds from each and their sources. Some VOCs have multiple sources while others may be characteristic of one source or another. The use of the multivariate statistics uses the whole suite to determine source allocation in this system.

One of the main problems with the data interpretation of VOCs in surface water is the very changeable environment affecting their production, release and distribution. Surface waters are vulnerable to changes in VOCs concentration due to this layer is in equilibrium with the atmospheric transport and for instance factor such a wind speed can remove the VOCs produced from the surface layer leading to false interpretations. As well during some periods compounds were detected very close to the limit of detections and also some of them have very short lifetimes limiting even more the detection of them. Is highly recommended and important to consider not only VOCs concentrations when a survey to detect the presence of them in seawaters is done, but also some other factors that may affect the removal or distribution of them to avoid making wrong conclusions.

Considering these factors data interpretation vary according to the extension of the period due to there are factors affecting in long or short term. When data is analyzed in a year period was possible to see that seasons with their proper characteristics lead the production of VOCs from different sources. On the other side, short period of time revealed that factors such a tide, seawater temperature and wind speed play an important role as well day/night cycle. However, no all the compounds are affected in the same way. Also is important to considerer that some gases tend to diffuse to the atmosphere quicker than others, and this affects the measurement of them in seawater as well some others tend to be highly accumulated in surface waters since there are produced such as bromoform. Despite of that consideration, models explained well the occurrence and sources of VOCs in the Menai Strait waters.

Table 3.5. Proposed source allocation for VOCs measured in Menai Strait seawater.

Sources	Type of compounds	Examples
Sediments	BTEXs	Toluene, benzaldehyde
	NMHC	Linear C_9-C_{11}
	Sulphur containing	DMS, DMS_2 and others
	Chlorinated	Dichloromethane, chloroform
	Aldehydes	Propanal, hexanal, decanal
Macroalgae	Brominated	Bromoform, dibromomethane
	Chlorinated	Tetrachloroethene, chloroform, dichloromethane
	Iodinated	Diiodomethane, iodoethane
	Mixed halogen	Bromodichloromethane
	Sulphur containing	DMS, DMS_2
Phytoplankton	Iodinated	Iodomethane, 1-iodobutane, diiodomethane
	Halogenated	1,1,2-trichloroethene, 2-chloropropane
	Mixed halogen	Chloroiodomethane, dibromochloromethane
	Brominated	1-bromopentane, 1-bromopropane
	NHMC	C_5-C_8
	Sulphur containing	DMS, DMS_2
	Aldehydes	Hexanal
	Others	2,4-dimethylfurane
Anthropogenic	Chlorinated	1,2-dichloroethane, 1,1,1-trichloroethane, trichloroethene, tetrachloroethene and carbon tetrachloride
	BTEXs	Xylenes, ethyl-benzene and others monoaromatics
	NMHC	Linear C_9-C_{11}

3.3 Conclusions

- Solid phase microextraction (SPME) has been shown to be a good tool to quantify a wide range of VOCs in seawater at trace levels using 4.5 L of seawater.

- In this study, the Menai Strait was a source of natural VOCs. VOCs that have not previously been reported from biogenic sources were also found in the Strait seawater such as 2,4-dimethylfuran and 1-bromopropane.

- Multivariate statistical analyses using PCA and PLS modelling were able to demonstrate the seasonal changes in the VOC signature (more BTEX and alkanes in the winter and halocarbons in the summer).

- PCA demonstrated that physico-chemical and meteorological factors such as wind speed, water temperature can influence the concentrations of VOCs in surface waters as well their productions. Also as the complex net of these factors, their interactions and the differential effects on VOC production lead to large temporal variability in seawater.

- Factors such as tidal cycle and wind speed also influence the short scale variation in concentrations of VOCs in the Strait.

- The PLS signature analysis highlighted the importance of the microalgae signature in spring while macroalgae and sediments dominated at other times.

3.4 References

Abrahamsson, K., Ekdahl, A., Collen, J. and Pedersen, M. (1995). Marine algae - A source of trichloroethylene and perchloroethylene. *Limnology and Oceanography* **40**(7): 1321-1326.

Abrahamsson, K., Loren, A., Wulff, A. and Wangberg, S. (2004). Air-sea exchange of halocarbons: the influence of diurnal and regional variations and distribution of pigments. *Deep-Sea Research II* (51): 2789-2805.

Baker, J. M., Reeves, C. E., Nightingale, P. D., Penkett, S. A., Gibb, S. W. and Hatton, A. D. (1999). Biological production of methyl bromide in the coastal waters of the North Sea and open ocean of the northeast Atlantic. *Marine Chemistry* **64**(4): 267-285.

Ballschmiter, K. (2003). Pattern and sources of naturally produced organohalogens in the marine environment: biogenic formation of organohalogens. *Chemosphere* **52**(2): 313-324.

Bianchi, A. P. and Varney, M. S. (1998). Volatile organic compounds in the surface waters of a British estuary. Part 1. Occurrence, distribution and variation. *Water Research* **32**(2): 352-370.

Blight, S. P., Bentley, T. L., Lefevre, D., Robinson, C., Rodrigues, R., Rowlands, J. and Williams, P. J. L. (1995). Phasing of autotrophic and heterotrophic plankton metabolism in a temperate coastal ecosystem. *Marine Ecology-Progress Series* **128**(1-3): 61-75.

Brimblecombe, P. and Shooter, D. (1986). Photooxidation of Dimethylsulfide in Aqueous-Solution. *Marine Chemistry* **19**(4): 343-353.

Broadgate, W. J., Malin, G., Kupper, F. C., Thompson, A. and Liss, P. S. (2004). Isoprene and other non-methane hydrocarbons from seaweeds: a source of reactive hydrocarbons to the atmosphere. *Marine Chemistry* **88**(1-2): 61-73.

Buckley, F. S. E. and Mudge, S. M. (2004). Dimethylsulphide and ocean-atmosphere interactions. *Chemistry & Ecology* **20**(2): 73-95.

Burkholder, J. B., Gilles, M. K., Gierczak, T. and Ravishankara, A. R. (2002). The atmospheric degradation of 1-bromopropane ($CH_3CH_2CH_2Br$): The photochemistry of bromoacetone. *Geophysical Research Letters* **29**(17): art. no.-1822.

Carpenter, L. J., Malin, G., Liss, P. S. and Kupper, F. C. (2000). Novel biogenic iodine-containing trihalomethanes and other short-lived halocarbons in the coastal East Atlantic. *Global Biogeochemical Cycles* **14**(4): 1191-1204.

Christof, O., Seifert, R. and Michaelis, W. (2002). Volatile halogenated organic compounds in European estuaries. *Biogeochemistry* **59**(1-2): 143-160.

Claeson, A. S., Levin, J. O., Blomquist, G. and Sunesson, A. L. (2002). Volatile metabolites from microorganisms grown on humid building materials and synthetic media. *Journal of Environmental Monitoring* **4**(5): 667-672.

Connan, O., LeCorre, P. and Marty, Y. (1997). Formation of dibromomethane and bromodichloromethane by phytoplankton in the coastal waters of the Western English Channel. *Comptes Rendus De L Academie Des Sciences Serie Ii Fascicule a- Sciences De La Terre Et Des Planetes* **324**(1): 25-31.

Cota, G. F. and Sturges, W. T. (1997). Biogenic bromine production in the Arctic. *Marine Chemistry* **56**(3-4): 181-192.

Dewulf, J., Drijvers, D. and Vanlangenhove, H. (1995). Measurement of Henrys Law Constant as Function of Temperature and Salinity for the Low-Temperature Range. *Atmospheric Environment* **29**(3): 323-331.

Diosady, L. L. and Ramarathnam, N. (1994). New Results in the Chemical Characterization of Meat Aroma. *Magyar Kemiai Folyoirat* **100**(2): 74-80.

Dumdei, B. E., Kenny, D. V., Shepson, P. B., Kleindienst, T. E., Nero, C. M., Cupitt, L. T. and Claxton, L. D. (1988). Ms Ms Analysis of the Products of Toluene Photooxidation and Measurement of Their Mutagenic Activity. *Environmental Science & Technology* **22**(12): 1493-1498.

Fogelqvist, E. and Krysell, M. (1986). The Anthropogenic and Biogenic Origin of Low-Molecular-Weight Halocarbons in a Polluted Fjord, the Idefjorden. *Marine Pollution Bulletin* **17**(8): 378-382.

Fogelqvist, E., Tanhua, T., Basturk, O. and Salihoglu, I. (1996). The distribution of man-made and naturally produced halocarbons in a double layer flow strait system. *Continental Shelf Research* **16**(9): 1185-1199.

Goodwin, K. D., North, W. J. and Lidstrom, M. E. (1997). Production of bromoform and dibromomethane by Giant Kelp: Factors affecting release and comparison to anthropogenic bromine sources. *Limnology and Oceanography* **42**(8): 1725-1734.

Gossett, J. M. (1987). Measurement of Henrys Law Constants for C1 and C2 Chlorinated Hydrocarbons. *Environmental Science & Technology* **21**(2): 202-208.

Gschwend, P. M., Zafiriou, O. C., Mantoura, R. F. C., Schwarzenbach, R. P. and Gagosian, R. B. (1982). Volatile Organic-Compounds at a Coastal Site .1. Seasonal-Variations. *Environmental Science & Technology* **16**(1): 31-38.

Haselmann, K. F., Laturnus, F., Svensmark, B. and Gron, C. (2000). Formation of chloroform in spruce forest soil - results from laboratory incubation studies. *Chemosphere* **41**(11): 1769-1774.

Itoh, N., Tsujita, M., Ando, T., Hisatomi, G. and Higashi, T. (1997). Formation and emission of monohalomethanes from marine algae. *Phytochemistry* **45**(1): 67-73.

Jeffrey, S. W., Mantoura, R. F. C. and Wright, S. W. (1997). *Phytoplankton pigments in oceanography: guidelines to modern methods*. Paris, Unesco, pp651.

Kiene, R. P. and Bates, T. S. (1990). Biological Removal of Dimethyl Sulfide from Sea-Water. *Nature* **345**(6277): 702-705.

Kind, I., Berndt, T., Boge, O. and Rolle, W. (1996). Gas-phase rate constants for the reaction of NO_3 radicals with furan and methyl-substituted furans. *Chemical Physics Letters* **256**(6): 679-683.

Krysell, M. (1991). Bromoform in the Nansen Basin in the Arctic-Ocean. *Marine Chemistry* **33**(1-2): 187-197.

Laturnus, F. (2001). Marine macroalgae in polar regions as natural sources for volatile organohalogens. *Environmental Science and Pollution Research* **8**(2): 103-108.

Laturnus, F., Giese, B., Wiencke, C. and Adams, F. C. (2000). Low-molecular-weight organoiodine and organobromine compounds released by polar macroalgae - The influence of abiotic factors. *Fresenius Journal of Analytical Chemistry* **368**(2-3): 297-302.

Liss, P. S. and Merlivat, L. (1986). The role of air-sea exchange in geochemical cycling. *Air-sea gas exchange rates: introduction and synthesis*. P. Buat-Menard, Dordrecht: D. Reidel: 113-127.

Liss, P. S., Watson, A. J., Liddicoat, M. I., Malin, G., Nightingale, P. D., Turner, S. M. and Upstill-Goddard, R. C. (1994). Chapter 12: Trace gases and air-sea exchanges. *Understanding the North Sea system*. H. Charnock, K. R. Dyer, J. M. Huthnance, P. S. Liss, J. H. Simpson and P. B. Tett. London, Chapman & Hall for The Royal Society: 153-163.

Manley, S. L. and delaCuesta, J. L. (1997). Methyl iodide production from marine phytoplankton cultures. *Limnology and Oceanography* **42**(1): 142-147.

Mantoura, R. F. C., Gschwend, P. M., Zafiriou, O. C. and Clarke, K. R. (1982). Volatile Organic-Compounds at a Coastal Site. 2 Short-Term Variations. *Environmental Science & Technology* **16**(1): 38-45.

Marti, S., Bayona, J. M. and Albaiges, J. (2001). A potential source of organic pollutants into the Northeastern Atlantic: The outflow of the Mediterranean deep lying waters through the Gibraltar Strait. *Environmental Science & Technology* **35**(13): 2682-2689.

McDonald, R. D., Zielinska, B., Fujita, E. M., Sagebiel, J. C., Chow, J. C. and Watson, J. G. (2000). Fine particle and gaseous emission rates from residential wood combustion. *Environmental Science & Technology* **34**(11): 2080-2091.

Moore, R. M., Geen, C. E. and Tait, V. K. (1995). Determination of Henry Law Constants for a Suite of Naturally- Occurring Halogenated Methanes in Seawater. *Chemosphere* **30**(6): 1183-1191.

Morris, A. W. (1974). Seasonal variations of dissolved metals in inshore waters of the Menai Strait. *Marine Pollution Bulletin* **5**: 54-59.

Nightingale, P. D., Malin, G. and Liss, P. S. (1995). Production of Chloroform and Other Low-Molecular-Weight Halocarbons by Some Species of Macroalgae. *Limnology and Oceanography* **40**(4): 680-689.

Ramarathnam, N., Rubin, L. J. and Diosady, L. L. (1993). Studies on Meat Flavor .3. A Novel Method for Trapping Volatile Components from Uncured and Cured Pork. *Journal of Agricultural and Food Chemistry* **41**(6): 933-938.

Scarratt, M. G. and Moore, R. M. (1996). Production of methyl chloride and methyl bromide in laboratory cultures of marine phytoplankton. *Marine Chemistry* **54**(3-4): 263-272.

Scarratt, M. G. and Moore, R. M. (1998). Production of methyl bromide and methyl chloride in laboratory cultures of marine phytoplankton II. *Marine Chemistry* **59**(3-4): 311-320.

Scarratt, M. G. and Moore, R. M. (1999). Production of chlorinated hydrocarbons and methyl iodide by the red microalga Porphyridium purpureum. *Limnology and Oceanography* **44**(3): 703-707.

Schall, C., Heumann, K. G. and Kirst, G. O. (1997). Biogenic volatile organoiodine and organobromine hydrocarbons in the Atlantic Ocean from 42 degrees N to 72 degrees S. *Fresenius Journal of Analytical Chemistry* **359**(3): 298-305.

Sharma, S., Vingarzan, R., Barrie, L. A., Norman, A., Sirois, A., Henry, M. and DiCenzo, C. (2003). Concentrations of dimethyl sulfide in the Strait of Georgia and its impact on the atmospheric sulfur budget of the Canadian West Coast. *Journal of Geophysical Research-Atmospheres* **108**(D15): art. no.-4459.

Shenoy, D. M., Paul, J. T., Gauns, M., Ramaiah, N. and Kumar, M. D. (2006). Spatial variations of DMS, DMSP and phytoplankton in the Bay of Bengal during the summer monsoon 2001. *Marine Environmental Research* **62**(2): 83-97.

Shepson, P. B., Edney, E. O. and Corse, E. W. (1984). Ring Fragmentation Reactions on the Photooxidations of Toluene and Ortho-Xylene. *Journal of Physical Chemistry* **88**(18): 4122-4126.

Tokarczyk, R. and Moore, R. M. (1994). Production of Volatile Organohalogens by Phytoplankton Cultures. *Geophysical Research Letters* **21**(4): 285-288.

Vernet, M. and Lorenzen, C. J. (1987). The presence of chlorophyll b and the estimatoin of phaeopigments in marine phytoplankton. *Journal of Plankton Research*(9): 255-265.

Wennberg, P. (1999). Atmospheric chemistry - Bromine explosion. *Nature* **397**(6717): 299-301.

Whitten, G. Z., Cohen, J. P., Myers, T. C. and Carter, W. P. L. (2003). The ozone formation potential of 1-bromo-propane. *Journal of the Air & Waste Management Association* **53**(3): 262-272.

Wolfe, G. V. and Steinke, M. (1996). Grazing-activated production of dimethyl sulfide (DMS) by two clones of Emiliania huxleyi. *Limnology and Oceanography* **41**(6): 1151-1160.

Wong, P. K. and Wang, Y. H. (1997). Determination of the Henry's law constant for dimethyl sulfide in seawater. *Chemosphere* **35**(3): 535-544.

Yokouchi, Y., Mukai, H., Yamamoto, H., Otsuki, A., Saitoh, C. and Nojiri, Y. (1997). Distribution of methyl iodide, ethyl iodide, bromoform, and dibromomethane over the ocean (east and southeast Asian seas and the western Pacific). *Journal of Geophysical Research-Atmospheres* **102**(D7): 8805-8809.

Young, D. N., McConnell, O. J. and Fenical, W. (1981). Invivo Biosynthesis of Tribromoheptene Oxide in Bonnemaisonia- Nootkana. *Phytochemistry* **20**(10): 2335-2337.

CHAPTER 4. VOLATILE ORGANIC COMPOUNDS PRODUCED BY MARINE MACROALGAE.

4.1 Introduction

Marine biota produce a great variety of volatile organic compounds (VOCs) (Gribble, 2003). Halogenated compounds may be produced by a range of marine organisms including marine bacteria, algae and several classes of marine invertebrates (Gribble, 2000). Marine biota produces a great variety of volatile organic compounds (VOCs) and these compounds are of diverse biosynthetic origins (Gribble, 2003). Halogenated compounds may be produced by a range of marine organisms including marine bacteria, algae and several classes of marine invertebrates (Gribble, 2000). These organisms excrete many organic compounds directly into the sea water as a mechanism for removal of metabolic wastes and as chemical communicants (Gagosian and Lee, 1981), for chemical protection (Laturnus, 1996), as secondary waste compounds formed with the help of peroxidases to lower the high concentration of hydrogen peroxide formed in algal cells (Collen and Pedersen, 1996), as a form of oxidative stress relief (Abrahamsson *et al.*, 2003), for anti-herbivory activity (Young *et al.*, 1981), antimicrobial action (Neidleman and Geigert, 1987) to facilitate food gathering or as hormones (Gribble, 2000) and other reasons not yet clearly understood.

Global production of halocarbons by marine algae generates an important controversy regarding their contributions to the global atmospheric flux; some authors have assumed that marine algae are apparently not the major source on a global scale *e.g.* Scarratt and Moore (1998), but may be more important on a local scale due to the occurrence at a high biomass in coastal regions *e.g.* Baker *et al.* (1999) and Laturnus (2001). On the other hand, other authors propose that marine algae may be a significant source of the total local and global production (Giese *et al.*, 1999; Carpenter and Liss, 2000). Macroalgae produce around the 70% of the world's bromoform (Carpenter and Liss, 2000) and combined emissions of macro and microalgae contribute substantial amounts of bromine to the global cycle, perhaps in the same order of magnitude as anthropogenic sources. Marine macroalgae may be the major source of the polybromomethanes in marine environments (Carpenter and Liss, 2000). Brominated and iodinated volatile halocarbons are principally from natural sources but several chlorinated compounds also have natural sources (Abrahamsson *et al.*, 1995).

The physiological mechanisms for VOC production are still not well understood but the formation of halocarbons by haloperoxidases enzymes (van Pee, 2001) through the oxidation of halogens in the presence of hydrogen peroxide is considered important. Hydrogen peroxide is a by-product result of photorespiration induced by photosynthesis, respiration and other metabolic processes (Figure 4.1). Hydrogen peroxide is an important substrate utilized by algae to produce halocarbons. Experiments developed with the artificial addition of H_2O_2 in algal cultures has shown increases in the production of some halocarbons (Collen *et al.*, 1994). Pedersen *et al.* (1996) have proposed that halogenated compounds are secondary compounds formed with the help of peroxidases in order to lower the high concentration of H_2O_2 formed in the algal cells. Hydrogen peroxide additions suggest that the brominated methane production during dark conditions is limited by bromine oxidant supply (Goodwin *et al.*, 1997). Collen *et al.* (1994) have indicated that chlorinated and brominated VOCs are formed as a result of H_2O_2 production and subsequent H_2O_2 scavenging activities by peroxidases, but iodine did not increase with H_2O_2 additions. Manley and Barbero (2001) suggest that the H_2O_2 is formed by photosynthetic activity and respiratory electron transport catalyzed by the enzyme superoxide dismutase. Sundstrom *et al.* (1996) provide evidence that the activity of the brominating peroxidases is dependent on the intracellular concentration of H_2O_2. Abrahamsson *et al.* (2003) found a strong correlation between the release of H_2O_2 with brominated and some iodinated compounds and they propose that the chlorinated compounds follow a different mechanism.

Several authors have found enzymatic activity in algae including bromoperoxidases (Manley and Barbero, 2001), chloroperoxidases (Almeida *et al.*, 2000), iodoperoxidases (Moore *et al.*, 1996) and methyltransferases (Ohsawa *et al.*, 2001). There is some evidence that the halocarbons are produced by other enzymatic mechanisms as well. For example, the production of halocarbons was reduced by addition of a metabolic inhibitor, such as sodium azide (NaN_3), a commercial herbicide dichlorophenyldimethyl urea (DCMU), a photosynthetic inhibitor, and sodium cyanide (NaCN) (Collen *et al.*, 1994; Sundstrom *et al.*, 1996; Cota and Sturges, 1997). The bromoperoxidases, according to Wever and Tromp (1991) constitute a class of enzymes that contain vanadium as a prosthetic group. These enzymes with a molecular mass around 90 kDa are in the presence of hydrogen peroxide able to oxidize bromide to hypobromous acid (HOBr). Their experiments reveal that the enzyme uses vanadium (V) and with the addition of hydrogen peroxide bound to the active site that bromide reacts with this enzyme peroxo-complex, resulting in the formation of

HOBr. When vanadium in the enzyme was reduced to the vanadium (IV) state, the enzyme lost its brominating activity. Moore *et al.* (1996) suggest that bromoperoxidases can produce some iodinated compounds. The enzymatic production of bromoform by bromoperoxidases is presented in Figure 4.2.

Some halogenases enzymes reported by van Pee and Holzer (1999) which instead of using hydrogen peroxide require NADH (the reduced form of nicotinamide adenine dinucleotide, a co-enzyme involved in biological oxidation-reduction processes). Due to their substrate specificity and regioselectivity, which is absent in haloperoxidases, halogenases are more likely to be the enzymes involved in halometabolite formation.

Other enzymes capable of mediating the production of halocarbons through methyltransferases enzyme reaction are discussed by Wuosmaa and Hager (1990), Saini *et al.* (1995) and Itoh *et al.* (1997). A methyltransferring enzyme isolated from marine macroalgae catalyzed the S-adenosyl-L-methionine-dependent (SAM) methylation of the halides Cl^-, Br^-, I^- to the respective methyl halides not requiring metallic ions to produce halocarbons (Ohsawa *et al.*, 2001). The production of methyl chloride by SAM is shown in Figure 4.3.

Another pathway may be the reaction of hypobromous acid (HBrO), an extremely reactive specie with organic matter to form volatile halocarbons. Hypobromous acid can be formed by haloperoxidases located near the macroalgal surface and then released into seawater. Wever *et al.* (1991) proposed that the HBrO is a strong biocide and the production of halocarbons by seaweed is part of a host defence system.

A direct incorporation of chlorine into organic matter may not be possible as chlorinating activity necessary for the enzymatic formation of organochlorine compounds was not detected in marine macroalgae (Laturnus *et al.*, 1997). However, Geigert *et al.* (1984) reported the formation of bromochlorocompounds in the presence of bromoperoxidases, evidence that chloroperoxidases may not be absolutely necessary for the formation of chlorinated compounds.

External factors such as light availability and desiccation can play an important role in the VOC production. The mechanisms involved in this production that act independently or with others to trigger the production of VOCs by marine algae can be seen in Figure 4.4. Results on the light influence by Laturnus *et al.* (2000) showed that light and dark periods had no influence on the release of volatile halocarbons. However, several authors have found an increment in the production of halocarbons under light conditions, due to algal photosynthetic activity (Ekdahl *et al.*, 1998). Laboratory experiments suggested that

release rates can be influenced by partial desiccation, light availability, tissue age, tissue wounding and grazing .

The aim of this research was to study the type of compounds produced by the dominant macroalgae (with emphasis on halogenated compounds) in the Menai Strait in response to exposure to light or partial desiccation.

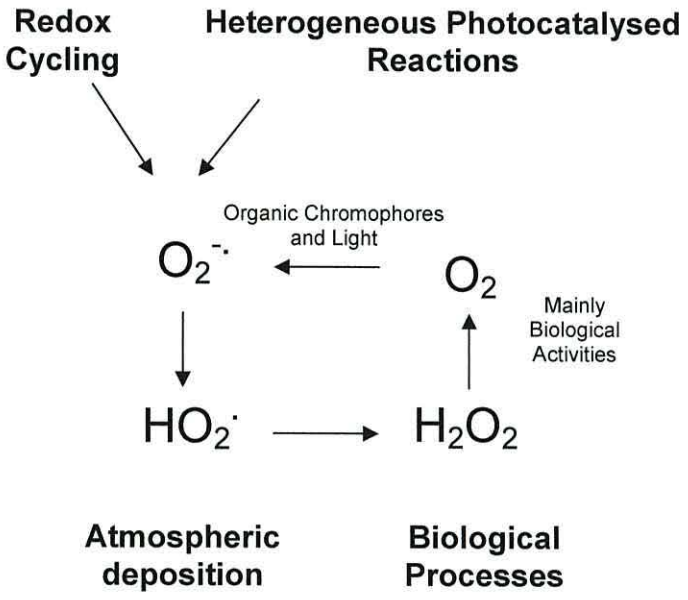


Figure 4.1. Hydrogen peroxide cycling in the ocean. From Price *et al.* (1992).

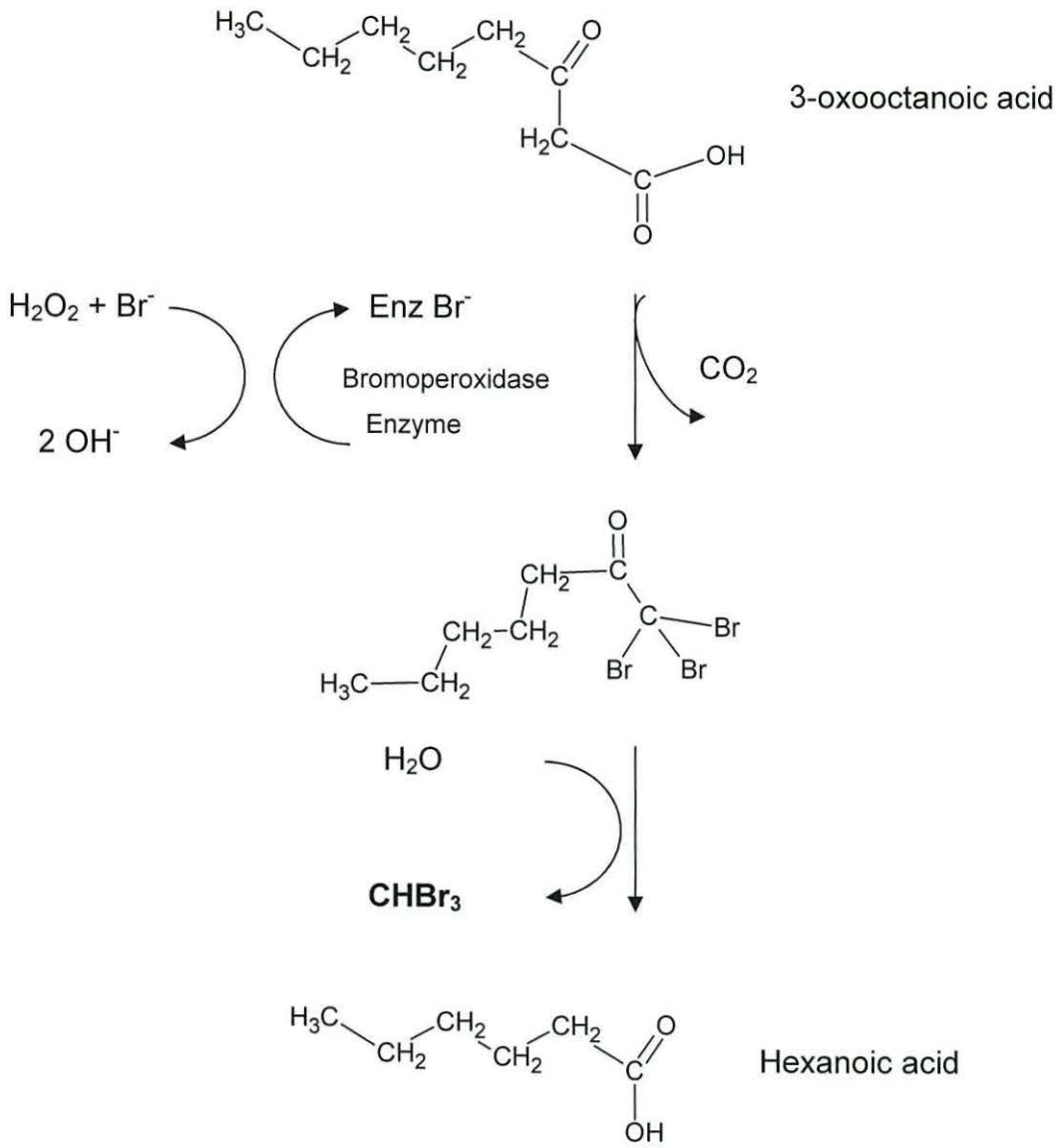


Figure 4.2. Enzymatic production of bromoform by bromoperoxidases. From Manley (2002).

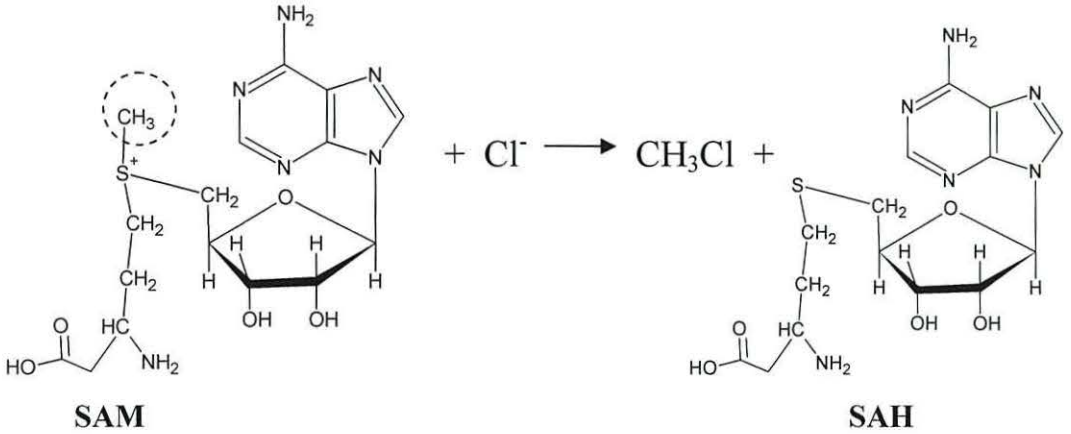


Figure 4.3. Reaction of SAM with chloride to form methyl chloride and SAH (S-Adenosylhomocysteine). From Manley (2002).

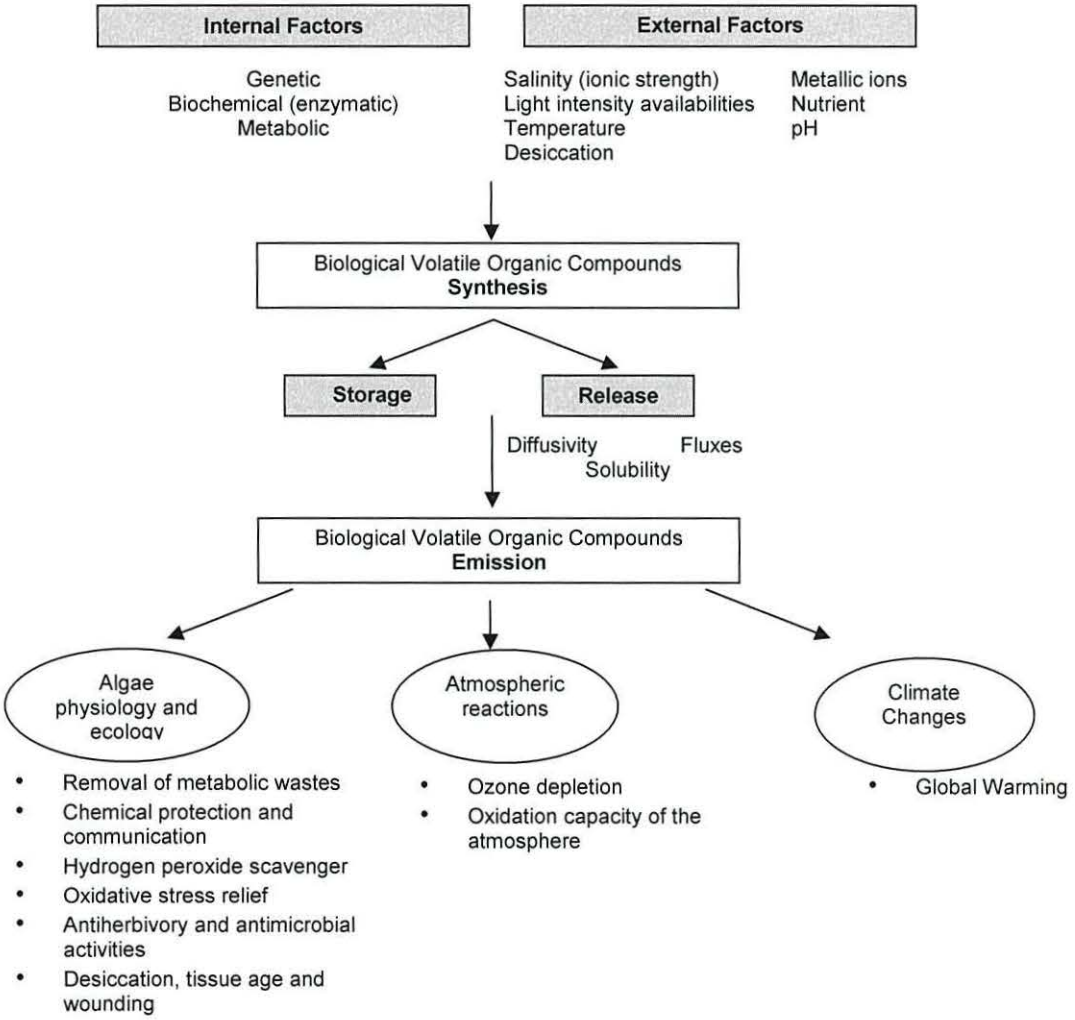


Figure 4.4. Factors driving VOC's emissions and biological and physico-chemical processes affected by these emissions and the possible consequences and reasons of this production. Modified from Peñuelas and Llusia (2003).

4.2 Results and discussion

4.2.1 Water content

The water content was variable with maximal values for red algaes. Table 4.1 shows the algae studied and their respective water content. In general, the red algae had more water in their tissue than either the green or brown algae.

Table 4.1. Water content of the algae investigated in percentage (n=5).

	Algal type	% of water	SD
Brown	*Ascophyllum nodosum*	68.7	1.3
	Fucus vesiculosus	76.7	0.6
	Fucus serratus	79.2	1.6
	Laminaria digitata	79.2	0.9
Green	*Ulva lactuca*	75.3	1.1
	Enteromorpha sp	78.9	1.2
Red	*Palmaria palmata*	86.2	0.3
	Griffithsia flocculosa	88.0	0.3

4.2.2. Blank analysis

The blank seawater used to incubate the macroalgae contained the target VOCs at trace levels (< 40 pg L^{-1}) despite the pre-treatment (filtration and sterilization). However, the concentrations were orders of magnitude less than those obtained from the experiments. This presence was not unexpected as the seawater used was originally taken from the deeper layers in the Menai Strait which naturally contains these compounds. The blank concentrations were subtracted from those obtained for each experiment. In the first experiment, the initial blank concentrations were similar to those after 12 hours indicating no net production or degradation over this period. Therefore, the blank concentrations at 0 and 12 hours were averaged and then subtracted from the corresponding samples.

4.2.3 Temporal evolution of VOCs

Forty seven different compounds were identified and quantified within the studied algae. Those compounds have previously been detected in local seawater samples, indicating that macroalgae are a potential sources of some VOCs to the bulk water. Not all algae produced all VOCs and some were specific to the type of algae and their general groups (brown, red or green). Figure 4.5 shows the production of selected VOCs throughout the incubation period under illumination and under dark conditions.

Bromoform (Figure 4.5a) was detected in all the algae studied and was produced in higher amounts by green algae (up to 25 times more than the other algae). Production in darkness was considerably lower than under illumination, this might be due the enzymatic production for this compound is nil or lower during dark conditions. Production was enhanced by longer incubation times and this agreed with findings of Collen *et al.* (1994) suggesting a constant production rate when algae are immersed in seawater. Fluxes of bromoform for all the studied algae ranged from 0.4 to 42.2 ng g^{-1} DW h^{-1}, lower values than those reported by Nightingale *et al.* (1995) of 0 to 1,250 ng g^{-1} DW h^{-1} with similar algae.

Diiodomethane (Figure 4.5b) behaved similarly to bromoform, and this agrees with findings saying that bromoperoxidases can also produce iodinated compounds. Its concentration was highest in *Laminaria*'s culture with a mean production rate of 4.38 ng g^{-1} DW h^{-1}. Carpenter *et al.* (2000) reported that diiodomethane was the main iodinated compound released by brown macroalgae.

Tetrachloroethene (Figure 4.5c) was only produced by brown macroalgae and its production was similar under both dark and light conditions. Evidences of natural production of this compound by marine macroalgae were given by Abrahamsson *et al.* (1995) who reported concentrations in the range of 0.003 to 8.2 ng g^{-1} FW h^{-1}; these data are much lower between 0.001 to 0.006 ng g^{-1} FW h^{-1}.

Bromodichloromethane (Figure 4.5d) also behaved similarly to bromoform, indicating a similar mechanism of formation. Production rates ranged from 0 to 0.68 ng g^{-1} DW h^{-1}.

Dimethylsulphide (DMS) and dimethyldisulphide (DMS_2) (Figure 4.5e, f) concentrations tended to increase under illumination. However, major releases were observed after dark conditions after 12 hours of incubation. Green algae had the highest production rate within the studied algae. Production of DMS for all the studied algae ranged from 0.005 to 7.61 ng g^{-1} DW h^{-1} under illumination and 0.019 to 13.36 ng g^{-1} DW h^{-1} under darkness, and for DMS_2 0.001 to 8.92 ng g^{-1} DW h^{-1} and 0.001 to 27.36 ng g^{-1} DW h^{-1} respectively. Apparently the production of sulphur containing compounds follow a different route as suggested by halocarbons, and may be related with respiration rather than photosynthesis. On the other hand, due to the dark condition was only performed after 12 hours of incubation, may be this time was very long for the algae provoking a stress in the algae and further production of sulphur containing compounds.

Figure 4.6 presents the total production of VOCs by group of chemicals and type of algae. Chlorinated compounds such as 1,1-dichloroethene, dichloromethane, chloroform, 1,1,1-trichloroethane, trichloroethene, 1,1,2-trichloroethane, tetrachloroethene, 1-chlorobutane, 2-chlorobutane and 2-chloropropane were all detected. They were produced in major proportions by *Ascophyllum nodosum* (Figure 4.6a). Production of halogenated compounds especially by *Ascophyllum nodosum* seems to be light dependant and related to photosynthesis (Klick, 1993).

Production under illumination was greater than under dark conditions. Mixed halogens (bromodichloromethane, dibromochloromethane and chloroiodomethane) and brominated (1-bromoethane, 1-bromopropane, 2,3-dibromopropene, dibromomethane, 1-bromopentane and bromoform) compounds are shown in Figure 4.6b and c. Bromoform was the main compound produced (up to 4,000 times more concentrated than others brominated compounds). Brominated compounds, particularly bromoform, have been reported as one of the main compound produced by marine macroalgae. According to

Klick (1993) the production of brominated compounds occurs mainly on exposure to the light which was confirmed in this research.

Iodinated compounds are shown in Figure 4.6d (iodoethane, 2-iodopropane, 1-iodobutane, diiodomethane and iodomethane). They were produced mainly by the brown alga *Laminaria digitata* and it is considered an important source of iodinated compounds from the ocean to the atmosphere (Leblanc *et al.*, 2006).

Sulphur containing compounds (DMS and DMS_2) (Figure 4.6e) were produced in greater amounts by algae during dark conditions, suggesting that these compounds are product of algal respiration rather than photosynthesis. Dimethylsulphoniopropionate (DMSP) is accumulated often in high concentrations as an osmoregulatory solute by many green macroalgae (Van Alstyne *et al.*, 2001). It acts as a precursor of DMS and this production can be mediated by marine bacteria living in the algae during algae decomposition (Castaldelli *et al.*, 2003).

Aldehydes detected including hexanal, heptanal, octanal and decanal (Figure 4.6f) were produced in major proportion under illumination together with oxygenated compounds such as 2,4-dimethylfuran and α-pinene (Figure 4.6g). Aldehydes have been reported to be toxic compounds produced by algae as a mechanism of defence (Paul and Puglisi, 2004).

Non-methane hydrocarbons from C_5 up to C_{11} (Figure 4.6h) were generated principally in dark conditions. Broadgate *et al.* (2004) observed that alkane emissions from macroalgae were generally greater in the dark and when photosynthesis was inhibited. They proposed that alkanes are produced in response to the stress imposed by the inhibition of photosynthesis at the time of day when light is normally abundant. This result agrees with findings in this research.

Total production of VOCs per algae type (Figures 4.6i) and the mean value per algae class (Figure 4.6j) show that the production of these compounds under illumination and darkness are not considerably different for green algae, similar findings were obtained by Collen *et al.* (1994). However, brown and red algaes produced more compounds under light exposure rather than dark.

VOC production was apparent under light and dark conditions, suggesting that the production of VOCs is present during algae photosynthesis as well in others metabolic processes such as respiration. The production of VOCs was dominated by green algae. However, their abundance and distribution are greater during spring time and then decay through the summer (Taylor *et al.*, 2001) and they are not the dominant species throughout

the year as brown macroalgae. Considering algal biomass, brown algae are probably the main contributors of VOCs to the Strait. Using PLS (Partial Least Squares) modelling to explain the variance of VOCs in the Menai Strait using individual contributions from green, brown and red macroalgae demonstrated that brown algae were a better predictor than other macroalgae, principally due to their abundance in the intertidal zone (see chapter 3).

Is also important to consider that even though all visible organisms were removed from the algal surface (*e.g.* snails), is not possible assume that all the volatiles found were produced by the algae themselves as some algae are covered by biofilms (*e.g.* marine bacteria) which may contribute to the production, but are unlikely to be greater than the algal production itself based on biomass alone.

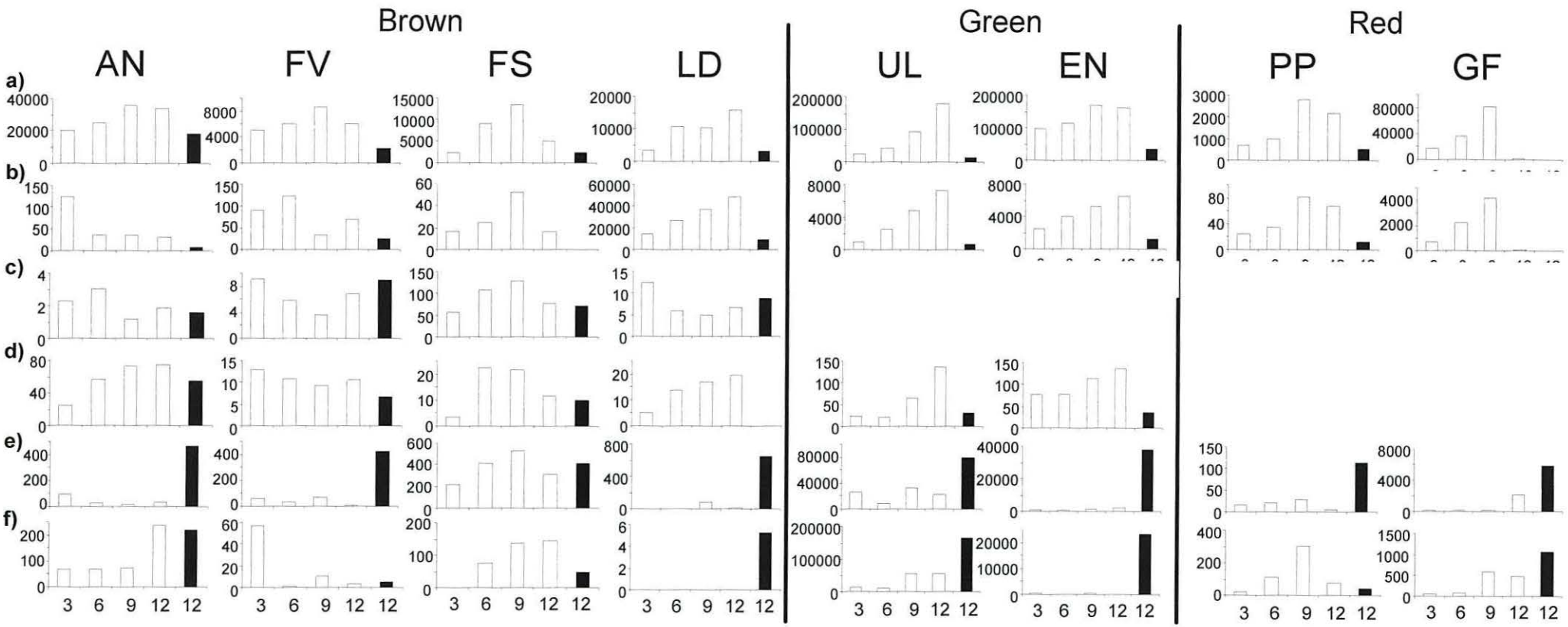


Figure 4.5. Examples of some of the VOCs produced by algae in the Menai Strait (pg g^{-1} DW): a) bromoform, b) diiodomethane, c) tetrachloroethene, d) bromodichloromethane, e) DMS and f) DMS_2 . White bars represent the concentrations obtained at 3, 6, 9 and 12 hours of immersion for each alga. Dark bars represent the dark condition after 12 hours. AN: *Ascophyllum nodosum*, FV: *Fucus vesiculosus*, FS: *Fucus serratus*, LD: *Laminaria digitata*, UL: *Ulva lactuca*, EN: *Enteromorpha sp*, PP: *Palmaria palmata* and GF: *Grifithsia flocculosa.* Blank spaces mean that the compound was not detected for a particular type of algae.

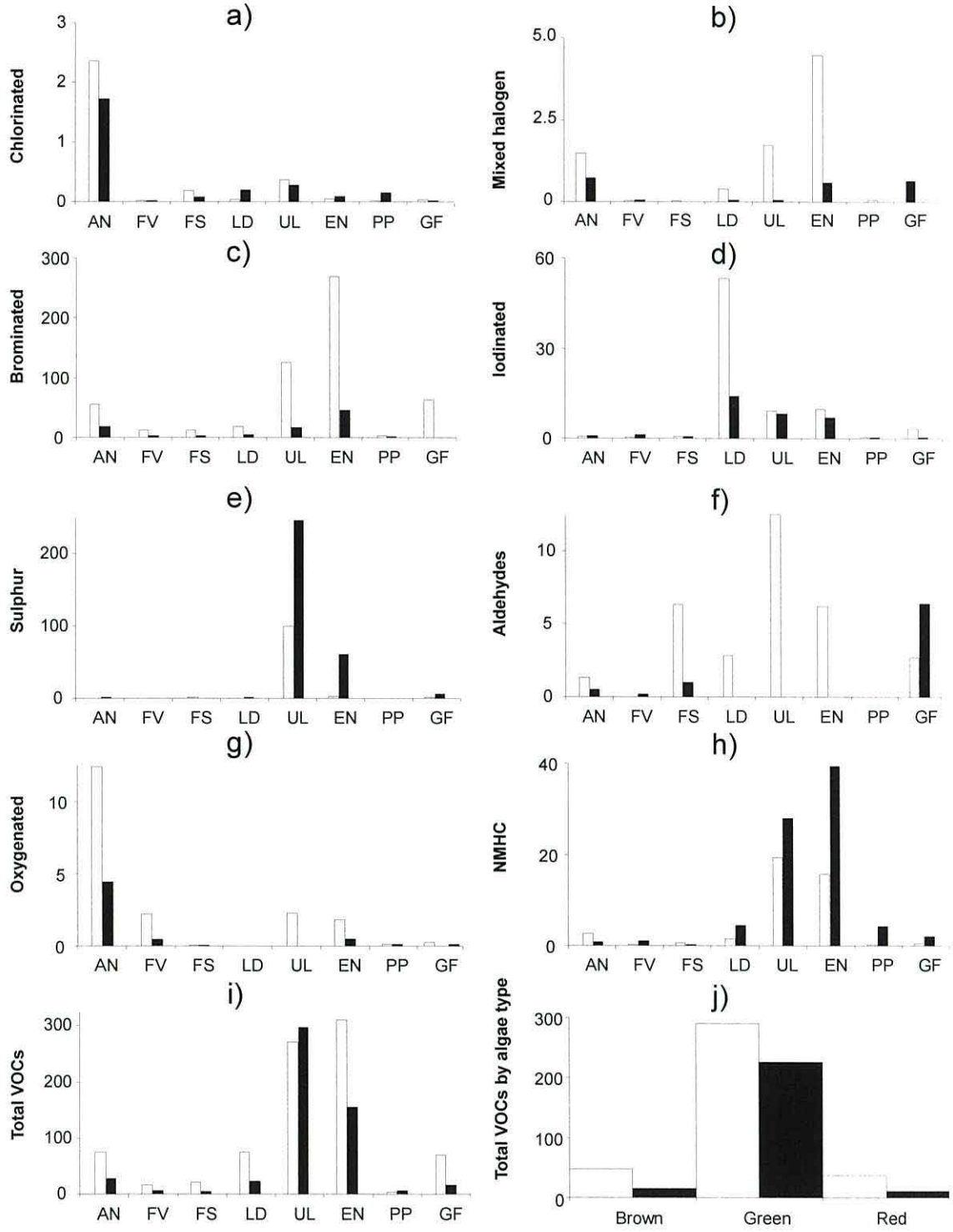


Figure 4.6. Fluxes of different groups of VOCs (ng g^{-1} DW 12 h^{-1}) produced under illuminated (open bars) and dark (black bars) conditions.

4.2.4 Losses of water

Losses of water due to natural desiccation of algae were practically linear (see Figure 4.7) over the 6 hours exposure time. Desiccation was greater in algae normally found low in the intertidal zone, with values of 72% for *Laminaria digitata* and 52% for *Ulva lactuca* after 6 hours of desiccation. This may be due to the large surface area, which is favourable for water evaporation. Losses of water were intermediate for the other brown algae (38 to 48%). *Enteromorpha* had the lowest value (28%) as its form facilitates the retention of water for longer periods.

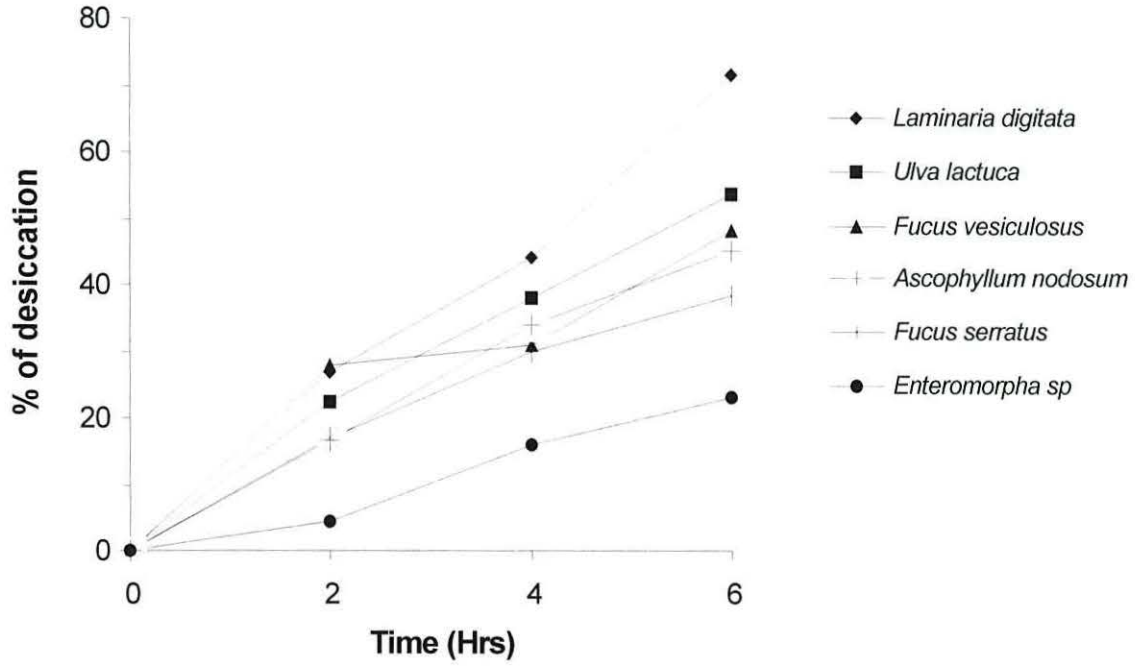


Figure 4.7. Weight losses for the algae after being left to dry for a period of 6 hours at 16-18 °C.

4.2.5 Desiccation induced VOC production

Results of the VOCs released after re-immersion are shown in Figure 4.8. The production of chlorinated and brominated compounds (Figures 4.8a and c) decreased after desiccation. The opposite was observed for mixed halogen and iodinated (Figures 4.8b and d). Iodinated compounds were greatly produced by *Laminaria digitata*. In addition, chloroform and the rest of the chlorinated compounds decreased, except in *Ascophyllum nodosum* whose production appeared to be independent of time (see Figure 4.8a). These results are at odds with the findings of Nightingale *et al.* (1995) who found enhancements in the production of chloroform, iodomethane and other halogenated compounds in *Ascophyllum nodosum*. *Laminaria digitata* produced much greater amounts of iodinated compounds, suggesting that for this alga desiccation produces and stimulates the production of these compounds. The findings of Palmer *et al.* (2005) with different oxidative stress on *Laminaria digitata* suggested that this alga releases a burst of volatile iodinated compounds and an even greater amount of molecular iodine.

Sulphur containing VOC production (Figure 4.8e) decreased with increasing desiccation time. *Ulva lactuca* produced more sulphur containing compounds than the other algae (in a weight based comparison), however due to the abundance of this alga in the Menai Strait is lower than brown algae, total contribution may be lower in terms of biomass.

NMHC (Figure 4.8f) decreased for *Ascophyllum nodosum*, *Fucus vesiculosus* and *Fucus serratus* and increased for *Ulva lactuca*, *Laminaria digitata* and *Enteromorpha sp.* Tendencies for aldehydes (Figure 4.8g) were not clear, except for *Laminaria digitata* whose production increased. In general, VOCs (Figure 4.8h) tended to increase with increasing desiccation; this indicates that VOC production by macroalgae is promoted by an oxidative stress produced by partial desiccation after being exposed to the air. This production changed according to the habitat range in the intertidal profile with lower production rates for high water algae (desiccation tolerant) and higher for low tide algae that are less tolerant to desiccation.

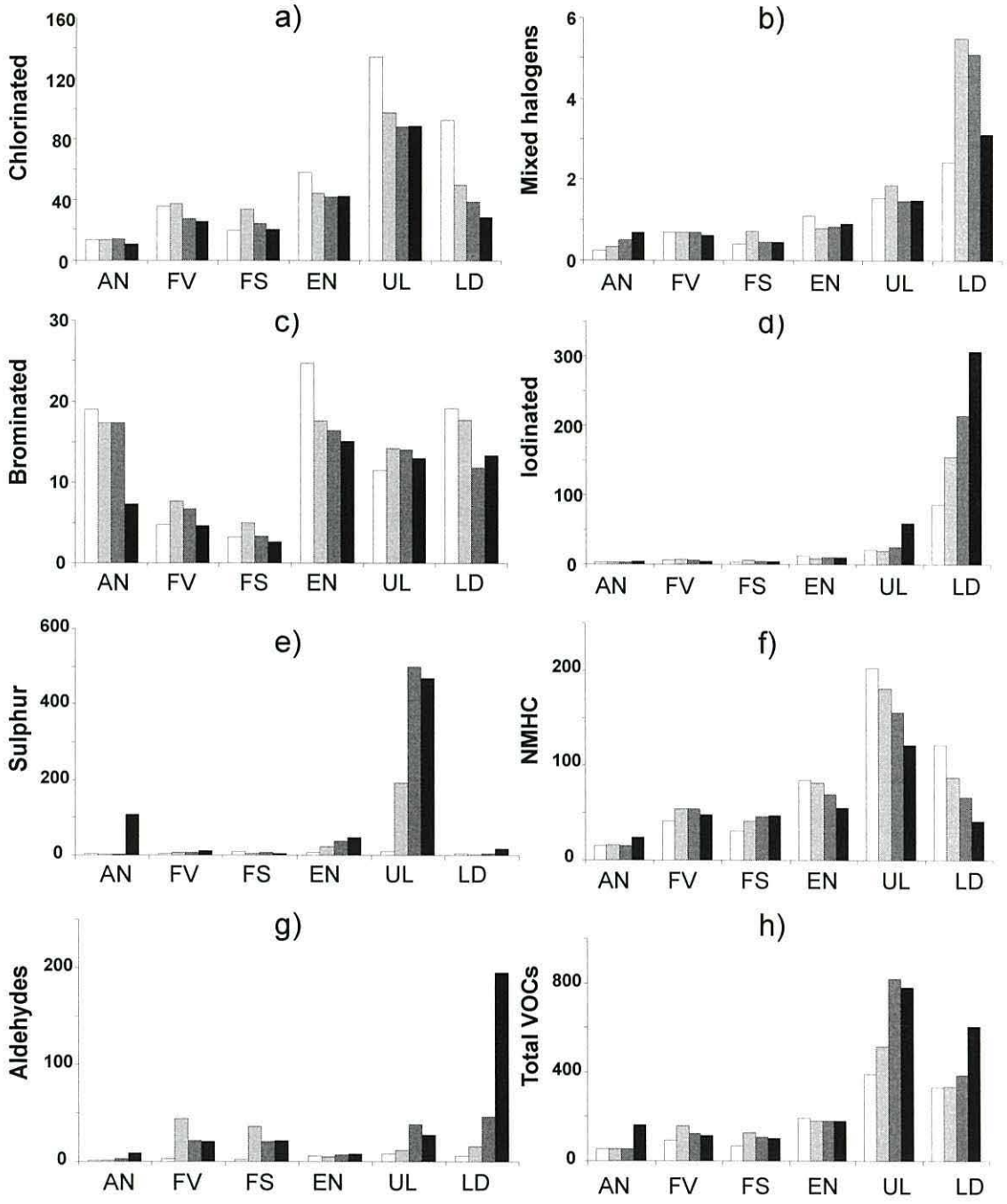


Figure 4.8. Summary of all VOCs per type in ng g^{-1} DW at 0 (white bras), 2 (light grey bars), 4 (grey bars) and 6 (black bars) hours of desiccation. Where: a) Total chlorinated compounds, b) Total mixed halogens compounds, c) Total brominated compounds, d) Total iodinated compounds, e) Total sulphur containing compounds, f) Total NMHC compounds, g) Total aldehydes compounds and c) Total VOCs detected.

Most of the studies report a limited amount of VOCs produced by macroalgae; however this is the first time that such amounts of compounds have been reported from temperate macroalgae. The algae studied are widely distributed in European coastal waters and clearly they are significant sources of VOCs to the atmosphere especially of brominated compounds (*e.g.* bromoform) and in a lower extent of iodinated compounds. In addition, some chlorinated compounds typically referred from anthropogenic sources such as tetrachloroethene were also produced.

The presence and the production of some VOCs by the studied algae seem to follow different mechanism and in the field they are affected by several external factors such as presence of predators, nutrients availability, desiccation and algal ecology leading to intra and extra-cellular production of VOCs triggered in different ways by these external factors. Also considering that some VOCs can be directly produced by the algae itself and others as secondary production due to the release for example of HOBr which can react with the organic matter present in the water to form bromoform.

Due to macroalgae are present all year through, they may not be the main sources of certain VOCs in the Menai strait, however they can be considered as a constant source.

Is important to highlight that species type/diversity results in different chemical profiles and quantities released. For example, chlorinated and oxygenated compounds are principally released by the brown alga *Ascophyllum nodosum*, while green algae represented by *Ulva lactuca* and *Enteromorpha* release much higher amount of brominated, sulphur containing compounds, aldehydes and non-methane hydrocarbons than the rest of the algae. On the other hand, kelps (e.g. *Laminaria digitata*) dominate the release of iodinated compounds such as diiodomethane. Consequently, this could dictate the presence of VOCs in seawater in different coastal regions where the species composition differs.

4.3 Conclusions

- Marine macroalgae can produce a broad variety of VOCs and this production can be enhanced by external factors such as light availability and desiccation.

- The production of compounds under illumination and darkness were not considerably different suggesting that the production of VOCs is possible during algal photosynthesis as well in others metabolic processes such as respiration.

- Desiccation play an important role in the production of VOCs, findings showed that VOCs tended to increase after desiccation indicating that VOCs production by macroalgae is promoted by an oxidative stress produced by partial desiccation after being exposed to the air. This production changed according to the habitat range in the intertidal profile with lower production rates for high water algae (desiccation tolerant) and higher for low tide algae that are less tolerant to desiccation.

4.4 References

Abrahamsson, K., Choo, K. S., Pedersen, M., Johansson, G. and Snoeijs, P. (2003). Effects of temperature on the production of hydrogen peroxide and volatile halocarbons by brackish-water algae. *Phytochemistry* **64**(3): 725-734.

Abrahamsson, K., Ekdahl, A., Collen, J. and Pedersen, M. (1995). Marine algae - A source of trichloroethylene and perchloroethylene. *Limnology and Oceanography* **40**(7): 1321-1326.

Almeida, M. G., Humanes, M., Melo, R., Silva, J. A., da Silva, J. and Wever, R. (2000). Purification and characterisation of vanadium haloperoxidases from the brown alga Pelvetia canaliculata. *Phytochemistry* **54**(1): 5-11.

Baker, J. M., Reeves, C. E., Nightingale, P. D., Penkett, S. A., Gibb, S. W. and Hatton, A. D. (1999). Biological production of methyl bromide in the coastal waters of the North Sea and open ocean of the northeast Atlantic. *Marine Chemistry* **64**(4): 267-285.

Broadgate, W. J., Malin, G., Kupper, F. C., Thompson, A. and Liss, P. S. (2004). Isoprene and other non-methane hydrocarbons from seaweeds: a source of reactive hydrocarbons to the atmosphere. *Marine Chemistry* **88**(1-2): 61-73.

Carpenter, L. J. and Liss, P. S. (2000). On temperate sources of bromoform and other reactive organic bromine gases. *Journal of Geophysical Research-Atmospheres* **105**(D16): 20539-20547.

Carpenter, L. J., Malin, G., Liss, P. S. and Kupper, F. C. (2000). Novel biogenic iodine-containing trihalomethanes and other short-lived halocarbons in the coastal East Atlantic. *Global Biogeochemical Cycles* **14**(4): 1191-1204.

Castaldelli, G., Welsh, D. T., Flachi, G., Zucchini, G., Colombo, G., Rossi, R. and Fano, E. A. (2003). Decomposition dynamics of the bloom forming macroalga Ulva rigida C. Agardh determined using a C-14-carbon radio-tracer technique. *Aquatic Botany* **75**(2): 111-122.

Collen, J., Ekdahl, A., Abrahamsson, K. and Pedersen, M. (1994). The Involvement of Hydrogen-Peroxide in the Production of Volatile Halogenated Compounds by Meristiella-Gelidium. *Phytochemistry* **36**(5): 1197-1202.

Collen, J. and Pedersen, M. (1996). Production, scavenging and toxicity of hydrogen peroxide in the green seaweed Ulva rigida. *European Journal of Phycology* **31**(3): 265-271.

Cota, G. F. and Sturges, W. T. (1997). Biogenic bromine production in the Arctic. *Marine Chemistry* **56**(3-4): 181-192.

Ekdahl, A., Pedersen, M. and Abrahamsson, K. (1998). A study of the diurnal variation of biogenic volatile halocarbons. *Marine Chemistry* **63**(1-2): 1-8.

Gagosian, R. B. and Lee, C. (1981). Processes Controlling the distribution of biogenic organic compounds in seawater. *Marine organic chemistry, evolution, composition, interactions and chemistry of organic mater in seawater*. E. K. Duursma and R. Dawson. New York, Elsevier: 91-107.

Geigert, J., Neidleman, S. L., Dewitt, S. K. and Dalietos, D. J. (1984). Halonium Ion-Induced Biosynthesis of Chlorinated Marine Metabolites. *Phytochemistry* **23**(2): 287-290.

Giese, B., Laturnus, F., Adams, F. C. and Wiencke, C. (1999). Release of volatile iodinated C-1-C-4 hydrocarbons by marine macroalgae from various climate zones. *Environmental Science & Technology* **33**(14): 2432-2439.

Goodwin, K. D., North, W. J. and Lidstrom, M. E. (1997). Production of bromoform and dibromomethane by Giant Kelp: Factors affecting release and comparison to anthropogenic bromine sources. *Limnology and Oceanography* **42**(8): 1725-1734.

Gribble, G. J. (2000). The natural production of organobromine compounds. *Environmental Science and Pollution Research* **7**(1): 37-49.

Gribble, G. W. (2003). The diversity of naturally produced organohalogens. *Chemosphere* **52**(2): 289-297.

Itoh, N., Tsujita, M., Ando, T., Hisatomi, G. and Higashi, T. (1997). Formation and emission of monohalomethanes from marine algae. *Phytochemistry* **45**(1): 67-73.

Klick, S. (1993). The Release of Volatile Halocarbons to Seawater by Untreated and Heavy-Metal Exposed Samples of the Brown Seaweed Fucus- Vesiculosus. *Marine Chemistry* **42**(3-4): 211-221.

Laturnus, F. (1996). Volatile halocarbons released from Arctic macroalgae. *Marine Chemistry* **55**(3-4): 359-366.

Laturnus, F. (2001). Marine macroalgae in polar regions as natural sources for volatile organohalogens. *Environmental Science and Pollution Research* **8**(2): 103-108.

Laturnus, F., Adams, F. C., Gomez, I. and Mehrtens, G. (1997). Halogenating activities detected in Antarctic macroalgae. *Polar Biology* **17**(3): 281-284.

Laturnus, F., Giese, B., Wiencke, C. and Adams, F. C. (2000). Low-molecular-weight organoiodine and organobromine compounds released by polar macroalgae - The influence of abiotic factors. *Fresenius Journal of Analytical Chemistry* **368**(2-3): 297-302.

Leblanc, C., Colin, C., Cosse, A., Delage, L., La Barre, S., Morin, P., Fievet, B., Voiseux, C., Ambroise, Y., Verhaeghe, E., Amouroux, D., Donard, O., Tessier, E. and Potin, P. (2006). Iodine transfers in the coastal marine environment: the key role of brown algae and of their vanadium-dependent haloperoxidases. *Biochimie* **88**(11): 1773-1785.

Manley, S. L. and Barbero, P. E. (2001). Physiological constraints on bromoform (CHBr3) production by Ulva lactuca (Chlorophyta). *Limnology and Oceanography* **46**(6): 1392-1399.

Moore, R. M., Webb, M., Tokarczyk, R. and Wever, R. (1996). Bromoperoxidase and iodoperoxidase enzymes and production of halogenated methanes in marine diatom cultures. *Journal of Geophysical Research-Oceans* **101**(C9): 20899-20908.

Neidleman, S. L. and Geigert, J. (1987). Biological Halogenation - Roles in Nature, Potential in Industry. *Endeavour* **11**(1): 5-15.

Nightingale, P. D., Malin, G. and Liss, P. S. (1995). Production of Chloroform and Other Low-Molecular-Weight Halocarbons by Some Species of Macroalgae. *Limnology and Oceanography* **40**(4): 680-689.

Ohsawa, N., Tsujita, M., Morikawa, S. and Itoh, N. (2001). Purification and characterization of a monohalomethane- producing enzyme S-adenosyl-L-methionine: Halide ion methyltransferase from a marine microalga, Pavlova pinguis. *Bioscience Biotechnology and Biochemistry* **65**(11): 2397-2404.

Palmer, C. J., Anders, T. L., Carpenter, L. J., Kupper, F. C. and McFiggans, G. B. (2005). Iodine and halocarbon response of Laminaria digitata to oxidative stress and links to atmospheric new particle production. *Environmental Chemistry* **2**(4): 282-290.

Paul, V. J. and Puglisi, M. P. (2004). Chemical mediation of interactions among marine organisms. *Natural Product Reports* **21**(1): 189-209.

Pedersen, M., Collen, J., Abrahamsson, K. and Ekdahl, A. (1996). Production of halocarbons from seaweeds: An oxidative stress reaction? *Scientia Marina* **60**: 257-263.

Penuelas, J. and Llusia, J. (2003). BVOCs: plant defense against climate warming? *Trends in Plant Science* **8**(3): 105-109.

Price, D., Worsfold, P. J. and Mantoura, R. F. C. (1992). Hydrogen-Peroxide in the Marine-Environment - Cycling and Methods of Analysis. *Trac-Trends in Analytical Chemistry* **11**(10): 379-384.

Saini, H. S., Attieh, J. M. and Hanson, A. D. (1995). Biosynthesis of Halomethanes and Methanethiol by Higher-Plants Via a Novel Methyltransferase Reaction. *Plant Cell and Environment* **18**(9): 1027-1033.

Scarratt, M. G. and Moore, R. M. (1998). Production of methyl bromide and methyl chloride in laboratory cultures of marine phytoplankton II. *Marine Chemistry* **59**(3-4): 311-320.

Sundstrom, J., Collen, J., Abrahamsson, K. and Pedersen, M. (1996). Halocarbon production and in vivo brominating activity of Eucheuma denticulatum. *Phytochemistry* **42**(6): 1527-1530.

Taylor, R., Fletcher, R. L. and Raven, J. A. (2001). Preliminary studies on the growth of selected 'Green tide' algae in laboratory culture: Effects of irradiance, temperature, salinity and nutrients on growth rate. *Botanica Marina* **44**(4): 327-336.

Van Alstyne, K. L., Wolfe, G. V., Freidenburg, T. L., Neill, A. and Hicken, C. (2001). Activated defense systems in marine macroalgae: evidence for an ecological role for DMSP cleavage. *Marine Ecology-Progress Series* **213**: 53-65.

van Pee, K. H. (2001). Microbial biosynthesis of halometabolites. *Archives of Microbiology* **175**(4): 250-258.

van Pee, K. H. and Holzer, M. (1999). Specific enzymatic chlorination of tryptophan and tryptophan derivatives. *Tryptophan, Serotonin and Melatonin.* New York, KLUWER ACADEMIC / PLENUM PUBL. **467:** 603-609.

Wever, R. and Tromp, M. G. M. (1991). Structural Studies of Vanadium Bromoperoxidases. *Abstracts of Papers of the American Chemical Society* **202**: 98-INOR.

Wever, R., Tromp, M. G. M., Krenn, B. E., Marjani, A. and Vantol, M. (1991). Brominating Activity of the Seaweed Ascophyllum-Nodosum - Impact on the Biosphere. *Environmental Science & Technology* **25**(3): 446-449.

Wuosmaa, A. M. and Hager, L. P. (1990). Methyl-Chloride Transferase - a Carbocation Route for Biosynthesis of Halometabolites. *Science* **249**(4965): 160-162.

Young, D. N., McConnell, O. J. and Fenical, W. (1981). Invivo Biosynthesis of Tribromoheptene Oxide in Bonnemaisonia- Nootkana. *Phytochemistry* **20**(10): 2335-2337.

CHAPTER 5. VOLATILE ORGANIC COMPOUNDS PRODUCED IN MARINE SEDIMENTS.

5.1. Introduction

Sediments are not well known as a source of VOCs. However, is important to consider that they can act as a source as well as sink of volatile organic compounds. Different methodologies have been developed in order to asses the types and amounts of VOCs present in sediments. There are many techniques applied to sediments and most involve taking the sample into the laboratory and use head-space (Bianchi *et al.*, 1991) purge-and-trap (Campillo *et al.*, 2004; Fu *et al.*, 2005) and many of them involve the use of solvents such as methanol in order to displace the VOCs present in the sample (Amaral *et al.*, 1994). However, the properties of the Solid-Phase Micro Extraction (SPME) make it amenable to *in situ* sampling. The majority of VOCs analyses in sediments involve sample collection with subsequent laboratory extraction. However, in the determination of VOCs, the loss of volatile components during sampling and sample handling and the small volume of the collected sample should be considered (Kuran *et al.*, 1994).

A wide variety of different types of VOCs have been detected in sediments such as BTEXs and monoaromatics compounds (Fu *et al.*, 2005); sulphur containing compounds represented by dimethyl sulphide (DMS) and dimethyl sulphoxide (DMSO), produced mainly by bacteria (Visscher *et al.*, 2003). Terpenes, aldehydes, alcohols, ketones, halogenated compounds are also commonly reported (Bianchi *et al.*, 1991). VOCs have a wide range of both natural and anthropogenic sources and their concentration in sediments may depend on the degree of contamination (see Chapter 3). The type of sediment also influences the type of VOCs produced. For example, anoxic and muddy sediments produce more reduced species such as DMS and methyl mercaptan (Kiene and Taylor, 1988). On the other hand, sandy sediments have less sorptive properties (Bianchi *et al.*, 1991) and may not be a significant source of VOCs if they are derived from surface bound organic matter (Sartin *et al.*, 2002).

The aim of this study was to determine the types, fluxes and concentration of VOCs in marine sediments using a new *in situ* SPME methodology and investigate any relationships with sediment type and properties.

5.2 Results and discussions

5.2.1 Sediment properties

Sediments of differing grain size and redox potential were investigated around the Menai Strait. The properties of the sediment are shown in Table 5.1. In general TOC% and particles <63μm correlated well. Temperature varied among samples and this may affect the volatilization of VOCs and subsequently the flux estimates.

Table 5.1. Locations and some properties of the sampling sites.

Place	Location (OS Grid, UK)	Moisture (%)	TOC (%)	Temperature (°C)	Mud (%)
Aberffraw	SH 35646 E/ 68827 N	27.96	1.20	18	3.6
Beaumaris Beach	SH 60760 E/ 76011 N	11.42	1.12	27	2.1
Menai Strait mud	SH 55927 E/ 72292 N	36.31	4.00	25	46.4
Menai Strait sand	SH 55717 E/ 71589 N	13.62	2.41	22	1.1
Menai Strait mud	SH 55945 E/ 72112 N	36.97	3.76	22	57.4
Salt Marsh Caernarfon	SH 45343 E/ 59713 N	20.56	1.26	25	1.8
Salt Marsh Caernarfon	SH 44496 E/ 58686 N	42.59	7.74	28	62.5

5.2.2 Preliminary sampling methodologies

A preliminary set of samples were collected in order to optimise the methodology, to characterize the sediments and also to identify the possible compounds present in the sediments. Different extraction methods were used to analyze VOCs present in marine sediments. About 4 to 20g of fresh weight sediments were taken and placed into modified volumetric flasks with headspace tops. Extraction was performed without using solvents or by addition of methanol to wet the sediments and force the VOCs to migrate to the headspace to be trapped by dynamic and static headspace/SPME. The results obtained varied from one sample to another. Best results were obtained using larger amounts of sediment, methanol and stirring. However, when the viscosity of the sediment was high, stirring was very difficult to perform, even after adding more methanol. In general, these

methodologies only detected the most concentrated compounds such as dichloromethane, chloroform, DMS, DMSO, some BTEXs and aliphatic hydrocarbons.

Sediment core samples were taken in the field from 1-3, 3-4, 9-10 cm and returned to the laboratory for VOCs analysis in depth. Findings showed that VOCs tend to be more concentrated in the surface rather than bottom sediments. This was also observed by Visscher *et al.* (1991) for DMS. Differences in concentration were found between the sediments from the high water mark compared to the low water mark. High water sediments had lower concentrations of VOC than low water sediments, both at the surface and 10 cm depth. This may be due to higher shore levels being exposed for longer periods of time to the air, and the diffusion and removal mechanisms are faster than in low levels, which are not always exposed and remain under water, it may also be due to lower waters may have higher deposition of organic matter which is one of the sources of VOCs for example by bacterial degradation.

Sensitivity and the number of VOCs detected were greatly increased when *in situ* sampling was performed (up to 50 times), it was decided to focus on *in situ* sampling rather than taking samples into the laboratory. Most of the literature about sediment analysis is based on the collection of the sample and posterior purging process using a gas stream (He, N_2, *etc.*) and VOC traps (Roose *et al.*, 2001). By collecting samples, however, the system might be disturbed and not be representative of what is really occurring. The SPME method does have advantages and disadvantages; advantages include the sample is not disturbed and the chance to contaminate it with chemicals from the laboratory is reduced to a minimum. Furthermore, the sample is representative of what is occurring at this moment in time. Some disadvantages are that is not possible to control some parameter such as quantity of sediment sampled or the temperature of extraction; also the volatiles inside the funnel may or may not be adsorbed by the fibre. On hot days, the funnel gets hot and the evaporation and condensation of water on the connectors might affect the extraction's yield. Findings of Larroque *et al.* (2006) showed that humidity may affect the adsorption of low molecular weight rather than heavier compounds using SPME methodology. An example trace for VOCs extracted from the Menai Strait can be seen in Figure 5.1.

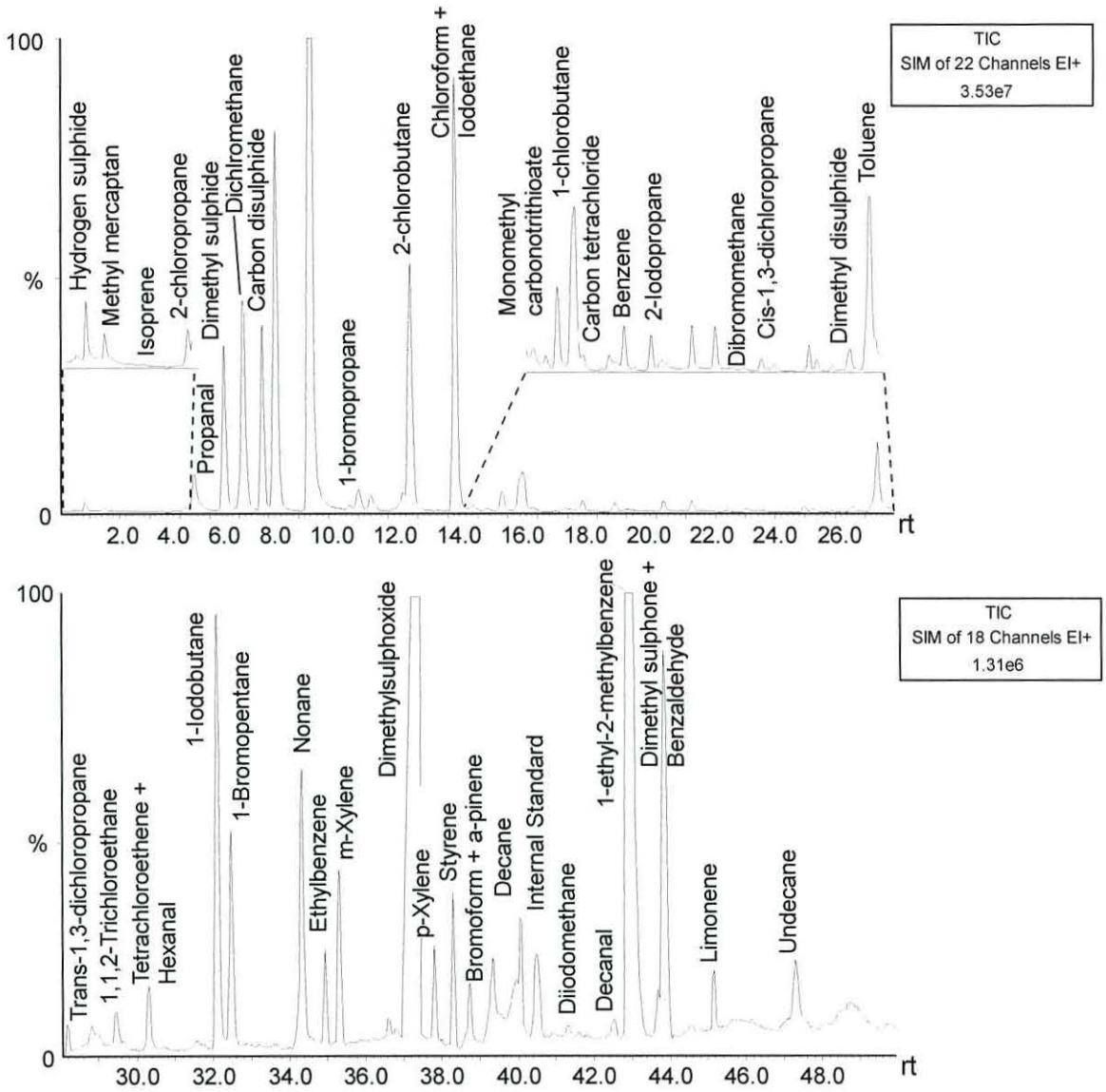


Figure 5.1. An example trace for VOCs extracted in one hour *in situ* from anoxic sediments in the Menai Strait.

5.2.3 Variability of VOCs analysis in sediments

Five VOC samples were taken sequentially from a $5m^2$ area of sediment that was visually level and homogeneous at the surface; one sample was taken from each corner plus a sample from the middle of the square. An example of selected compounds from a range of compound classes can be seen in Figure 5.2. The degree of variability of the compounds detected was moderate to high, with values ranging from 43 up to 270% RSD although this may be considered reasonable when such a wide range of compounds are quantified in a single analysis. The range measured may be due to natural variation induced by spatial and temporal effects including the time of day (Visscher *et al.*, 2003) as replicate water samples had considerably less variability (see Chapter 3). In contrast, the variation in the recovery of the internal standard for 11 samples expressed as a relative standard deviation was ~15%. This is higher than anticipated and may be due to the internal standard, which was applied directly onto the sediment's surface being partially adsorbed. Temperature also affects the evaporation rate and this may induce differences. An assumption made is that the internal standard is totally evaporated and retrieved during the sampling. According to Bianchi *et al.* (1991) the performance of sediment purge-and-trap methods is primarily dependent on the physico-chemical properties of the analytes, rather than intrinsic properties of the sediments. Three of the most important physico-chemical properties in this regard are their boiling points, vapour pressures and aqueous solubilities.

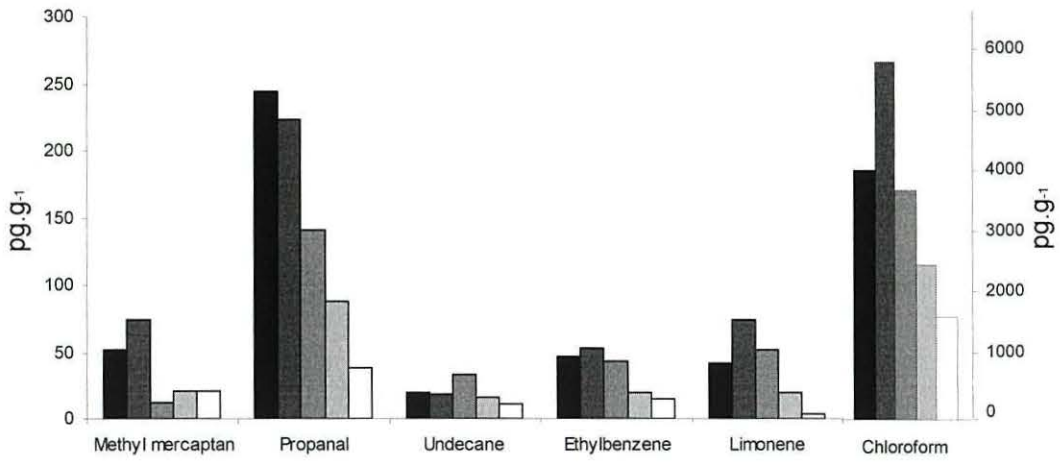


Figure 5.2. Variability in the sediment of selected VOC concentrations expressed per unit weight of sediment. The five samples were all collected within a 5 m^2 visually homogeneous muddy area of the Menai Strait. (Chloroform is shown on the right hand axis).

5.2.4 Sediments samples collected in the Menai Strait

Samples were collected on different days from marine sediments in the Menai Strait. The 61 identified compounds were classified and their fluxes were determined (Table 5.2). Fluxes were calculated from the area under the funnel for the one hour sampling period. Identification was made using several samples and running them in scan mode (47 – 270 *m/z*) on the GC-MS. The chromatographic retention times and the *m/z* chosen for each VOC for single ion monitoring analysis are shown in Table 5.2. VOCs found were classified in groups: halogenated, hydrocarbons and NMHC (non-methane hydrocarbons), BTEXs and mono-aromatic hydrocarbons, aldehydes, terpenes and sulphur containing compounds.

Redox potential for the first 5 centimetres showed that muddy sediments in the Menai Strait are characterized by having an oxic layer in the first two centimetres (1 cm: +320 mV, 2cm: +5 mV) then anoxic layers in the next 3, 4, 5 centimetres with values of -354, -403, -535 mV respectively. The first two centimetres may be exposed to the air (via diffusion); however, the 2nd cm is almost neutral and represents a transition layer. The anoxic condition increased with depth and those are the layers where the reduced VOCs might be produced, especially sulphur containing compounds.

Since the sampler was placed onto the surface of the sediment, is difficult to know from which depth (below the sediment surface) the VOCs were originated. Therefore, it was assumed that all the VOCs analyzed were produced within the first 5 cm of sediment based on the laboratory studies with sediment cores. To estimate the amount of sediment and calculate concentrations a core sample was taken from the first 5 cm of sediment and weighed. The estimated average fluxes, mean concentrations and ranges for the Menai Bridge samples are shown in Table 5.2.

5.2.4.1 BTEXs and mono-aromatic hydrocarbons

In general, the BTEX are not expected to be produced by biological sources. However, the incorporation of them from anthropogenic sources may lead to their adsorption onto the sediment surface. Nevertheless, compounds such as toluene, which had the highest fluxes from muddy sediments, can be produced naturally by bacteria in anoxic environments (Juttner, 1991; Mrowiec *et al.*, 2005). In general, compounds such as benzaldehyde, styrene, ethylbenzene have been reported in sediments, although the concentration reported in this research are much lower than those reported by Roose *et al.* (2001) and Bianchi *et al.* (1991). The fate of the different BTEXs components in anoxic sediments is dependent on the sediment conditions as well as on the characteristics and pollution history of the sediment. For instance during the summer the uses of petrol and diesel-powered engines used for recreations increased during the summer in the Menai Strait, leading to find BTEXs and mono-aromatic benzenes in waters and sediments in major concentrations.

5.2.4.2 Halogenated compounds

Twenty one halogenated compounds were found; chloroform and dichloromethane were present in the highest concentrations. Bianchi *et al.* (1991) found concentrations of dichloromethane in estuary sediment in ranges of 20-2,742 pg g^{-1} similar to the concentrations detected in this investigation (see Table 5.2). Roose *et al.* (2001) reported concentration of chloroform in sediment of 100 pg g^{-1} and Amaral *et al.* (1994) of 600 pg g^{-1} both of which are low compared with mean concentration reported in this study of 4,742 pg g^{-1}. These compounds might be produced in sediments by bacteria rather than arising from anthropogenic inputs to the Menai Strait. Other chlorinated compounds

normally considered anthropogenic in origin such as 1,2-dichloroethane, *cis*-1,3-dichloropropene, *trans*-1,3-dichloropropene, 1,1,2-trichloroethane and tetrachloroethene were found in low concentrations (<1 – 12 pg g^{-1}), almost below the limits of detection (LOD). Carbon tetrachloride was detected at 5 pg g^{-1} which may be low compared with other reported values of 200 pg g^{-1} (Amaral *et al.*, 1994), 50 pg g^{-1} (Roose *et al.*, 2001) and 75 to 1,856 pg g^{-1} (Bianchi *et al.*, 1991). Other halogenated compounds were detected such as iodinated (iodoethane, diiodomethane), brominated (1-bromopentane, bromoform) and mixed halogens (bromodichloromethane, dibromochloromethane). These are not commonly reported from anthropogenic sources and their sources are thought to be principally natural (see Chapter 6).

5.2.4.3 Sulphur containing compounds

Although the emanations from marine coastal sediments are not an important contribution to the global sulphur cycle (Andreae, 1990), production rates of methylated sulphur compounds in sediments may be high (Kiene and Capone, 1988). Microbial decomposition of sulphur-containing amino acids and the osmolyte dimethylsulphoniopropionate (DMSP) are the major processes by which volatile organic sulphur compounds are produced (Kiene and Capone, 1988). Seven different reduced sulphur compounds were detected with dimethyl sulphide (DMS) and dimethyl sulphoxide (DMSO) the most concentrated. Concentrations of DMS of 10,105 to 350,900 pg g^{-1} were reported by Bianchi *et al.* (1991), much higher values than those observed in this study. However, this difference might be due to the different methodologies employed and their use of temperature in the analysis of the sample. DMSO is formed naturally from degradation of phytoplankton in marine environments (Griebler and Slezak, 2001), from microbially mediated oxidation of DMS (Griebler, 1997) and from photo-oxidation of DMS in water surface layers (Bentley and Chasteen, 2004). In anoxic marine sediment, sulphate-reducing bacteria and methanogenic bacteria are involved in the metabolism of methylated sulphur compounds (Jonkers *et al.*, 1998; Bentley and Chasteen, 2004). Methyl mercaptan and carbon disulphide are indicators of the anoxic condition of the sediments (Lomans *et al.*, 1999). These compounds were found in all the samples in the Menai Strait in mean concentrations of 32 and 50 pg g^{-1} respectively. Methyl mercaptan is formed in large amounts by living systems (*e.g.* algae, bacteria) particularly in marine environments (Bentley and Chasteen, 2004). Demethiolation of DMSP and other materials also leads to

the production of methyl mercaptan (Bentley and Chasteen, 2004). Dimethyl sulphone was also detected in relatively high concentrations (424 pg g^{-1}); this compound originates from oxidation of DMS by hydroxyl and nitrate radicals (Bentley and Chasteen, 2004).

No reports of the environmental occurrence of monomethyl carbonotrithioate (Figure 5.3) were found in the literature. It might be a compound produced by marine bacteria from fatty acids under anoxic conditions. All samples from reducing areas of the Menai Strait had measurable amounts (Table 5.2).

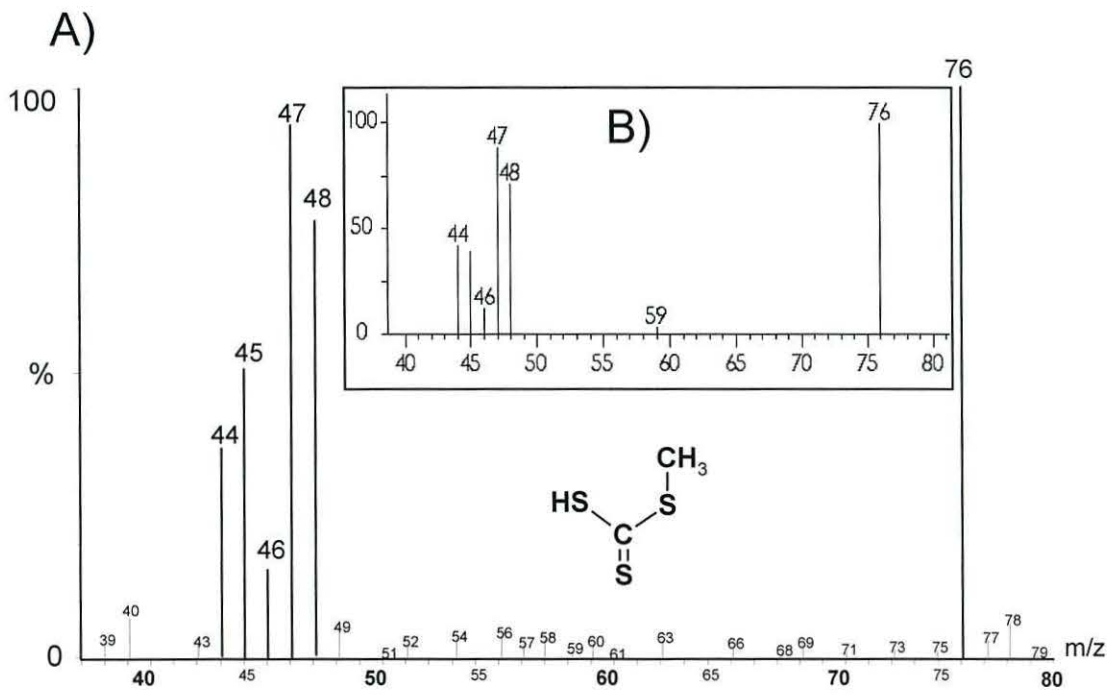


Figure 5.3. Structure of monomethyl carbonotrithioate. A) Mass spectrum of an environmental sample ran in scan mode. B) Mass spectrum for this compound from NIST library (v1.6d).

5.2.4.4 Aliphatic hydrocarbons, aldehydes and terpenes

Aldehydes such as propanal, hexanal, decanal and benzaldehyde were detected in the marine sediments. These have been reported as biogenic VOCs produced in sediments (Bianchi and Varney, 1989). The highest flux rates were for benzaldehyde and propanal with values of 2,455 and 3,003 pg h^{-1} m^{-2} respectively. These may be formed from the degradation of fatty acids under aerobic conditions. Terpenes and aliphatic hydrocarbons were generally detected at low concentrations. Hydrocarbons have an anthropogenic as well natural source and these samples indicate a low production rate and subsequent flux to the atmosphere.

Table 5.2. List of compounds found in the Menai Strait sediment samples and their respective retention time (RT) and the fragment utilized for single ion monitoring (*m/z*), fluxes, mean concentrations and ranges. n=8.

Compounds	RT (min)	*m/z*	Flux pg h^{-1} m^{-2}	Concentration* pg g^{-1} w/w	Range pg g^{-1} w/w	
					Min	Max
Chlorinated						
2-chloropropane	4.11	43	45	137.4	0.6	1,078.1
Dichloromethane	6.67	49	37,055	2,023.0	2.0	6,268.5
2-chlorobutane	11.40	57	1,868	76.2	<0.1	136.8
Chloroform	13.16	83	106,557	4,741.5	<0.1	13,435.7
1-chlorobutane	15.42	56	13,350	526.9	<0.1	974.4
Carbon tetrachloride	16.50	117	173	4.8	2.9	8.7
1.2-dichloroethane	17.29	62	33	1.3	<0.1	3.5
Cis-1,3-dichloropropene	23.47	75	301	11.6	0.44	21.0
Trans-1,3-dichloropropene	28.30	75	30	0.9	<0.1	3.4
1,1,2-trichloroethane	29.02	97	26	0.8	<0.1	1.8
Tetrachloroethene	30.50	166	25	1.0	<0.1	1.9
Mixed halogenated						
Bromodichloromethane	22.67	83	34	0.6	<0.1	1.1
Dibromochloromethane	31.43	127	603	25.5	<0.1	57.7
Iodinated						
Iodoethane	13.18	156	6,048	248.1	1.7	642.7
2-Iodopropane	18.49	43	2,114	91.3	<0.1	195.6
1-Iodobutane	31.95	184	1,243	48.1	<0.1	120.8
Diiodomethane	41.78	268	98	1.6	0.2	4.0
Brominated						
1-Bromopropane	9.65	43	48	44.7	<0.1	155.4
Dibromomethane	22.83	93	610	1.9	<0.1	4.7
1-Bromopentane	32.80	43	1,170	54.2	<0.1	111.3
Bromoform	38.80	173	457	14.5	0.4	37.9
Aldehydes						
Propanal	4.40	58	3,003	173.4	38.6	462.5
Hexanal	30.21	43	367	17.6	1.4	36.0
Decanal	42.30	43	245	40.7	1.5	252.0
Sulphur containing compounds						
Methyl mercaptan	1.34	47	499	32.5	1.5	74.0
Dimethyl sulphide	5.37	62	10,848	1,220.5	66.2	5,671.2
Carbon disulphide	6.77	76	714	49.8	2.5	204.4
Monomethyl carbonotrithioate	14.76	76	1,451	56.8	2.6	207.0
Dimethyl disulphide	26.40	94	237	15.9	1.1	49.2
Dimethyl sulphoxide	37.25	63	34,278	1,474.3	40.7	4,900.8
Dimethyl sulphone	43.15	79	11,694	424.5	17.0	1,945.5

Compounds	RT (min)	*m/z*	Flux pg h^{-1} m^{-2}	Concentration* pg g^{-1} w/w	Range pg g^{-1} w/w	
					Min	Max
Mono-aromatics						
Benzene	17.50	78	1,108	65.6	8.6	176.7
Toluene	27.27	91	8,484	374.9	<0.1	886.9
Ethylbenzene	34.82	91	543	24.4	<0.1	53.1
m-Xylene	35.20	91	640	33.0	<0.1	104.2
p-Xylene	37.20	91	257	11.2	<0.1	37.9
Styrene	37.29	104	1,681	63.3	9.6	164.5
n-propylbenzene	40.79	91	400	10.1	<0.1	24.0
1,3,5-trimethylbenzene	41.29	105	236	8.6	<0.1	26.8
1,2,4-trimethylbenzene	41.58	105	75	3.2	<0.1	11.6
1-ethyl-2-methylbenzene	42.89	105	87	10.1	<0.1	45.1
1,2,3-trimethylbenzene	43.64	105	2,699	99.7	20.3	296.8
Benzaldehyde	44.09	77	2,455	102.8	19.2	296.0
1-ethyl-3-methylbenzene	47.51	105	33	6.2	<0.1	39.0
sec-butylbenzene	47.71	105	41	6.9	<0.1	42.7
Aromatic unknown 1	48.05	105	18	7.6	<0.1	56.0
Aromatic unknown 2	49.44	105	46	8.7	<0.1	63.7
Terpenes						
α-pinene	38.46	93	107	3.3	<0.1	8.8
Limonene	45.03	93	521	24.6	<0.1	74.2
Hydrocarbons						
Isoprene	3.69	67	25	1.9	0.4	7.3
Nonane (C_9)	34.40	57	202	18.9	<0.1	58.4
C_{10} Branched 1	36.58	43	210	8.3	<0.1	26.6
C_{10} Branched 2	37.19	43	399	26.4	<0.1	90.4
C_{10} Branched 3	37.34	43	328	9.6	<0.1	43.0
C_{10} Branched 4	39.34	43	267	15.9	<0.1	33.8
Decane (C_{10})	40.00	57	547	61.9	1.1	195.4
C_{11} Branched 1	41.14	57	28	27.9	<0.1	119.9
C_{11} Branched 2	44.02	57	49	1.0	<0.1	4.0
C_{11} Branched 3	44.25	57	38	0.7	<0.1	2.1
C_{11} Branched 4	44.54	57	190	3.6	<0.1	9.7
Undecane (C_{11})	47.28	57	275	14.4	0.6	33.7

* These concentrations are assumed that were produced in the first 5cm of sediment.

5.2.5 The effect of sediment type

Samples were collected at a range of sites with similar properties in the Menai Strait. Properties of the sediments sampled are shown in Table 5.1. Results show that sites with similar properties such as sediment type and redox conditions have similar VOC signatures. Figure 5.4 shows that samples collected in a muddy/anoxic environment had similar signatures to other taken in similar environment; they are characterised by having a major presence of halogenated, sulphur and mono-aromatic compounds. Bianchi *et al.* (1991) reported that VOCs content increased in samples with a greater content of silt potentially due to the higher surface area available either as a sorbent or as an organic carbon food source. Sandy samples are as less effective sorbents for VOCs and their production is low compared with muddy environment; the presence of compounds such as BTEXs and halogenated compounds may be explained by anthropogenic inputs. To further investigate which compounds are characteristic of a specific type of sediments, Principal Component Analysis was performed.

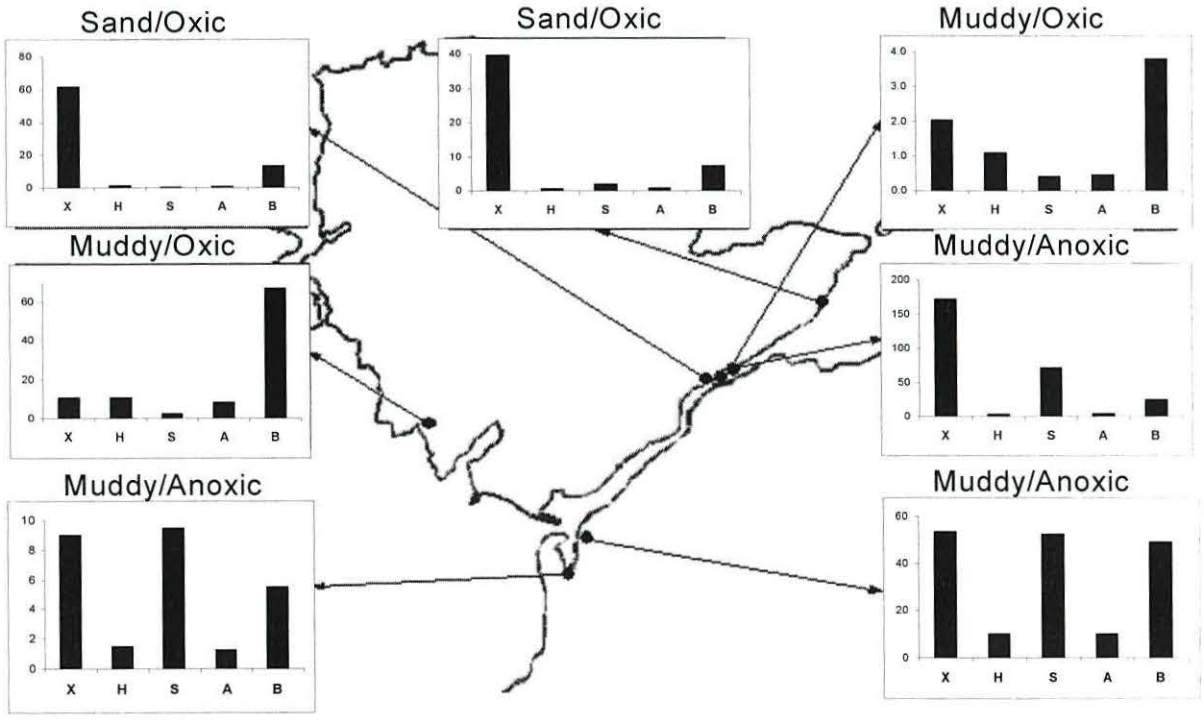


Figure 5.4. Signatures found in different samples expressed as a sumatory of all the VOCs types per sample in pg g^{-1}; where X: Total halogenated compounds, H: Total hydrocarbons, S: Total sulphur containing compounds, A: Total aldehydes, B: Total BTEXs and mono-aromatic compounds.

5.2.6 Principal Component Analysis (PCA)

PCA was used to identify the relationships between VOCs collected in the different areas. The concentrations were standardized using proportions to remove concentration effects (Mudge, 2007). The loadings and scores from the PCA (Figure 5.5) indicated that VOCs are grouped according to the sediment properties. For instance, all the muddy samples are in the same group; the same is true for the muddy/sandy and sandy. Therefore, the substrate characteristics have an effect on the types as well the amount of the VOCs generated and produced in sediments. Muddy sediments are in the majority of the cases anoxic and concentrations of the reduced sulphur containing compounds are produced in greater proportions in such sediments. Other factors that may influence the production of VOCs are redox potential, sediment temperature and organic matter input. Mixed mud/sand sites overlap the two end members with VOCs from both environments. Sandy samples were characterized by having a major presence of BTEXs, hydrocarbons, aldehydes and terpenes. The presence of these compounds may be indicative of the sub-surface biochemical processes. For instance, the aldehydes may result from the aerobic degradation of fatty acids (Goni *et al.*, 2000).

A sample was also collected from the terrestrial environment and a similar range of VOCs was measured. However, the profile was different to all the marine samples and a diagnostic signature was different to the rest of the marine samples. It had higher proportions of carbon tetrachloride (from anthropogenic as well from bacterial production), terpenes and isoprene (from trees and terrestrial plants). This means that marine sediments may have similar compounds that soil sample, but the proportions of them are different giving different signatures.

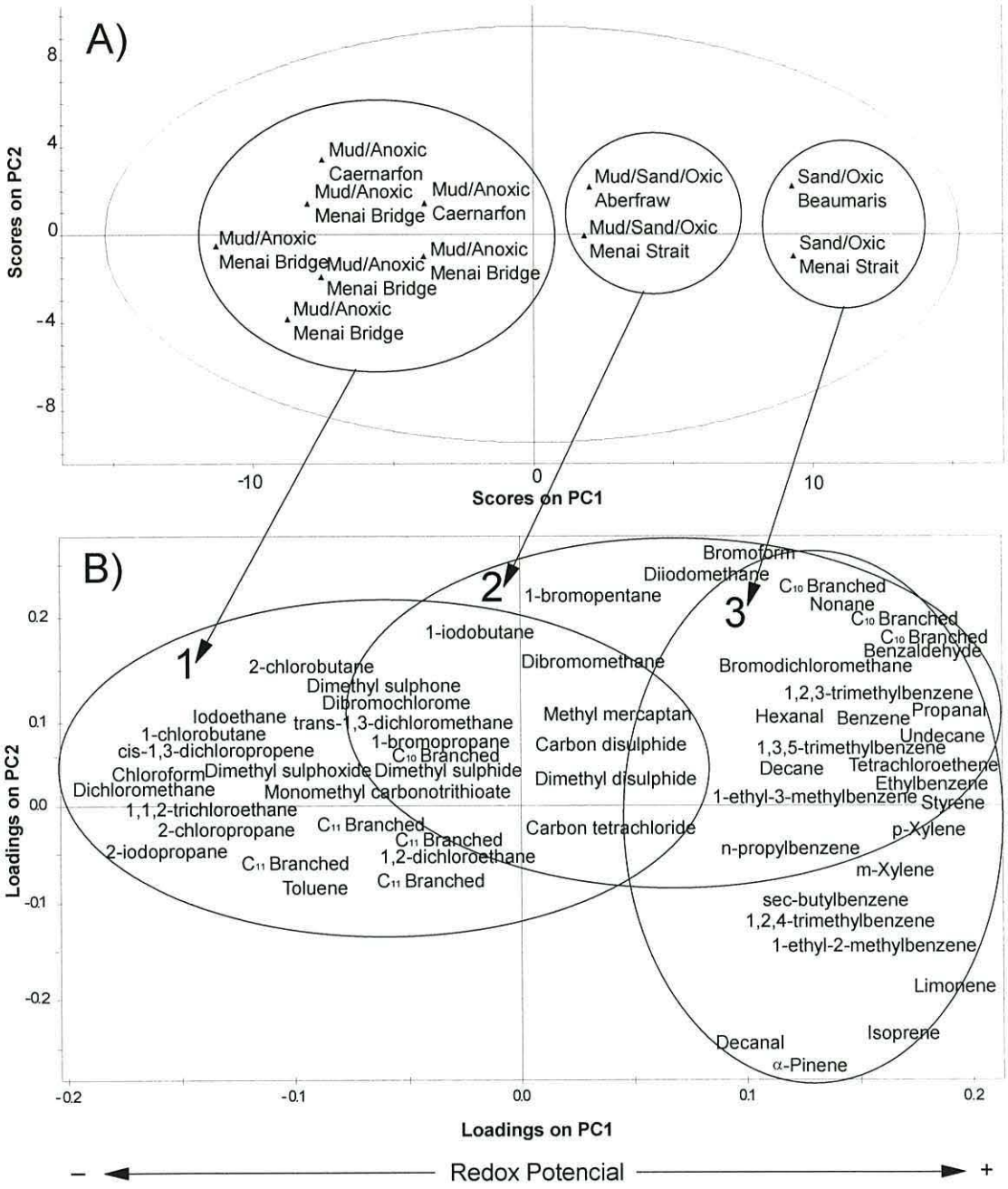


Figure 5.5. PCA analysis for the samples collected in different sites. A) Score plot for sediment samples showing the grouping of sites according to sediment properties, B) Loading plot for sediment samples showing the groups of VOCs formed according to the substrate characteristics. Grouping in circles are related to sediments 1) muddy/anoxic, 2) muddy/sandy oxic and 3) sandy/oxic.

Sediments can be a potential natural source of reduced sulphur compounds to the atmosphere as well other compounds. Sulphur containing compounds are involved in several chemical reactions in the atmosphere leading to different atmospheric processes such as acid rain and cloud condensation nuclei (CNN).

Signatures can be obtained from different kind of sediments but is difficult to differentiate chemicals that are produced in the sediments and those who are adsorbed, considering that they can act as a source as well as a sink of VOCs. For example, is difficult to determine if chlorinated compounds were originated in the sediments or were adsorbed after production of macro/microalgae or anthropogenic sources and released to the atmosphere during low tides by evaporation.

The compounds produced in sediments are released direct to the atmosphere in coastal sites at low tides; however in deeper water they are released into the water column and may have certain modification (chemical degradation or oxidation, *etc.*) as analysis of seawater did not show as many sulphur containing compounds as sediment did. As well production of VOCs in coastal zones may be higher than open ocean due to the higher input or organic matter with subsequent bacterial degradation.

5.3 Conclusions

- This study showed that SPME coupled with the vacuum sampling system and GC-MS analysis is a sensitive technique to measure *in situ* VOCs in coastal sediments. This methodology allows a large number of VOCs to be quantified simultaneously and permits estimation of the fluxes.

- The sediment type was a major influence on the production rates and the suite of VOCs present. The VOC profile appears to be similar in samples with the same physico-chemical characteristics. For instance, muddy and anoxic sediments are rich in reduced sulphur containing compounds and halogenated VOCs, while sandy areas have more hydrocarbons and BTEX compounds. If these VOCs reflect the active sub-surface biochemical processes, this form of analysis may enable characterisation of the sediment "status" and contamination by particular chemicals.

- Further experimentation would be needed to determine the effect of pollution on the VOC signature. It may also be possible to track sub-surface contamination moving as a non-aqueous phase layer within an aquifer provided the contaminant has some volatility and there is no impermeable barrier between the layer and the surface.

5.4 References

Amaral, O. C., Olivella, L., Grimalt, J. O. and Albaiges, J. (1994). Combined Solvent-Extraction Purge-and-Trap Method for the Determination of Volatile Organic-Compounds in Sediments. *Journal of Chromatography A* **675**(1-2): 177-187.

Andreae, M. O. (1990). Ocean-Atmosphere Interactions in the Global Biogeochemical Sulfur Cycle. *Marine Chemistry* **30**(1-3): 1-29.

Bentley, R. and Chasteen, T. G. (2004). Environmental VOSCs - formation and degradation of dimethyl sulfide, methanethiol and related materials. *Chemosphere* **55**(3): 291-317.

Bianchi, A. and Varney, M. S. (1989). Analysis of Methyl Tert-Butyl Ether and 1,2-Dihaloethanes in Estuarine Water and Sediments Using Purge-and-Trap Gas-Chromatography. *Hrc-Journal of High Resolution Chromatography* **12**(3): 184-186.

Bianchi, A. P., Varney, M. S. and Phillips, J. (1991). Analysis of Volatile Organic-Compounds in Estuarine Sediments Using Dynamic Headspace and Gas-Chromatography Mass- Spectrometry. *Journal of Chromatography* **542**(2): 413-450.

Campillo, N., Aguinaga, N., Vinas, P., Lopez-Garcia, I. and Hernandez-Cordoba, M. (2004). Speciation of organotin compounds in waters and marine sediments using purge-and-trap capillary gas chromatography with atomic emission detection. *Analytica Chimica Acta* **525**(2): 273-280.

Fu, J. H., Ai, X. T., Liu, H. S., Han, D. Q., Chen, D. Y. and Ma, W. Y. (2005). Determination of trace benzene, toluene, ethylbenzene and xylenes in seabed sediments and seawater by purge and trap gas chromatography. *Chinese Journal of Analytical Chemistry* **33**(12): 1753-1756.

Goni, M. A., Yunker, M. B., Macdonald, R. W. and Eglinton, T. I. (2000). Distribution and sources of organic biomarkers in arctic sediments from the Mackenzie River and Beaufort Shelf. *Marine Chemistry* **71**(1-2): 23-51.

Griebler, C. (1997). Dimethylsulfoxide (DMSO) reduction: A new approach to determine microbial activity in freshwater sediments. *Journal of Microbiological Methods* **29**(1): 31-40.

Griebler, C. and Slezak, D. (2001). Microbial activity in aquatic environments measured by dimethyl sulfoxide reduction and intercomparison with commonly used methods. *Applied and Environmental Microbiology* **67**(1): 100-109.

Jonkers, H. M., Koopmans, G. F. and van Gemerden, H. (1998). Dynamics of dimethyl sulfide in a marine microbial mat. *Microbial Ecology* **36**(1): 93-100.

Juttner, F. (1991). Formation of Toluene by Microorganisms from Anoxic Fresh-Water Sediments. *Fresenius Journal of Analytical Chemistry* **339**(10): 785-787.

Kiene, R. P. and Capone, D. G. (1988). Microbial Transformations of Methylated Sulfur-Compounds in Anoxic Salt-Marsh Sediments. *Microbial Ecology* **15**(3): 275-291.

Kiene, R. P. and Taylor, B. F. (1988). Demethylation of Dimethylsulfoniopropionate and Production of Thiols in Anoxic Marine-Sediments. *Applied and Environmental Microbiology* **54**(9): 2208-2212.

Kuran, P., Kubinec, R., Ostrovsky, I. and Sojak, L. (1994). Purge-and-trap injection capillary gas chromatgraphic determination of volatile aromatic hydrocarbons in river sediment. *Journal of Chromatography A*(665): 133-138.

Larroque, V., Desauziers, V. and Mocho, P. (2006). Development of a solid phase microextraction (SPME) method for the sampling of VOC traces in indoor air. *Journal of Environmental Monitoring* **8**(1): 106-111.

Lomans, B. P., den Camp, H., Pol, A. and Vogels, G. D. (1999). Anaerobic versus aerobic degradation of dimethyl sulfide and methanethiol in anoxic freshwater sediments. *Applied and Environmental Microbiology* **65**(2): 438-443.

Mrowiec, B., Suschka, J. and Keener, T. C. (2005). Formation and biodegradation of toluene in the anaerobic sludge digestion process. *Water Environment Research* **77**(3): 274-278.

Mudge, S. M. (2007). Multivariate statistical methods in environmental forensics. *Environmental forensics* **8**(1-2): 155-163.

Roose, P., Dewulf, J., Brinkman, U. A. T. and Van Langenhove, H. (2001). Measurement of volatile organic compounds in sediments of the Scheldt Estuary and the Southern North Sea. *Water Research* **35**(6): 1478-1488.

Sartin, J. H., Halsall, C., Hayward, S. and Hewitt, C. N. (2002). Emission rates of C-8-C15VOCs from seaweed and sand in the inter-tidal zone at Mace Head, Ireland. *Atmospheric Environment* **36**(34): 5311-5321.

Visscher, P. T., Baumgartner, L. K., Buckley, D. H., Rogers, D. R., Hogan, M. E., Raleigh, C. D., Turk, K. A. and Des Marais, D. J. (2003). Dimethyl sulphide and

methanethiol formation in microbial mats: potential pathways for biogenic signatures. *Environmental Microbiology* **5**(4): 296-308.

Visscher, P. T., Quist, P. and Vangemerden, H. (1991). Methylated Sulfur-Compounds in Microbial Mats - Insitu Concentrations and Metabolism by a Colorless Sulfur Bacterium. *Applied and Environmental Microbiology* **57**(6): 1758-1763.

CHAPTER 6. VOLATILE ORGANIC COMPOUNDS IN LIVERPOOL BAY, IRISH SEA.

6.1 Introduction

Oceans act as a sink or reservoir of VOCs (Chester, 1990) and the marine boundary layer is one of the most important places for gas exchange between water/atmosphere (Jones, 1980).

The incidence and distribution of halocarbons and other VOCs in marine water, have been widely studied *e.g.* in South Asian and Western Pacific Oceans (Yokouchi *et al.*, 1997), the Atlantic Ocean baker (Baker *et al.*, 2000), the Northwest Atlantic and Pacific Oceans (Tokarczyk and Saltzman, 2001), the Arctic Ocean (Krysell, 1991), the North Sea (Huybrechts *et al.*, 2000), estuaries (Christof *et al.*, 2002) and bays (Yamamoto *et al.*, 2001). The VOCs distribution and concentration depended greatly on the location and, for biogenic sources, whether or not an algal bloom was present in ocean system or macroalgae in coastal zones. In relation to anthropogenic inputs, concentrations are dependent on the proximity of production near the sampling site.

No studies of the incidence and distribution of these compounds in seawater have been reported in the area of Liverpool Bay or Irish Sea. Liverpool Bay and especially the Mersey River are areas of intense human and industrial activity (Fox *et al.*, 2001). The port and rivers have played a major role in the city development and many industries are next to the river and oil/gas extraction activities occur offshore. This bay is influenced by several rivers including Conwy, Dee, Ribble and Mersey. Tide plays an important role in water mass mixing in this area with ranges up to 10 metres.

The aim of this research was to quantify the distribution of halocarbons and some selected volatile organic compounds which have both natural and anthropogenic sources in the area of Liverpool Bay and Irish Sea.

6.2 Results and discussion

6.2.1 Conditions during sampling

Across the sampling area, water depth varied from 8 to 47 metres. Salinity varied according to the influences of the rivers, with stations far from rivers having higher values (32 to 33) and stations close or in the River Mersey had lower values (19 to 30). Surface water temperature was relatively constant ranging from 5.7 to 7.9°C. A wider fluctuation was observed with air temperature ranging from of 2.4 to 11.7°C. Wind speed, one of the main factors affecting the gas transference, varied from 3.6 to 26.2 m s^{-1}. Atmospheric pressure was uniform (*ca.* 1000 mbar) and solar irradiation reached 868 W m^{-2}. Weather in general was changeable, and this in some ways made it difficult or impossible to follow the planned sampling grid. All the physico-chemical and meteorological data can be found in Appendix 8.

6.2.2 VOCs in surface waters

Seventeen surface seawater samples were collected. Only one sample per station was sampled. Variograms suggest that a classed posting is a better method of displaying the results than contour plots as there was no systematic gradient across the region of interest. The plots were generated with Surfer 8.0 (Golden Software). Fifty eight different compounds were detected and quantified. Concentrations for the entire VOC suite can be found in Appendix 10. Compounds detected were classified as follow:

6.2.2.1 Halocarbons

Twenty one different halogenated compounds were detected during the sampling period in a range of 0.2 to 1,400 ng L^{-1}. The compounds were consistent with the use of chlorinated solvents in industrial processes and biological production. In addition, brominated and iodinated VOCs that are rarely reported as industrial chemicals and are more likely to be produced from biogenic sources were also identified. Some chlorinated compounds (see Figure 6.1a-e) were clearly coincident with riverine inputs especially the River Mersey; these included 1,2-dichloroethane, 1,1,1-trichloroethane, trichloroethene, tetrachloroethene and carbon tetrachloride. Carbon tetrachloride was one of the compounds

whose production was phased out in the Montreal Protocol (Buchmann *et al.*, 2003). However, it is still found in the environment due to its long lifetime in seawater of approximately 30 years (Huhn *et al.*, 2001) and its production from natural sources (see Chapter 3). The mean measured concentration of carbon tetrachloride of 2.3 ng L^{-1} is similar to those reported by Schall *et al.* (1997) and Class *et al.* (1986) in the Atlantic and South Atlantic Ocean respectively.

The remaining halogenated compounds were heterogeneously distributed and are known to be produced from biological sources; these were brominated, iodinated or contained mixed halogens. Table 6.1 shows that halogenated compounds found in this cruise are commonly reported from biogenic sources and have similar concentration with those reported in the literature. However, there are some compounds which were also detected and they might be novel compounds detected in the marine environment such as 2-chloropropane, 1-bromoethane and 1-chlorobutane.

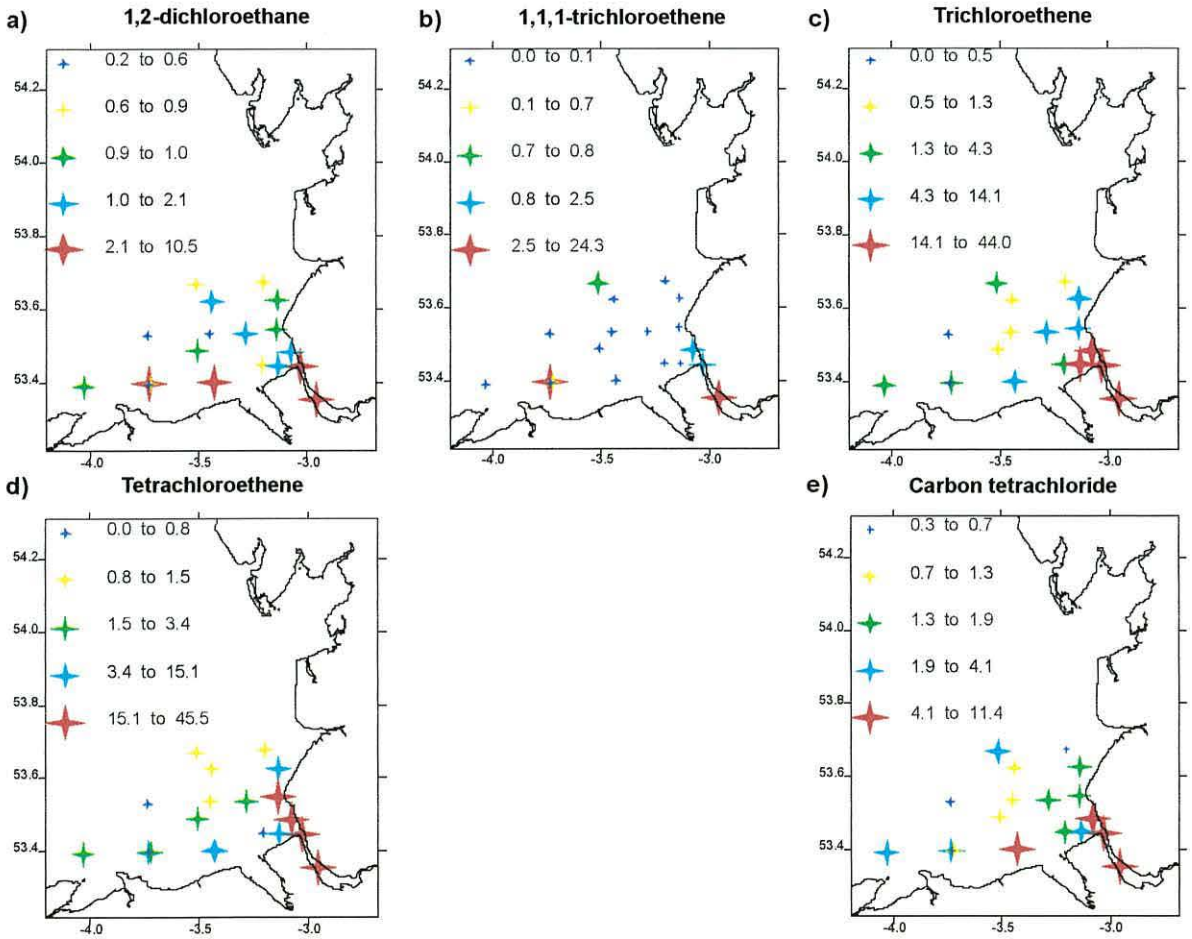


Figure 6.1. Distributions for some chlorinated compounds (ng L^{-1}) across Liverpool Bay and the River Mersey.

Table 6.1. Concentrations of halogenated compounds commonly reported from natural sources in this study compared with others places.

Compound	Range (ng L^{-1})	Mean (ng L^{-1})	Place	Reference
$CHBr_3$	<LoD-4.30	0.74	Irish Sea	This study
	3-7		Arctic Ocean	Krysell (1991)
		0.80	South Atlantic	Class *et al.* (1986)
	0.8- >6		North Atlantic	Class *et al.* (1986)
	<0.03-15		Atlantic Ocean	Schall *et al.* (1997)
	1-100		Eastern Arctic Ocean	Dyrssen and Fogelqvist (1981)
	100.29-110,376		Coastal east Atlantic	Carpenter *et al.* (2000)
CH_3CH_2Br	<LoD -1.42	0.26	Irish Sea	This study
	0.049-20.73		Coastal east Atlantic	Carpenter *et al.* (2000)
CH_3I	<LoD -1.52	0.43	Irish Sea	This study
	1.60-17.75		Coastal east Atlantic	Carpenter *et al.* (2000)
CH_3CH_2I	<LoD -183.06	30.51	Irish Sea	This study
	0.14-49.29		Coastal east Atlantic	Carpenter *et al.* (2000)
$CHBrCl_2$	<LoD -1.68	0.16	Irish Sea	This study
	<0.03-15		Atlantic Ocean	Schall *et al.* (1997)
		0.10	South Atlantic	Class *et al.* (1986)
$CHBr_2Cl$	<LoD -13.98	2.90	Irish Sea	This study
	6.90-12,463		Coastal east Atlantic	Carpenter *et al.* (2000)
	<0.03-15		Atlantic Ocean	Schall *et al.* (1997)
	0.1-2.2		North Atlantic	Class *et al.* (1986)
		0.12	South Atlantic	Class *et al.* (1986)

<LoD: Below the limit of detection

6.2.2.2 BTEXs and mono-aromatic compounds

At least 13 different mono-aromatic compounds were found in a range of 1.5 to 2,900 ng L^{-1}. The sources of BTEX are diverse and, due to this, their distribution is not clear. Some originate from terrestrial sources (combustion of fuel oils, solvents, *etc.*) and also from oil and gas extraction facilities in the Irish Sea; the high maritime traffic of fossil fuel powered vessels in this particular area may also contribute. Selected distribution plots are shown in Figure 6.2a-i. Results from the Menai Strait (see Chapter 3), an isolated portion of the Irish Sea ranged between 0.038 to 4,282 ng L^{-1}. Gschwend *et al.* (1982) and Mantoura *et al.* (1982) have reported a maximum concentration of 500 ng L^{-1} in coastal waters ostensibly free from anthropogenic inputs. However, Marti *et al.* (2001) found aromatic hydrocarbons in surface seawater in the North-eastern Atlantic in a range of 23 to 68 pg L^{-1}, values very low in comparison with that found in the Irish Sea. The amounts found at each place depend intimately on local contamination and the uses of the water: the highest concentrations were found near the river mouths and close to the port activities. Lowest concentrations were found in cleaner waters towards the west.

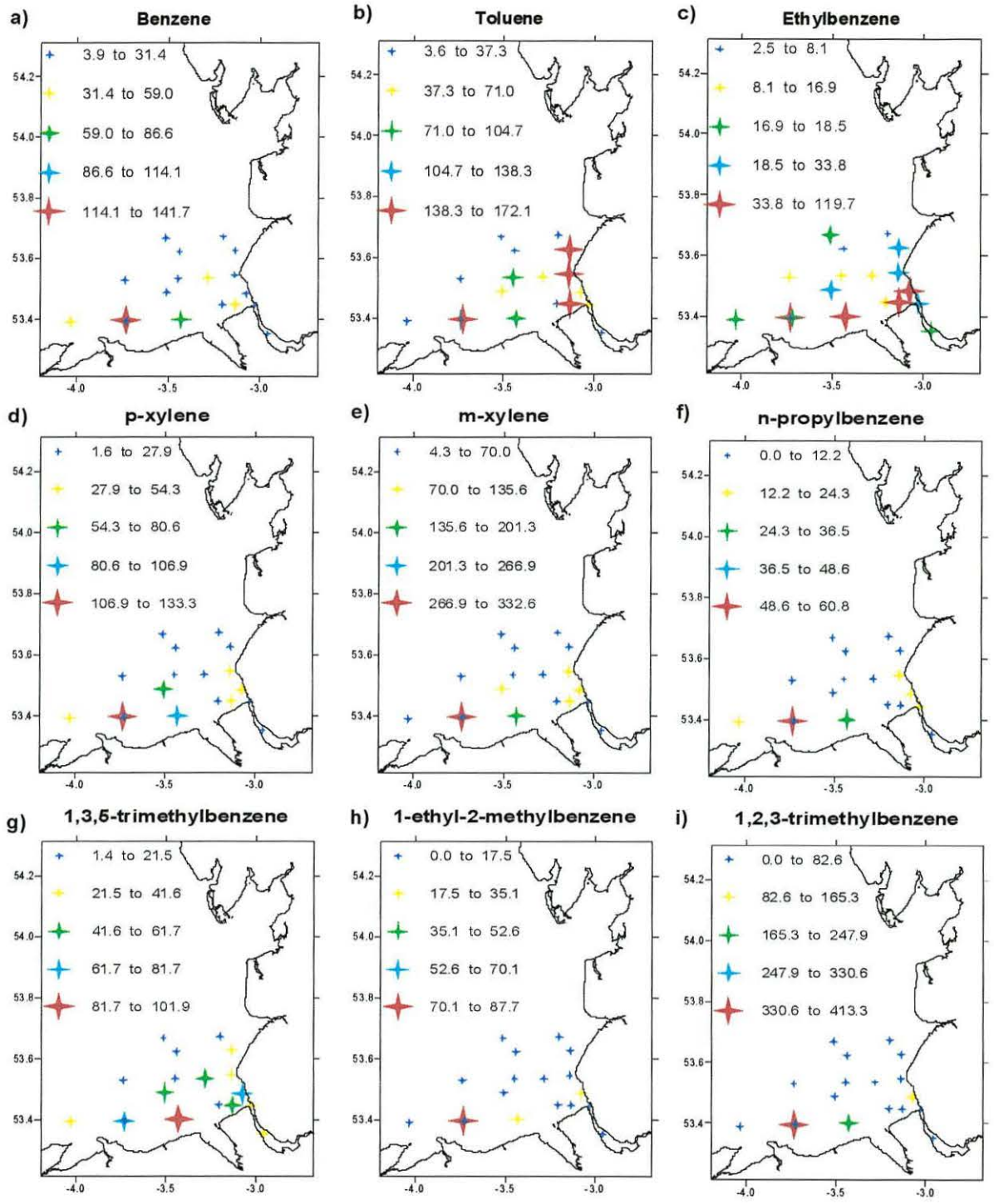


Figure 6.2. Distributions for some BTEXs and monoaromatic compounds (ng L^{-1}) across Liverpool Bay and the River Mersey.

6.2.2.3 NMHC and others VOCs

Distribution plots for some hydrocarbons detected are shown in Figure 6.3a-l. Their concentrations ranged between 0.6 and 15,800 ng L^{-1}. Results in the relatively clean area of the Menai Strait had values much lower than those found in this study (see Chapter 3), suggesting a greater impact of anthropogenic hydrocarbons in the Liverpool Bay area.

In this study n-C_5 correlated with other small hydrocarbons such as cyclohexane (R=0.886) and C_6 branched (R=0.793) and they behaved differently to longer chain hydrocarbons such as n-C_9, n-C_{10}, n-C_{11} and branched aliphatic hydrocarbons. McDonald *et al.* (1988) suggested that hydrocarbons n-C_6 to n-C_{10} are the dominant alkanes in areas effected by petroleum sources and the n-C_5 has a presumably biogenic source. Thurman (1985) attributed the presence of n-C_5 and n-C_7 to marine phytoplankton and n-C_8, n-C_9, n-C_{10} and n-C_{11} were concentrated in areas with activities involving oil.

Isoprene (Figure 6.3a) was found in a range between 0.62 to 14.24 ng L^{-1}, with a mean concentration of 3.49 ng L^{-1}. Similar quantities (0.66 to 3.45 ng L^{-1}) of isoprene were detected by Milne *et al.* (1995) in the Gulf Stream off the Florida coast. Isoprene was reported as an indicator of phytoplankton presence by Yokouchi *et al.* (1999). However, no correlation was found with isoprene and chlorophyll *a* in this study (R=0.063, P=0.798). Gist and Lewis (2006) found alkenes, such as ethene (0.47 to 26.62 ng L^{-1}) and propene (0.54 to 13.86 ng.L^{-1}), in the North Sea. Their results demonstrated that their marine concentrations and the processes controlling their production are heterogeneous.

Aldehydes detected were hexanal (2.22 to 526.23 ng L^{-1}), heptanal (<LoD to 62.98 ng L^{-1}) and octanal (<LoD to 332.69 ng L^{-1}). Distribution patterns are heterogeneous, not showing a clear source or similarities among them (see Figure 6.3h-j). Jalliffiermerlon *et al.* (1991) suggested that productions of aldehydes are via degradation of phytoplankton fatty acids, and also found a good correlation with pigments. No correlation was found with pigments and presence of aldehydes in this study. Bianchi and Varney (1998) detected aldehydes in total concentrations of 620 to 7,205 ng L^{-1} suggesting a biogenic production by marine phytoplankton and in minor extent an input from anthropogenic sources. This range is much higher than the range of total aldehydes in this research of 3.16 to 216.06 ng L^{-1}. The low range might be due to the sampling was performed before the main algal bloom and higher concentration might be expected later.

The terpenes found were α-pinene (1.03 to 103.96 ng L^{-1}) and limonene (4.97 to 164.90 ng L^{-1}). Bianchi and Varney (1993) stated that presence of limonene is basically

due to run-off from terrestrial sources. However there were also detected in macroalgae cultures (see chapter 4)

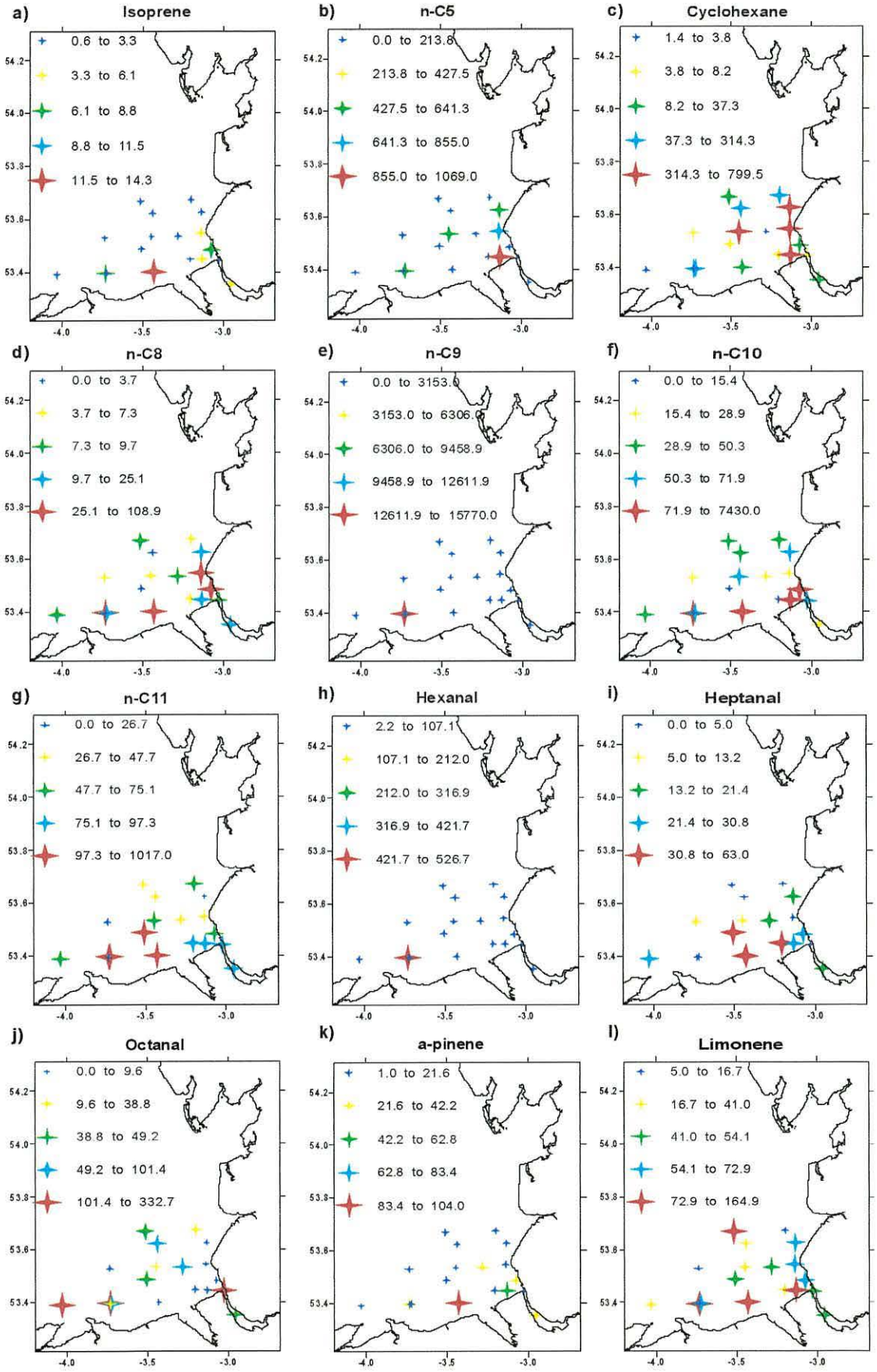


Figure 6.3. Distributions for some NMHC and oxygenated compounds (ng L^{-1}) across Liverpool Bay and the River Mersey.

6.2.2.4 Sulphur containing compounds

Dimethyl sulphide was the only sulphur containing compound detected (Figure 6.4). Its concentration ranged between 1.7 and 19 ng L^{-1} with a mean concentration of 5.6 ng L^{-1}. It is well known that this compound is produced by marine phytoplankton (Simo, 2001) and higher concentrations might be expected during algal bloom periods. Turner *et al.* (1996) measured a concentration of 8.06 ng L^{-1} during the winter time and 1,550 ng L^{-1} during the spring bloom in May in the North Sea. Other investigators have measured 124 ng L^{-1} in Antarctic waters (Turner *et al.*, 1995) and 68 ng L^{-1} in the East Atlantic (Andreae *et al.*, 2003). The concentrations of DMS are strongly influenced by the seasons. This work was conducted in early spring and suggests the early stages of a phytoplankton bloom. Higher concentration may be expected during May with presence of *Phaeocystis* and other microflagellates. Good correlations were found by Shenoy *et al.* (2006) between the phytoplankton population and chlorophyll *a* : phaeopigments ratios and DMS production; no correlation (R=0.013, P=0.968) was found in this study between chlorophyll *a* and DMS concentrations. Results from the Menai Strait (see Chapter 3) suggested a large seasonal variation thoughtout the year, with very low values during the winter and high values during the algal bloom period ranging from 0.078 to 71 ng L^{-1}. A recent review of DMS in seawater by Buckley and Mudge (2004) showed there are wide spatial differences in DMS concentrations and it might not practical to compare results from different places.

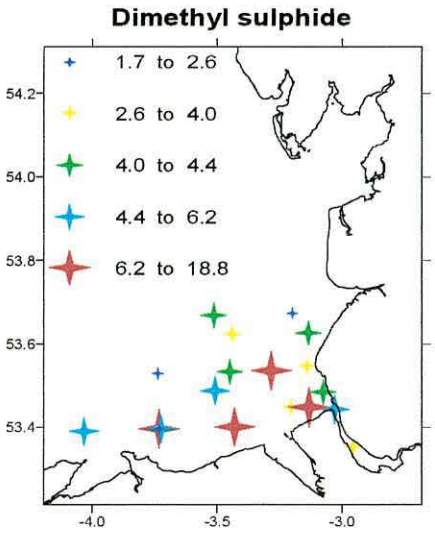


Figure 6.4. Distribution of DMS (ng L^{-1}) across Liverpool Bay and the River Mersey.

6.2.3 Surface seawater sampling for pigments

During the period of sampling (end of March) chlorophyll *a* concentrations were low (1.50 to 8.91 μg L^{-1}) compared to peak blooms periods a month later. The distributions of selected marine pigments are presented in Figure 6.5. Satellite images from Remote Sensing Data Analysis Service – RSDAS - (Figure 6.6) for the corresponding period (29th March – 4th April 2006) were obtained. The presence of clouds during the exact dates of sampling meant no coverage was available but these are within a few days. These images showed concentrations of chlorophyll *a* between 2 to 8 μg L^{-1}. However, is possible to see higher values in the coastal zone, although this may be due to the high suspended solid loadings coming from the rivers or resuspension in this area and not necessarily to a high primary production. Despite that, values of chlorophyll *a* were similar to the ones found in this investigation.

Major pigments such as chlorophyll *a* (1.50-8.91 μg L^{-1}), chlorophyll *b* (0.06-037 μg L^{-1}), *β,β*-carotene (0.02-0.10 μg L^{-1}) and fucoxanthin (0.05-0.72 μg L^{-1}) were present in all the samples. Minor pigments such as chlorophyllide *a* (0.10-1.46 μgL^{-1}), 19'-butanoyloxyfucoxanthin (0.48-4.42 μg L^{-1}), 19'-hexanoyloxyfucothanthin (0.11-0.73 μg L^{-1}), cis-19'-hexanoyloxyfucothanthin (0.11-0.79 μg L^{-1}), diadinoxanthin (0.04-0.17 μg L^{-1}), diatoxanthin (0.01-0.22 μg L^{-1}) and chlorophyll allomer (0.10-0.82 μg L^{-1}) were also detected.

The findings of Gowen *et al.* (2000) in Liverpool Bay and Irish Sea suggest that the main phytoplankton bloom occurs at the beginning of April and lasts to the middle of May according to the chlorophyll *a* values. Concentrations of chlorophyll *a* during the spring bloom in coastal and offshore waters of the western Irish Sea can reach 23 and 16 μg L^{-1} respectively; values of up to 44 μg L^{-1} in Liverpool Bay, dominated by *Phaeocystis* and other microflagellates (Gowen and Stewart, 2005), also occur. The small concentrations of some accessory pigments (chlorophyll *b*, fucoxanthin, diadinoxanthin, diatoxanthin, *etc.*) suggest that the phytoplankton were at an early stage of bloom development and may be principally diatoms.

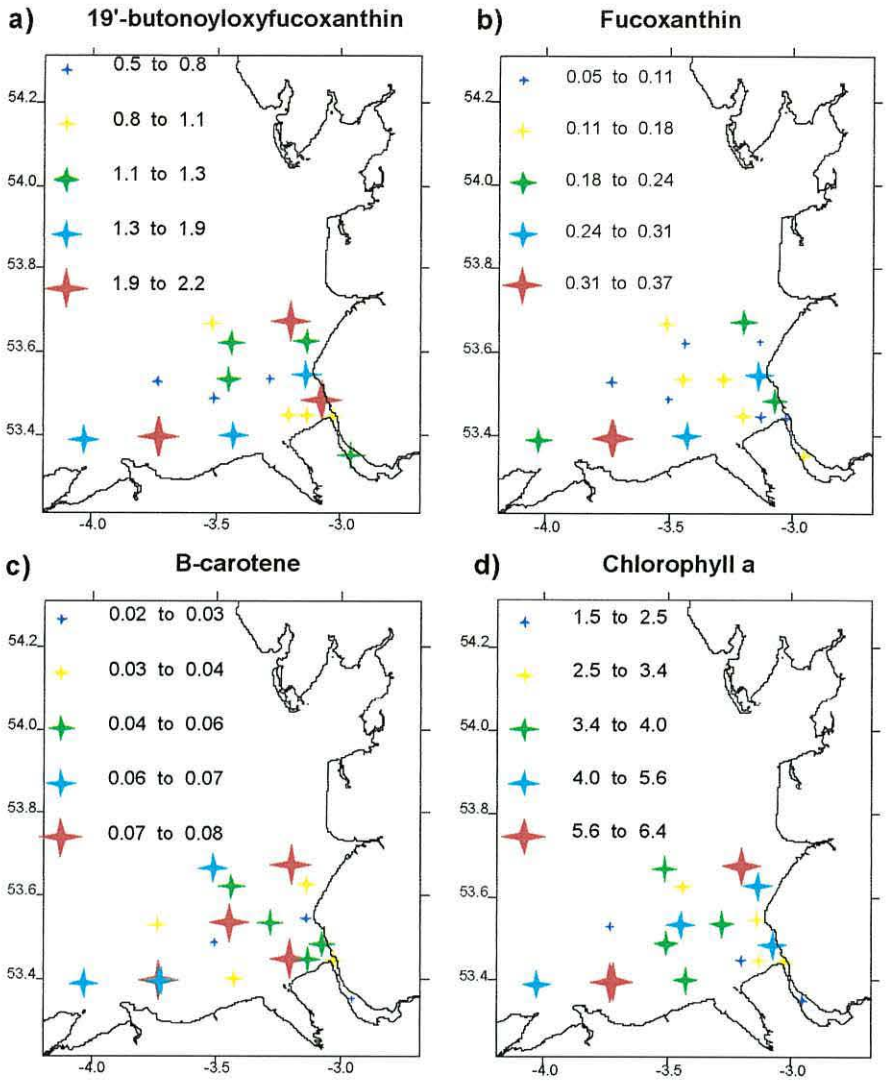
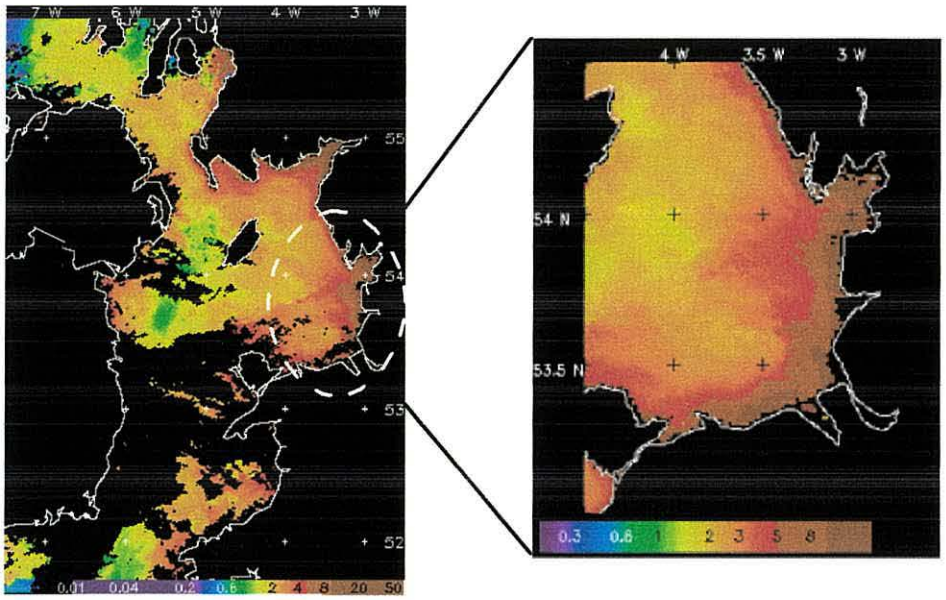


Figure 6.5. Distribution of the main pigments detected during the sampling period (μg L^{-1}). a) 19'butanoyloxyfucoxanthin, b) Fucoxanthin, c) *β,β*-carotene and d) Chlorophyll *a*.

a)



b)

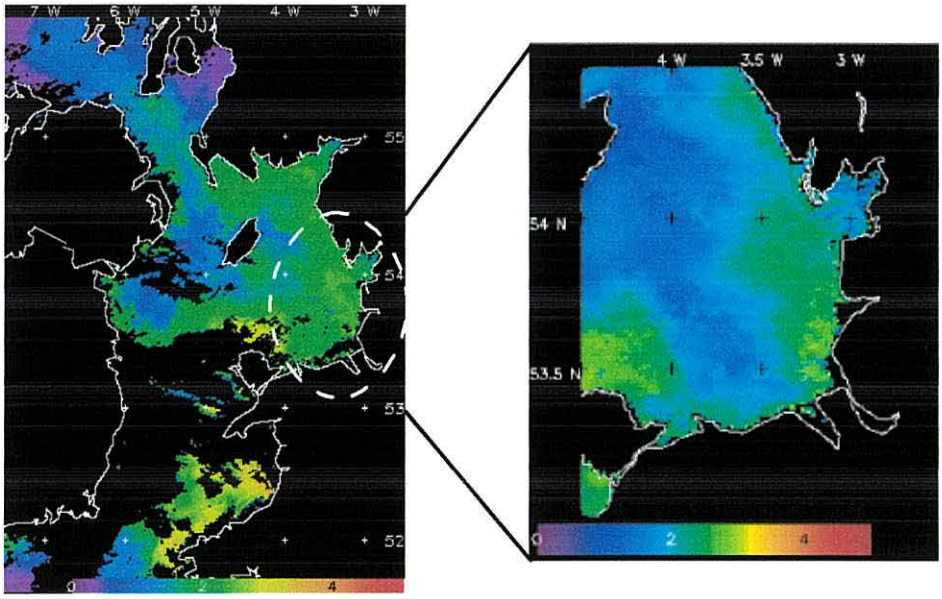


Figure 6.6. Satellite image of a) chlorophyll *a* (μg L^{-1}) and b) suspended particulate matter (mW cm^{-2} μm^{-1} sr^{-1}) for the period 29th March – 4th April 2006. Satellite data were acquired and processed by NERC Earth Observation Data Acquisition and Analysis Service (NEODAAS: www.neodaas.ac.uk).

6.2.4 Samples variability

6.2.4.1 VOCs variability

In order to measure the variability of VOCs concentrations, three samples were collected at station 2 on different days during the sampling period. The concentrations of VOCs in surface water were highly variable with a relative standard deviation (RSD%) of ~ 380% although these differences were not unexpected as the VOCs fluxes are highly affected by physicochemical variables such as wind speed (Liss *et al.*, 1993) which varied considerably over this period. For instance, the highest concentrations of hydrocarbons and BTEXs were coincident with high solar irradiation and low wind speeds; the opposite was found for halogenated compounds. This suggests different sources, mechanisms of formation or different physical and chemical properties. The meteorological conditions also lead to different stripping mechanisms.

6.2.4.2 Pigment variability

The same sampling procedure was followed to see the variability of pigments at the same station. The variability ranged from 11 to 170 RSD% being the lowest values for major pigments and higher values for minor pigments. This might be due to mixing of water masses with different properties under the influence of tides. Another factor is the influence of the river's discharge near this station, diluting and mixing the water.

6.2.5 Statistical analysis

Principal Component Analysis (PCA) was employed as a tool to investigate the relationships among compounds. The concentrations of the VOCs analyzed were standardized using proportions and, since most of them were not normally distributed, a logarithmic transformation was performed.

6.2.5.1 Halocarbon sources

The loadings plot for the halocarbons alone is shown in Figure 6.7. The results show that compounds such as carbon tetrachloride, tetrachloroethene, trichloroethene, 1,2-dichloroethane and 1,1,1-trichloroethane clearly separate on PC1 from the other (natural–source) halocarbons. From the scores plot (inset to Figure 6.7) is possible to see a gradient of different compounds with sampling sites in the River Mersey characterized by the chlorinated solvents above; a group of samples characterized by having bromoform, DMS and 2-chloropropane were seen in the coastal environment. A third offshore area had a diverse variety of halogenated compounds brominated and iodinated with a primarily biogenic source.

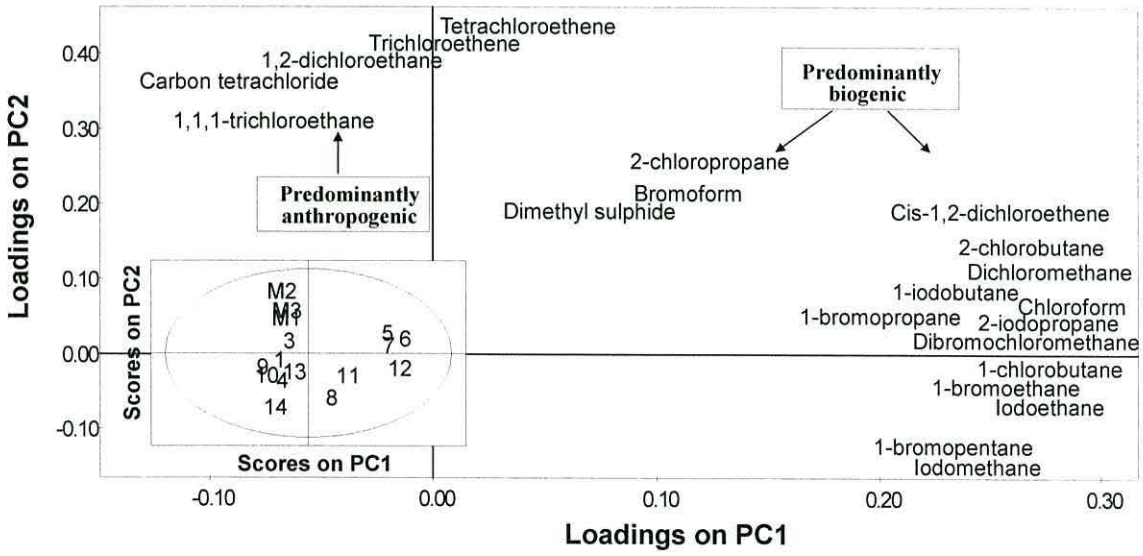


Figure 6.7. PCA loadings plot for halogenated compounds showing a separation on the first major axis of those compounds from biogenic or anthropogenic sources. Scores plot are included inside the figure.

Figure 6.8 was done using the codes derived from the quadrants of the score plot in Figure 6.7. It shows the areas where VOCs have major presence or concentrations. The area in blue is characterized for having a major presence of heavier hydrocarbons (from C_9 up to C_{11}) and coincides with the location of oil platforms. The zone in red exhibits a higher concentration and presence of iodinated, brominated and lighter hydrocarbons (C_5-C_8). The zone in yellow has a main presence of DMS, toluene and terpenes probably coming from sediments. The green zone corresponding to area of the rivers shows the higher presence of chlorinated solvents, BTEXs and aldehydes possibly coming from the industrial area placed in the River Mersey.

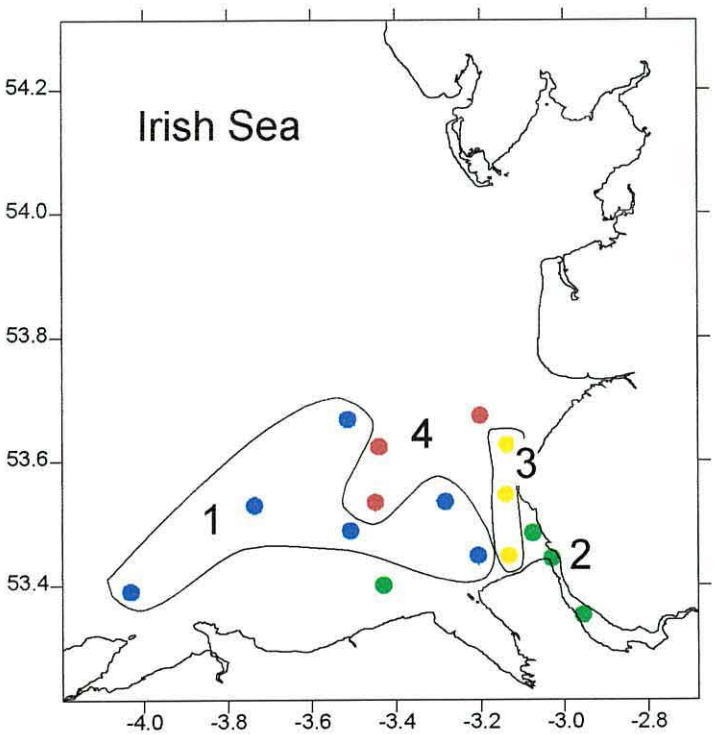


Figure 6.8. Scores values obtained from the first two components in a PCA analysis including all the VOCs found plotted on the map.

6.2.5.2 Correlation with pigments

Chlorophyll *a* is usually used as an indicator for phytoplankton, one of the main producers of halocarbons in the open oceans (Tokarczyk and Moore, 1994). Although it is improbable that chlorophyll *a* is directly involved in the marine production of halocarbons, it was found that it could be used as an indicator for the biogenic production of these compounds (Schall *et al.*, 1997). The correlation between chlorophyll *a* and iodocarbons is not high (Schall *et al.*, 1997). However, in the surface water of the Southern North Sea. Liss *et al.* (1994) found a correlation between iodomethane and chlorophyll *a* concentrations. Moore *et al.* (1996) did not find a correlation between chlorophyll and methyl chloride. Connan *et al.* (1997) observed a good correlation between the plankton and chlorophyll *a* concentration and suggested that the occurrence of bromocarbons in coastal zones is associated with phytoplankton growth or simply their presence. The correlation between halocarbons might indicate the same sources and origins; good correlations have been found among bromocarbons compounds by Yokouchi *et al.* (1997) and Schall *et al.* (1997) proving the same biogenic origin and mechanism of formation. PCA was performed using the halogenated compounds and the marine phyto-pigments. In Figure 6.9 it is possible to see the projections of those compounds from biogenic sources such as bromoform, dimethylsulphide, *etc* and the major pigments such as chlorophyll *a*, fucoxanthin, *etc*. Interestingly, the degradation pigments such as phaeophytin *a* and chlorophyllide *a* correlated with the chlorinated solvents predominantly produced by anthropogenic sources. This correlation may suggest that those chemical might be produced, in part, by senescent phytoplankton cells, zooplankton faecal pellets (grazing activity) or due to the presence of greater amounts of terrestrial detritus in the river area.

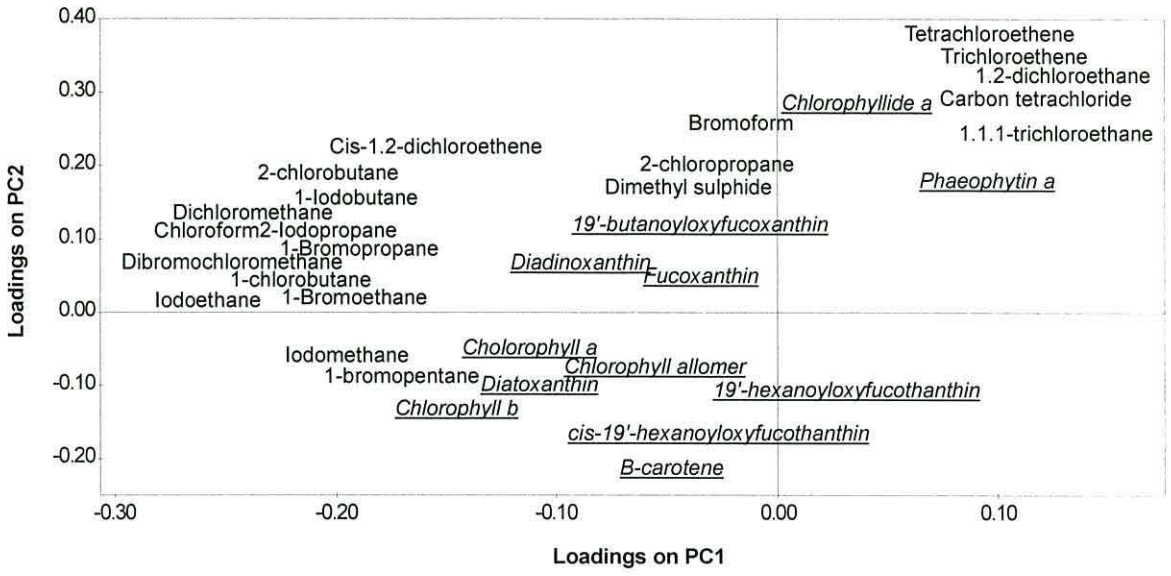


Figure 6.9. PCA Loadings plot for halogenated compounds and pigments (underlined and italics).

6.2.6 Day and night sampling

Samples for VOCs and pigments analysis were collected over a day/night cycle at station 15 (see Figure 2.3). Meteorological as well physico-chemical parameters were recorded at the time that the samples were taken. The sampling period started at midday and finished at 05:00 AM the following morning. The sampling interval was three hours except for the sample between midnight and morning with a gap of 5 hours.

Figure 6.10 shows how some VOCs behaved during the day/night sampling. Pentane behaved differently to the C_8 to C_{11} hydrocarbons (Figure 6.10e); its concentration decreased considerably from day to night. C_8 and C_9 maintained their concentration during the sampling; C_{10} and C_{11} correlated well, with a lowering of their concentration during the day and relatively constant through the night. The differences among the hydrocarbons might be due to different sources or due to the lighter hydrocarbons being influenced by sunlight or produced during photosynthesis.

BTEXs are more likely to be produced by anthropogenic sources. However, toluene behaved differently to other BTEXs (Figure 6.10c) and this might be due to its biological production in anoxic environments as well anthropogenic sources. It has been reported by Mrowiec *et al.* (2005) that toluene can be produced during the acidity phase of anaerobic

degradation in sludge; similar process may happen with anoxic sediments or micro-anaerobic sites in the water column.

The concentrations of some halogenated compounds decreased dramatically after dark (Figure 6.10d). Similar results were found by Ekdahl *et al.* (1998) in a diurnal study and concluded that it was due to losses to the atmosphere. Dimethylsulphide (Figure 6.10d) did not vary significantly during the day cycle and it seems to not be affected by day and night transitions. Compounds which were identified as chlorinated solvents such as carbon tetrachloride did not vary considerably throughout the sampling. Marine phytopigments did not correlate with the production of VOCs. Figure 6.10b shows that they are inversely correlated with tide cycle, probably owing to water masses movement with different characteristics. A CTD cast at the station (see Figure 6.11) revealed the influences of the river inputs, with water with higher temperature and low salinity.

Factor such as water and air temperature, wind speed, solar irradiation and tide height are shown in Figure 6.10a.

In order to see if these differences in concentration through the day are due to physical or biological factors, PCA was performed (Figure 6.12). The VOC's concentrations were standardized using proportions (to avoid concentration effect) and the values of physico-chemical parameters and pigments were used without modifications. Since the VOCs were normally distributed, no further transformations were necessary. PCA with VOCs showed a day/night pattern of distribution on PC1.

Iodinated, brominated, light hydrocarbons and some chlorinated compounds, previously identified as predominantly from biogenic sources, correlated well with solar irradiation. This suggests that some of them might be produced as a product of photoproduction or photodegradation as well by photosynthesis. Bromoform correlated with tide. At high tide the macroalgae near to the coast are covered with water and compounds, especially bromoform, are released into the water (Carpenter and Liss, 2000). Chlorophyll *a* and pigments in general did not have a clear relationship with the VOCs measured.

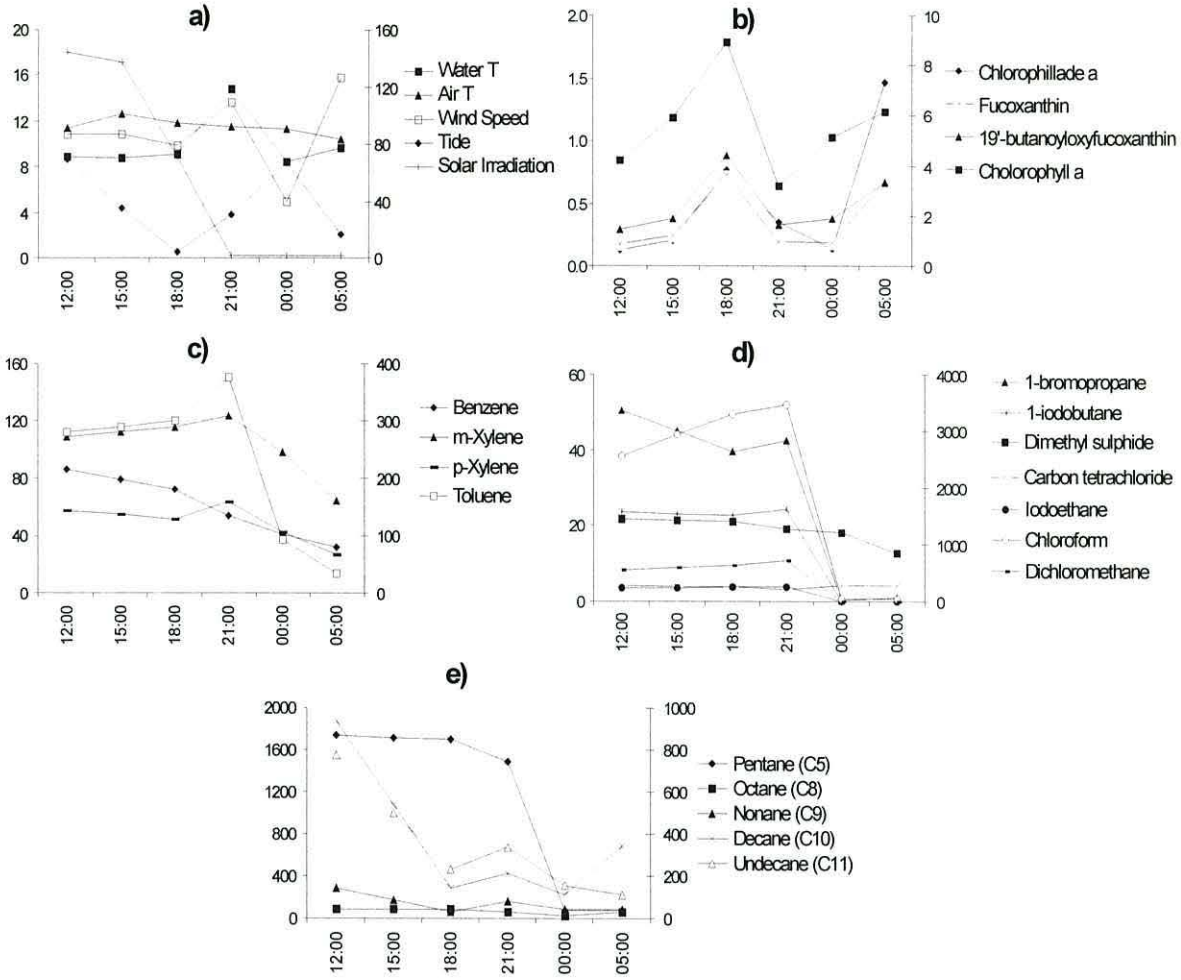


Figure 6.10. Tendencies during the day and night sampling. a) Physico-chemical and meteorological parameters, solar irradiation (W m^{-2}) right axis and seawater, air temperature (°C) and wind speed (m s^{-1}) left axis. b) Some marine photopigments (μg L^{-1}), Chlorophyll *a* and 19'-butanoeloxyfucoxanthin plotted against right axis. c to e) Selected VOCs in ng L^{-1} (iodoethane, chloroform, dichloromethane, C_8 to C_{11} and toluene are plotted against the right axis).

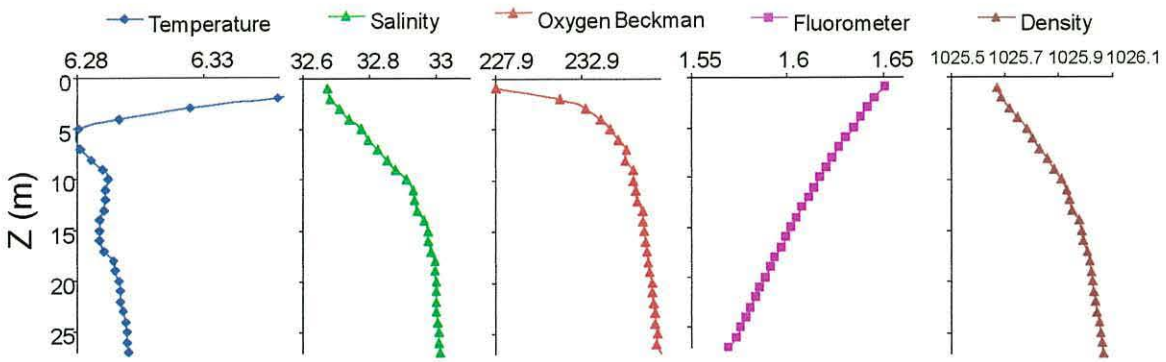


Figure 6.11. Depth Profiles for temperature (°C), salinity (PSU), oxygen Beckman (μmol Kg^{-1}), fluorometer (V) and density (Kg m^{-3}) obtained from the CTD cast at the station 9; showing the influences of fresh water coming from the rivers in Liverpool Bay.

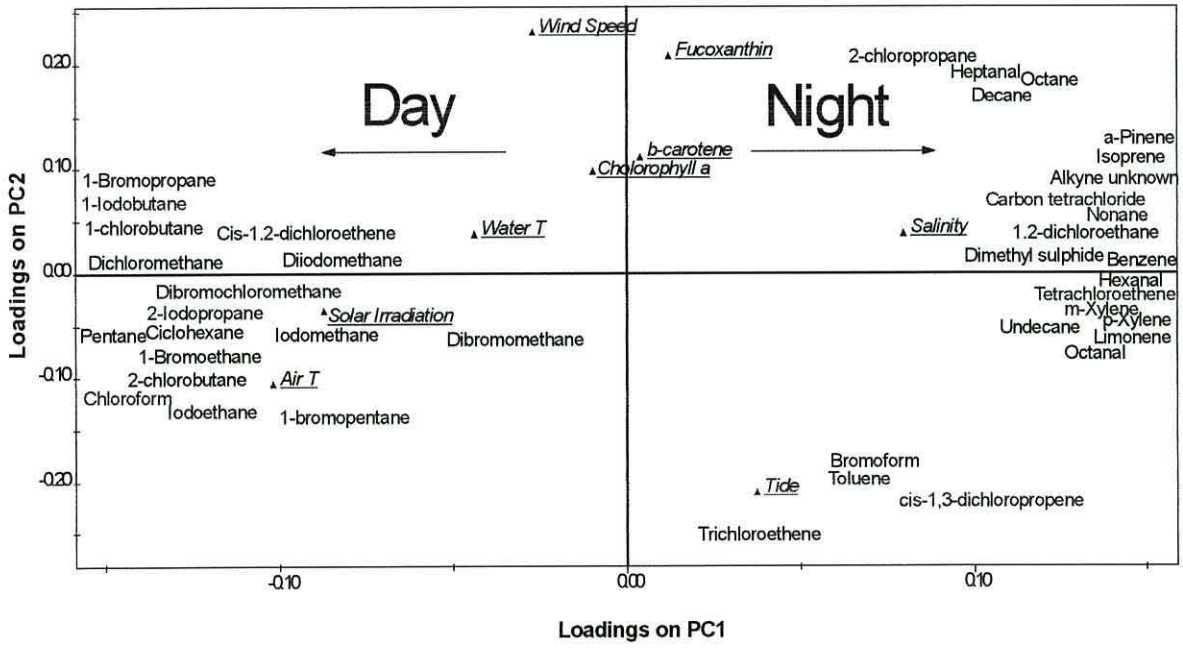


Figure 6.12. PCA analysis showing how physicochemical, meteorological and some pigments (underlined and italics) correlate with the distribution and production of some selected VOCs for a day/night pattern.

Due to Liverpool Bay waters circulate through the Menai Strait this might be an explanation of the presence of some chlorinated solvents possible originated from anthropogenic sources. However, due to dilution and an increment in the salinity from the river inputs to the sea the compounds the solubility might be reduced and possibly released to the atmosphere.

The inputs of VOCs from terrestrial sources can especially be seen near to the coast in highly urbanized and industrialized areas. Water can be contaminated with VOCs coming from diffuse and punctual sources such as wet and dry deposition, industrial wastes, sewage treatment works, oil spills, etc. Chlorinated solvents coming from industrial sources are ubiquitous and are known to be widely used in industrial processes for organic synthesis and solvents. They can also be produced as sub-products of water disinfection (e.g. chloroform). Their river inputs in this area are more likely to be anthropogenic in origin rather than biogenic, especially in the River Mersey. Compounds such as carbon tetrachloride, tetrachloroethene and 1,1,1-trichloroethane are compounds that were phased out or restricted and consequently their production and use have been minimised during the last decade; however they can still be detected in this area, proving that they are yet being used or produced.

When sampling during different seasons is so important to consider that the presence of phytoplankton blooms may change the amounts of halogenated compounds produced, and for instance production of some compounds with mixed sources (natural and anthropogenic) can be enhanced from natural production being equal or higher to anthropogenic sources.

Is important to highlight that the correlation of VOCs with pigments presence is not easy to achieve, and this might be due to once they are released they can be quickly degraded, transformed into other chemical or transferred into the atmosphere, so when sampling is done not a real picture can be performed. However if the stripping mechanisms are known and a good correlation with pigments can be done, satellite images of chlorophyll can be used as a predictor of VOCs in open oceans.

6.3 Conclusions

- Liverpool Bay, especially the area influenced by the River Mersey have significant concentrations of halogenated compounds such as 1,2-dichloroethane, 1,1,1-trichloroethane, trichloroethene, tetrachloroethene and carbon tetrachloride which are widely used as a industrial solvents.

- Biogenic sources of VOCs, with special emphasis on the halogenated ones, may also be an important source in this area. These results indicated that three halogenated compounds might be novel to the marine environment; these are 2-chloropropane, 1-bromoethane and 1-chlorobutane.

- Sampling in the same station and with different conditions may dramatically affect the presence of VOCs basically affected by factors such a wind speed, day light and tide.

- Day and night sampling, showed that for this area, halogenated as well other VOCs typically from natural sources decreased noticeably after sunset; this can be explained due to lower production or transference of these compounds to the atmosphere during the night.

- Marine pigments may indicate the presence of phytoplankton but do not have a direct relationship with VOCs presence in this survey.

- SPME is a good technique for ship borne analysis and enables quantification of wide range of VOCs in seawater at low concentrations.

- Further seasonal sampling is needed to understand the annual processes of production and distribution of volatile organic compounds in the Irish Sea.

6.4 References

Andreae, M. O., Andreae, T. W., Meyerdierks, D. and Thiel, C. (2003). Marine sulfur cycling and the atmospheric aerosol over the springtime North Atlantic. *Chemosphere* **52**(8): 1321-1343.

Baker, A. R., Turner, S. M., Broadgate, W. J., Thompson, A., McFiggans, G. B., Vesperini, O., Nightingale, P. D., Liss, P. S. and Jickells, T. D. (2000). Distribution and sea-air fluxes of biogenic trace gases in the eastern Atlantic Ocean. *Global Biogeochemical Cycles* **14**(3): 871-886.

Bianchi, A. P. and Varney, M. S. (1993). Sampling and Analysis of Volatile Organic-Compounds in Estuarine Air by Gas-Chromatography and Mass-Spectrometry. *Journal of Chromatography* **643**(1-2): 11-23.

Bianchi, A. P. and Varney, M. S. (1998). Volatile organic compounds in the surface waters of a British estuary. Part 1. Occurrence, distribution and variation. *Water Research* **32**(2): 352-370.

Buchmann, B., Stemmler, K. and Reimann, S. (2003). Regional emissions of anthropogenic halocarbons derived from continuous measurements of ambient air in Switzerland. *Chimia* **57**(9): 522-528.

Buckley, F. S. E. and Mudge, S. M. (2004). Dimethylsulphide and ocean-atmosphere interactions. *Chemistry & Ecology* **20**(2): 73-95.

Carpenter, L. J. and Liss, P. S. (2000). On temperate sources of bromoform and other reactive organic bromine gases. *Journal of Geophysical Research-Atmospheres* **105**(D16): 20539-20547.

Carpenter, L. J., Malin, G., Liss, P. S. and Kupper, F. C. (2000). Novel biogenic iodine-containing trihalomethanes and other short-lived halocarbons in the coastal East Atlantic. *Global Biogeochemical Cycles* **14**(4): 1191-1204.

Chester, R. (1990). Dissolved gases in sea water. *Marine Geochemistry*. London, Unwin Hyman Ltd: 233-269.

Christof, O., Seifert, R. and Michaelis, W. (2002). Volatile halogenated organic compounds in European estuaries. *Biogeochemistry* **59**(1-2): 143-160.

Class, T., Kohnle, R. and Ballschmiter, K. (1986). Chemistry of Organic Traces in Air .7. Bromochloromethanes and Bromochloromethanes in Air over the Atlantic-Ocean. *Chemosphere* **15**(4): 429-436.

Connan, O., LeCorre, P. and Marty, Y. (1997). Formation of dibromomethane and bromodichloromethane by phytoplankton in the coastal waters of the Western English Channel. *Comptes Rendus De L Academie Des Sciences Serie Ii Fascicule a- Sciences De La Terre Et Des Planetes* **324**(1): 25-31.

Dyrssen, D. and Fogelqvist, E. (1981). Bromoform Concentrations of the Arctic Ocean in the Svalbard Area. *Oceanologica Acta* **4**(3): 313-317.

Ekdahl, A., Pedersen, M. and Abrahamsson, K. (1998). A study of the diurnal variation of biogenic volatile halocarbons. *Marine Chemistry* **63**(1-2): 1-8.

Fox, W. M., Connor, L., Copplestone, D., Johnson, M. S. and Leah, R. T. (2001). The organochlorine contamination history of the Mersey estuary, UK, revealed by analysis of sediment cores from salt marshes. *Marine Environmental Research* **51**(3): 213-227.

Gist, N. and Lewis, A. C. (2006). Seasonal variations of dissolved alkenes in coastal waters. *Marine Chemistry* **100**(1-2): 1-10.

Gowen, R. J., Mills, D. K., Trimmer, M. and Nedwell, D. B. (2000). Production and its fate in two coastal regions of the Irish Sea: the influence of anthropogenic nutrients. *Marine Ecology-Progress Series* **208**: 51-64.

Gowen, R. J. and Stewart, B. M. (2005). The Irish Sea: Nutrient status and phytoplankton. *Journal of Sea Research* **54**(1): 36-50.

Gschwend, P. M., Zafiriou, O. C., Mantoura, R. F. C., Schwarzenbach, R. P. and Gagosian, R. B. (1982). Volatile Organic-Compounds at a Coastal Site .1. Seasonal-Variations. *Environmental Science & Technology* **16**(1): 31-38.

Huhn, O., Roether, W., Beining, P. and Rose, H. (2001). Validity limits of carbon tetrachloride as an ocean tracer. *Deep-Sea Research Part I-Oceanographic Research Papers* **48**(9): 2025-2049.

Huybrechts, T., Dewulf, J., Moerman, O. and Van Langenhove, H. (2000). Evaluation of purge-and-trap-high-resolution gas chromatography-mass spectrometry for the determination of 27 volatile organic compounds in marine water at the ng l(-1) concentration level. *Journal of Chromatography A* **893**(2): 367-382.

Jalliffiermerlon, E., Marty, J. C., Denant, V. and Saliot, A. (1991). Phytoplanktonic Sources of Volatile Aldehydes in the River Rhone Estuary. *Estuarine Coastal and Shelf Science* **32**(5): 463-482.

Jones, E. P. (1980). Gas Exchange. *Air-Sea interaction (instrument and methods)*. F. Dobson, L. Hasse and R. Davis. New York, Plenum Press.: 433-445.

Krysell, M. (1991). Bromoform in the Nansen Basin in the Arctic-Ocean. *Marine Chemistry* **33**(1-2): 187-197.

Liss, P. S., Watson, A. J., Liddicoat, M. I., Malin, G., Nightingale, P. D., Turner, S. M. and Upstillgoddard, R. C. (1993). Trace Gases and Air-Sea Exchanges. *Philosophical Transactions of the Royal Society of London Series a-Mathematical Physical and Engineering Sciences* **343**(1669): 531-541.

Liss, P. S., Watson, A. J., Liddicoat, M. I., Malin, G., Nightingale, P. D., Turner, S. M. and Upstill-Goddard, R. C. (1994). Chapter 12: Trace gases and air-sea exchanges. *Understanding the North Sea system*. H. Charnock, K. R. Dyer, J. M. Huthnance, P. S. Liss, J. H. Simpson and P. B. Tett. London, Chapman & Hall for The Royal Society: 153-163.

Mantoura, R. F. C., Gschwend, P. M., Zafiriou, O. C. and Clarke, K. R. (1982). Volatile Organic-Compounds at a Coastal Site .2. Short-Term Variations. *Environmental Science & Technology* **16**(1): 38-45.

Marti, S., Bayona, J. M. and Albaiges, J. (2001). A potential source of organic pollutants into the Northeastern Atlantic: The outflow of the Mediterranean deep lying waters through the Gibraltar Strait. *Environmental Science & Technology* **35**(13): 2682-2689.

McDonald, T. J., Kennicutt, M. C. and Brooks, J. M. (1988). Volatile Organic-Compounds at a Coastal Gulf of Mexico Site. *Chemosphere* **17**(1): 123-136.

Milne, P. J., Riemer, D. D., Zika, R. G. and Brand, L. E. (1995). Measurement of Vertical-Distribution of Isoprene in Surface Seawater, Its Chemical Fate, and Its Emission from Several Phytoplankton Monocultures. *Marine Chemistry* **48**(3-4): 237-244.

Moore, R. M., Groszko, W. and Niven, S. J. (1996). Ocean-atmosphere exchange of methyl chloride: Results from NW Atlantic and Pacific Ocean studies. *Journal of Geophysical Research-Oceans* **101**(C12): 28529-28538.

Mrowiec, B., Suschka, J. and Keener, T. C. (2005). Formation and biodegradation of toluene in the anaerobic sludge digestion process. *Water Environment Research* **77**(3): 274-278.

Schall, C., Heumann, K. G. and Kirst, G. O. (1997). Biogenic volatile organoiodine and organobromine hydrocarbons in the Atlantic Ocean from 42 degrees N to 72 degrees S. *Fresenius Journal of Analytical Chemistry* **359**(3): 298-305.

Shenoy, D. M., Paul, J. T., Gauns, M., Ramaiah, N. and Kumar, M. D. (2006). Spatial variations of DMS, DMSP and phytoplankton in the Bay of Bengal during the summer monsoon 2001. *Marine Environmental Research* **62**(2): 83-97.

Simo, R. (2001). Production of atmospheric sulfur by oceanic plankton: biogeochemical, ecological and evolutionary links. *Trends in Ecology & Evolution* **16**(6): 287-294.

Thurman, E. M. (1985). *Organic geochemistry of natural waters*. Boston, Kluwer Academic Publishers,

Tokarczyk, R. and Moore, R. M. (1994). Production of Volatile Organohalogens by Phytoplankton Cultures. *Geophysical Research Letters* **21**(4): 285-288.

Tokarczyk, R. and Saltzman, E. S. (2001). Methyl bromide loss rates in surface waters of the North Atlantic Ocean, Caribbean Sea, and eastern Pacific Ocean (8 degrees-45 degrees N). *Journal of Geophysical Research-Atmospheres* **106**(D9): 9843-9851.

Turner, S. M., Malin, G., Nightingale, P. D. and Liss, P. S. (1996). Seasonal variation of dimethyl sulphide in the North Sea and an assessment of fluxes to the atmosphere. *Marine Chemistry* **54**(3-4): 245-262.

Turner, S. M., Nightingale, P. D., Broadgate, W. and Liss, P. S. (1995). The Distribution of Dimethyl Sulfide and Dimethylsulphoniopropionate in Antarctic Waters and Sea-Ice. *Deep-Sea Research Part Ii-Topical Studies in Oceanography* **42**(4-5): 1059-1080.

Yamamoto, H., Yokouchi, Y., Otsuki, A. and Itoh, H. (2001). Depth profiles of volatile halogenated hydrocarbons in seawater in the Bay of Bengal. *Chemosphere* **45**(3): 371-377.

Yokouchi, Y., Li, H. J., Machida, T., Aoki, S. and Akimoto, H. (1999). Isoprene in the marine boundary layer (Southeast Asian Sea, eastern Indian Ocean, and Southern Ocean): Comparison with dimethyl sulfide and bromoform. *Journal of Geophysical Research-Atmospheres* **104**(D7): 8067-8076.

Yokouchi, Y., Mukai, H., Yamamoto, H., Otsuki, A., Saitoh, C. and Nojiri, Y. (1997). Distribution of methyl iodide, ethyl iodide, bromoform, and dibromomethane over the ocean (east and southeast Asian seas and the western Pacific). *Journal of Geophysical Research-Atmospheres* **102**(D7): 8805-8809.

CHAPTER 7. GENERAL DISCUSSION AND CONCLUSIONS

7.1 General Discussion

Solid phase micro-extraction (SPME) has proven to be a good methodology to analyse a wide range of VOCs with a wide range of chemical and physical properties. It is solvent free, fast and can be reutilized several times. Although the efficiency of the fibre employed may be dependent on heating, stirring and type of purging gas used. Heating was not considered important as every time that the temperature was modified; the nitrogen purge gas cooled the waters down to a constant temperature after 20 minutes, making it difficult to raise the temperature by more than 5 degrees above this value. Also is known that increasing the temperature of the samples moisture content increases and subsequently the extraction yield can be reduced due to competition of water and VOCs for fibre's absorption. The volume of sample employed also played an important role in the amount retrieved; preliminary experiments using 10 mL, 100 mL, *etc.* allowed quantification of only the most concentrated compounds such as dichloromethane, DMS, chloroform and bromoform. Using 4.5 L, the sensitivity increased greatly such that the method was able to detect more than 50 compounds at trace levels in the order of 30 – 50 pg L^{-1}. The memory effect with the fibre after conditioning for one hour before re-using it with the next sample was very low and no discernible peaks from the last sample were detected.

The purging time was initially an issue although several preliminary experiments with several times showed that 1 hour was the optimal period; longer or shorter periods could be used depending on the kind of sample. However, there is no need to achieve complete equilibrium concentrations if only the exposure time of the fibre is kept exactly constant. Considering the nature of the samples and concentration of VOCs it was not worth extending this time here. In addition, experiments were done with previously purged samples and very few compounds were above the limit of detections, implicating that the time chosen was the correct. What permitted very low limits of detection was the use of single ion monitoring (SIM) on the MS (mass spectrometer) which increased the sensitivity by at least ten times over scan mode. The fibres did produce small peaks of substrate bleeding (siloxane compounds) but these did not interfere or co-eluted with the target compounds. Chemical and physical inspections were performed with the fibres in order to ensure the quality of the obtained results, as well the use of internal standard permitted understanding of the efficiency of the purging procedure within samples and recovery of the VOCs in the sample; these had little changes in concentrations over the experimental period.

The SPME methodology employed can be further applied to other systems. For example, the system to extract VOCs in sediments could track contaminated aquifers and ground water systems if the permeability of the above soil permits the diffusion of it. It may also be applied to measure atmospheric VOCs. The system employed to purge VOCs has since been used to measure trihalomethanes (THMs) in drinkable water in Chile with good results.

Novels VOCs were detected in the seawater during this research such as 2,4-dimethylfuran and 1-bromopentane which were probably produced by marine algae and phytoplankton as well as a sulphur compound (mono-methyl carbonotrithioate) suspected to be produced by microbial activity in sediments, which may be from biogenic origins. An interesting compound not initially expected to be from biological sources was toluene; this compound is normally referred as an anthropogenic compound, however, it was found to be produced biogenically in marine anoxic sediments and also its production increased during the bloom period which may facilitate the growing of bacterial films on sediments.

Figure 7.1 illustrates the major sources of VOCs in the Menai Strait and how external factors affect their production and distribution. Three of the main sources (sediments, macroalgae and microalgae) were investigated and the results revealed that the signatures obtained from these sources can help to explain the variance and their seasonal importance. Models used did not explain 100% of the variance during the year long sampling. This may be explained by three different reasons: firstly, there are missing inputs which were not considered in the model; secondly, the models may not be sufficiently strong to estimate the total variance; and thirdly, which seems to be the most important, are the external factors affecting the removal of VOCs from the surface since they are produced and released to the seawater.

External factors such as the physico-chemical properties of the water (salinity, temperature, *etc.*) and meteorological conditions (wind speed, solar irradiation, temperature, *etc.*) influenced the production and release of VOCs in the marine environments. However, was difficult to attribute a particular effect to any of them, because many of them correlate and take part of a complex network of relationships. For instance, solar irradiation triggers the growing of phytoplankton which subsequently release VOCs and at the same time increases the temperature of the water affecting the solubility of them and simultaneously plays an important role on photochemical transformations and abiotic productions. Other important factor is wind speed; it is higher during winter and may lead to a rapid removal of VOCs from the surface waters to the atmosphere, so when a sample of water is taken only few compounds will be detected and maybe the difference in production from summer and winter seasons for some compounds are not very different.

Due to these reasons, it is not easy to construct numerical models with an adequate accuracy to interpret what is occurring in the studied system. Despite this, the multivariate models generated in this research lead to clear conclusions of what is affecting the releases and production of these compounds in seawater. However, is easy to over interpret them as there are factors affecting daily (short term) variability and those factors affecting the annual (long term) cycle.

These inter-relationships may be one of the reasons why it is so difficult in open oceans to find a relationship between VOCs and chlorophyll measurements. In the case of the Irish Sea sampling, the scenario could dramatically change if samples were taken in other periods such as winter/autumn; even so, within the same week period the concentration of VOCs in the water can dramatically change due to changes in the weather (*e.g.* wind speed). Perhaps during the algal bloom, the compounds that are known to be produced by anthropogenic sources could be enhanced to greater amounts due to biological sources. Atmospheric sampling would be needed to study the air/ocean exchanges of these chemicals.

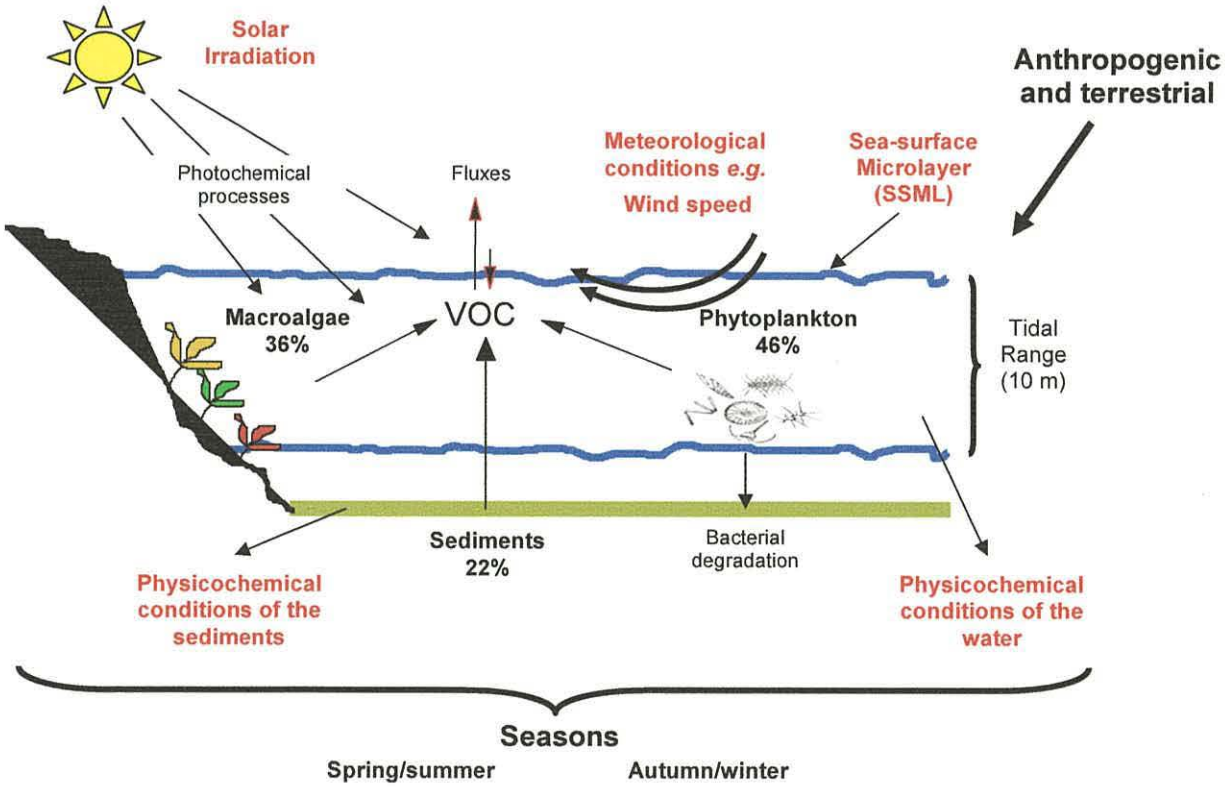


Figure 7.1. Diagram showing all the possible sources of VOCs in the Menai Strait and how external factors affect their production and distribution. Values in percentage are the maximal values of Q^2 (explained variance) obtained from the signatures in macroalgae, microalgae and sediments in Chapter 3.

7.2 General Conclusions

On the basis of the VOCs analysis in seawater and the multivariate statistical techniques, it can be concluded that:

- SPME is a good technique to analyse a wide range of different VOCs in seawater and marine sediments with very low limit of detections and with reasonable replication. It can also be applied for ship borne analysis and *in situ* sampling.

- The Menai Strait is a natural source of VOCs and some new compounds probably produced naturally such as such as 2,4-dimethylfuran, 1-bromopropane and mono-methyl carbonotrithioate were detected.

- Marine macroalgae can produce a broad variety of VOCs proving to be an important contributor of VOCs in the Menai Strait water, principally for brominated compounds such as bromoform. This production can be enhanced by external factors such as light availability or dark conditions depending on the kind of compound, proving that algae release compounds during photosynthetic activity as well during respiration. Desiccation also play an important role, indicating that VOCs production by macroalgae is promoted by an oxidative stress produced by partial desiccation after being exposed to the air. This release is higher from algae that are less tolerant to desiccation.

- Sediments release a great variety of VOCs being enriched in reduced sulphur containing compounds. The VOCs composition varied according to the type of sediment and samples with similar physico-chemical properties showed very similar signatures.

- Natural sources were investigated such as macroalgae, marine sediments and microalgae highlighting that the importance of the microalgae signature was in spring time while macroalgae and sediments dominated at other times. Multivariate statistical analyses using PCA and PLS demonstrated that the release from those sources mentioned above as well other not included in this study are driven by seasons (with their characteristic changes on meteorological and physicochemical properties of the water) having different suites of VOCs during spring/summer and autumn/winter periods.

- The River Mersey area has significant concentrations of halogenated compounds such as 1,2-dichloroethane, 1,1,1-trichloroethane, trichloroethene, tetrachloroethene and carbon tetrachloride which are widely used as a industrial solvents. These waters also contained some novel compounds from biogenic sources not reported before such as 2-chloropropane, 1-bromoethane and 1-chlorobutane.

- Marine pigments may indicate the presence of phytoplankton but did not have a direct relationship with VOCs presence in the Liverpool Bay waters; although better correlations were found in the Menai Strait waters, especially during the algal bloom period.

- Day and night sampling, showed that for Liverpool Bay, halogenated as well other VOCs typically from natural sources decreased noticeably after sunset; this can be explained due to lower production or transference of these compounds to the atmosphere during the night. In addition, in the Menai Strait waters the main factor affecting the daily production were tidal height and wind speed.

7.3 Recommendations for future work

- Do a more intensive winter/summer sampling through out the year.

- Incorporate atmospheric measurements of VOCs at different altitudes.

- Validate the SPME methodology with other well known techniques such as purge and trap and improve the SPME purging system in order to shorten the purging time and reach the equilibrium faster allowing to analyze more samples in shorter periods.

- Organize a cruise to the Irish Sea during the algal bloom period to see the differences in concentration of biogenic VOCs out of this period, also incorporate vertical profiles and atmospheric measurements of VOCs.

- Estimate the macroalgae biomass in the Menai Strait in order to quantify the annual fluxes of VOCs released to the atmosphere.

- Identify other possible sources of VOCs into the Menai Strait such as sewage treatment waters released into the strait as well other sources such as rivers and atmospheric deposition coming from big cities such as Liverpool and Manchester.

- Use other calibration methods such as deuterated chemicals to quantify VOCs.

- Use stable isotope ratios to try to identify the origins of VOCs in seawater.

- Incorporate satellite images of chlorophyll *a* in order to associate the presence of phytoplankton in open oceans to certain VOCs produced by them.

- Incorporate measurements such as dissolved organic carbon (DOC) and oxygen concentrations (as indicator of phytoplankton presence) and try to relate them to the presence of VOCs in seawater.

- Test other models than can also explain how external factors drive the production and release of VOCs in seawater.

- Incorporate the VOC's signatures of different kind of microalgae present in the strait such as Phaeocystis *sp*.

- Increase the number of sediment samples in order to construct a stronger model and try to relate the VOCs in different kind of sediments with some other properties such as organic matter content, grain size, etc.

7.4 Papers to be published

Bravo-Linares C and Mudge S. (2007). Analysis of volatile organic compounds (VOCs) in sediments using in situ SPME sampling. Journal of Environmental Monitoring 9 (5): 411- 418. (See enhanced version on http://xlink.rsc.org/?doi=b617215f)

Bravo-Linares C, Mudge S, and Loyola R. (*accepted)*. Occurrence of Volatile Organic Compounds (VOCs) in Liverpool Bay, Irish Sea. Marine Pollution Bulletin.

Bravo-Linares C and Mudge S. (*submitted)*. Temporal variation of Volatile Organic Compounds (VOCs) in seawater. Marine Chemistry.

Bravo-Linares C and Mudge S. (*submitted)*. Production of halogenated compounds and other volatile organic compounds (VOCs) by macroalgae. European Journal of Phycology.

Appendix 1: Concentration of pigments [μg L^{-1}] for the time series experiment.

Pigment	15/10/2004	21/10/2004	26/10/2004	27/10/2004	12/11/2004	15/11/2004	18/11/2004	22/11/2004	24/11/2004	26/11/2004	29/11/2004	01/12/2004	26/01/2005	03/02/2005	04/02/2005	05/02/2005
Carotenoid P468	0.034															
Chlorophillade b																
Chlorophillade a	0.182	0.138	0.133	0.147	0.178											
Chlorophyll c3																
Chlorophyll c2	0.412			0.091												
Chlorophyll c1+c2	0.135	0.125	0.085	0.072												
Peridinin																
19'-butanoyloxyfucoxanthin	0.377	0.074		0.066									0.079		0.058	0.102
Fucoxanthin	0.440	0.151	0.193	0.197	0.356	0.153	0.142	0.163	0.312	0.319	0.368	0.152	0.166	0.197	0.182	0.243
19'-hexanoyloxyfucothanthin				0.055												
cis-fucoxanthin	0.086			0.048							0.064		0.035	0.047		
cis-19'-hexanoyloxyfucothanthin	0.078															
Prasinoxanthin	0.059	0.059									0.042		0.038			
Violaxanthin	0.059	0.043			0.035											
Dinoxanthin		0.032														
Diadinoxanthin	0.044		0.039		0.055											0.035
Antheraxanthin																
Alloxanthin	0.025	0.026	0.023		0.022											
Monadoxanthin																
Diatoxanthin																
Lutein		0.029												0.022		
Zeaxanthin		0.025														
Canthaxanthin																
Chlorophyll b	0.116	0.142	0.079		0.238	0.100			0.076	0.100				0.148	0.078	0.104
Chlorophyll allomer	0.098	0.095	0.116		0.102									0.123		
Cholorophyll a	1.715	0.892	0.860	0.843	1.727	0.817	0.650	0.753	0.972	1.129	0.961	0.581	0.916	1.463	1.402	1.926
Lycopene																
Pheophytin b																
Phaeophytin a																
β-carotene	0.025	0.032	0.038	0.024	0.037	0.030	0.051	0.054	0.012	0.016	0.019		0.011	0.016	0.029	0.020

Appendix 1: Concentration of pigments [μg L^{-1}] for the time series experiment. (Continuation)

Pigment	06/02/2005	07/02/2005	07/03/2005	08/03/2005	09/03/2005	14/03/2005	15/03/2005	16/03/2005	17/03/2005	21/03/2005	22/03/2005	23/03/2005	29/03/2005	04/04/2005	05/04/2005	06/04/2005
Carotenoid P468																
Chlorophillade b																
Chlorophillade a																
Chlorophyll c3																
Chlorophyll c2																
Chlorophyll c1+c2			0.089													
Peridinin																
19'-butanoyloxyfucoxanthin	0.138	0.161									0.086		0.099		0.131	
Fucoxanthin	0.306	0.449	0.236	0.279	0.169	0.294	0.277	0.232	0.305	0.334	0.160	0.347	0.508	0.555	0.434	0.585
19'-hexanoyloxyfucothanthin										0.065			0.073			
cis-fucoxanthin	0.065	0.065	0.048			0.038			0.033	0.028	0.027	0.051	0.054	0.125	0.080	0.149
cis-19'-hexanoyloxyfucothanthin						0.054			0.064	0.078						
Prasinoxanthin		0.036											0.033			
Violaxanthin			0.031													
Dinoxanthin																
Diadinoxanthin	0.065	0.061				0.057	0.046	0.043	0.055	0.037	0.017	0.034	0.083	0.067	0.039	0.044
Antheraxanthin																
Alloxanthin	0.029					0.022	0.024		0.030	0.040	0.021	0.026	0.037	0.036	0.034	0.026
Monadoxanthin																
Diatoxanthin	0.024	0.029														
Lutein	0.030									0.041						
Zeaxanthin	0.027															
Canthaxanthin	0.095															
Chlorophyll b	0.133	0.158		0.046	0.036	0.060	0.052	0.058	0.065	0.268	0.101	0.157	0.144	0.166	0.091	0.095
Chlorophyll allomer	0.075	0.063	0.066	0.037	0.068	0.166	0.098	0.084	0.099	0.073		0.092	0.105	0.263	0.251	0.230
Cholorophyll a	0.791	1.012	0.435	0.383	0.811	1.758	1.497	1.202	1.825	2.402	1.020	1.887	2.336	3.668	2.257	2.739
Lycopene										0.020						
Pheophytin b																
Phaeophytin a																
β-carotene	0.036	0.079	0.021	0.014	0.009	0.033	0.019	0.022	0.027	0.039	0.007	0.022	0.029	0.032	0.014	0.030

Appendix 1: Concentration of pigments [μg L^{-1}] for the time series experiment. (Continuation)

Pigment	13/04/2005	14/04/2005	16/04/2005	18/04/2005	19/04/2005	26/04/2005	28/04/2005	29/04/2005	03/05/2005	04/05/2005	06/05/2005	08/05/2005	10/05/2005	12/05/2005	14/05/2005	16/05/2005
Carotenoid P468									0.027							0.040
Chlorophillade b									1.562	2.580	3.334	2.155	0.670	0.112		0.185
Chlorophillade a							0.116		2.331	4.086	4.411	3.111	1.441	0.623	0.267	0.585
Chlorophyll c3										0.245	0.759	0.150	0.250	0.340	0.129	
Chlorophyll c2									0.297	0.401	1.007	0.565	0.256	0.102		
Chlorophyll c1+c2						0.120	0.067	0.169	0.178	0.260	1.178	0.601	0.449	0.155	0.157	
Peridinin												0.214		0.076		
19'-butanoyloxyfucoxanthin										0.057	0.591	0.073	0.189	0.100		0.094
Fucoxanthin	0.535	0.411	0.442	0.499	0.323	0.920	1.648	1.352	7.872	9.262	11.221	10.014	6.629	5.317	4.915	3.872
19'-hexanoyloxyfucothanthin							0.530	0.410								0.171
cis-fucoxanthin	0.076	0.047	0.112	0.114	0.052	0.263			2.654	2.700	4.789	4.050	2.652	1.998	1.536	1.314
cis-19'-hexanoyloxyfucothanthin							0.095		4.287	5.545	9.029	8.048	4.117	2.827		1.862
Prasinoxanthin				0.040												
Violaxanthin										0.052	0.146	0.087				
Dinoxanthin									0.137	0.156	0.170	0.163	0.133	0.089	0.090	
Diadinoxanthin	0.062	0.049	0.065	0.058	0.055	0.105	0.189	0.164	1.110	1.363	1.461	1.498	1.003	0.659	0.830	0.609
Antheraxanthin							0.035									
Alloxanthin	0.031	0.024	0.020	0.030	0.021	0.030	0.046	0.019	0.022	0.029	0.022					
Monadoxanthin									0.026	0.037	0.034					
Diatoxanthin									0.111	0.125		0.044	0.047	0.086	0.099	0.047
Lutein					0.022											
Zeaxanthin																
Canthaxanthin																
Chlorophyll b	0.086	0.115	0.078	0.157	0.112	0.199	0.224	0.155	0.608	2.117	2.383	2.345	0.261	0.129	0.528	0.100
Chlorophyll allomer	0.207	0.164	0.243	0.146	0.139	0.182	0.404	0.377	1.816	0.182	0.177	0.088	1.987	1.345		0.646
Cholorophyll a	2.725	2.497	2.463	3.339	2.060	4.267	7.694	5.763	29.749	37.865	48.209	38.374	24.248	16.833	18.616	15.352
Lycopene																
Pheophytin b									0.776	1.196	1.431	0.895	0.626		0.495	0.491
Phaeophytin a									0.449	0.321	0.416	0.399	0.302			
β-carotene	0.020	0.026	0.023	0.062	0.029	0.084	0.093	0.064	0.325	0.403	0.497	0.276	0.217	0.143	0.080	0.096

Appendix 1: Concentration of pigments [μg L^{-1}] for the time series experiment. (Continuation)

Pigment	18/05/2005	20/05/2005	22/05/2005	24/05/2005	26/05/2005	28/05/2005	30/05/2005	01/06/2005	03/06/2005	05/06/2005	07/06/2005	09/06/2005	11/06/2005	13/06/2005	15/06/2005	17/06/2005
Carotenoid P468				0.068	0.082									0.032		
Chlorophillade b	0.407	0.511	0.346	2.099	2.121	0.357	0.307									
Chlorophillade a	0.756	1.663	0.611	1.984	1.022	0.244	0.620	0.186		0.220		0.161			0.230	
Chlorophyll c3		0.131			0.967				1.171	1.280	0.692	0.873	0.836	0.504	0.450	0.508
Chlorophyll c2				0.646	0.508										0.184	
Chlorophyll c1+c2				0.345				1.388							0.218	
Peridinin																
19'-butanoyloxyfucoxanthin	0.108	0.156		0.157	0.251	0.198			0.129	0.148			0.082	0.223	0.081	0.081
Fucoxanthin	3.689	6.102	3.468	9.917	11.193	10.625	7.055	4.610	2.388	2.229	1.038	1.324	0.975	1.155	1.376	0.602
19'-hexanoyloxyfucothanthin	0.201	0.266							0.133	0.227		0.183	0.194	0.317	0.110	
cis-fucoxanthin	1.441	2.385	0.875	3.258	3.822	4.084	2.477	0.860	0.395	0.370	0.188	0.361	0.253	0.103	0.338	0.133
cis-19'-hexanoyloxyfucothanthin	2.405	4.474		2.727	0.331		1.197							0.176	0.225	0.273
Prasinoxanthin																
Violaxanthin																
Dinoxanthin	0.071	0.097		0.173	0.242	3.815	0.111		0.083							0.041
Diadinoxanthin	0.564	0.796	0.451	1.435	1.589	1.599	0.975	0.614	0.380	0.366	0.210	0.157	0.104	0.185	0.205	0.099
Antheraxanthin		0.091														
Alloxanthin								0.063					0.036			
Monadoxanthin				0.059												
Diatoxanthin	0.059	0.061	0.072	0.091	0.076	0.122	0.154			0.097						
Lutein																
Zeaxanthin																
Canthaxanthin																
Chlorophyll b	0.705	1.147	0.510	2.256	2.534	1.823								0.110		0.108
Chlorophyll allomer					0.328	0.266	0.968	0.849	0.515	0.424	0.344	0.298		0.349	0.229	0.189
Cholorophyll a	13.983	23.789	13.454	44.991	52.920	46.010	26.870	18.551	10.700	10.366	4.158	4.881	3.907	5.784	4.950	2.595
Lycopene							1.150									
Pheophytin b		0.803		1.751	2.429	2.055	0.527	1.141	1.052	0.947						
Phaeophytin a														0.226		
β-carotene	0.081	0.144	0.099	0.371	0.463	0.251	0.183	0.158	0.073	0.100		0.032	0.018	0.101	0.062	0.113

Appendix 1: Concentration of pigments [μg L^{-1}] for the time series experiment. (Continuation)

Pigment	19/06/2005	21/06/2005	23/06/2005	25/06/2005	27/06/2005	29/06/2005	01/07/2005
Carotenoid P468							
Chlorophillade b	0.203	0.116	0.209	0.185			0.094
Chlorophillade a	0.424						
Chlorophyll c3	0.537	0.351	0.160	0.395	0.173	0.272	0.126
Chlorophyll c2	0.240						0.305
Chlorophyll c1+c2							
Peridinin							
19'-butanoyloxyfucoxanthin	0.447	0.453					
Fucoxanthin	3.043	2.775	1.312	0.919	0.642	1.158	1.129
19'-hexanoyloxyfucothanthin							
cis-fucoxanthin	0.686	0.536	0.297	0.214	0.077	0.220	0.302
cis-19'-hexanoyloxyfucothanthin	0.070	0.130	0.192		0.263	0.143	0.345
Prasinoxanthin							
Violaxanthin							
Dinoxanthin							
Diadinoxanthin	0.440	0.423	0.178	0.171	0.170	0.135	0.209
Antheraxanthin							
Alloxanthin	0.035	0.045		0.037	0.067	0.051	0.040
Monadoxanthin		0.033					
Diatoxanthin							
Lutein	0.028	0.051					
Zeaxanthin							
Canthaxanthin							
Chlorophyll b		0.175				0.131	0.406
Chlorophyll allomer	0.898	1.332	0.576	0.307	0.201	0.321	0.112
Cholorophyll a	11.282	12.577	5.404	4.627	3.168	6.047	5.651
Lycopene	0.492						
Pheophytin b	0.466						
Phaeophytin a	0.249					0.373	
β-carotene	0.156	0.160	0.049	0.031	0.042	0.083	0.060

Appendix 2: Concentration of VOCs [pg L^{-1}] for the time series experiment.

Compound	06/08/2004	10/08/2004	11/08/2004	13/08/2004	16/08/2004	17/08/2004	19/08/2004	15/10/2004	15/10/2004	21/10/2004	26/10/2004	27/10/2004	12/11/2004	15/11/2004	18/11/2004	22/11/2004	24/11/2004	26/11/2004	29/11/2004	01/12/2004	26/01/2005	03/02/2005	04/02/2005	05/02/2005
1,1-dichloroethene	27	21	58	11	39	15	35	59	97	90	87	75	76	39	29	105	56	45	56	96	2	38	15	19
Dichloromethane	6892	4369	3917	6381	3327	2595	2312	883	532	1177	1392	1039	2809	2670	2881	4424	3687	3743	5024	1624	1564	7454	3024	4662
Cis-1,2-dichloroethene	100	108	322	127	412	126	107	53	88	44	73	95	65	200	13	73	28	48	167	82	48	359	104	334
Chloroform	3218	2199	1978	2948	2044	2225	2194	6639	6877	9522	14312	12354	11202	9719	14637	24055	22063	23188	36211	2947	7171	36376	16241	24295
1,1,1-trichloroethane	92	195	73	89	59	38	12	101	66	64	50	51	58	62	48	72	132	139	117	48	28	221	87	141
Carbon tetrachloride	944	1407	1207	1276	1283	556	682	471	289	75	97	464	73	302	262	303	317	324	531	60	80	799	311	438
1,2-dichloroethane	88	9	247	59	264	37	84	116	65	73	873	65	92	212	179	244	36	114	308	51	47	393	189	14
Trichloroethene	61	79	754	122	89	329	314	430	435	124	575	632	83	148	268	261	357	304	323	130	104	552	117	147
Bromodichloromethane	761	728	425	370	807	680	302	162	160	91	116	275	57	301	223	241	581	446	910	31	84	51	33	11
cis-1,3-Dichloropropene	69	39	31	16	97	62	12	50	121	286	44	75	43	44	94	78	62	22	45	38	29	139	34	17
trans-1,3-Dichloropropene	105	16	26	32	55	60	170	87	63	298	78	23	55	13	416	96	224	73	52	28	12	75	16	119
1,1,2-trichloroethane	9	416	1652	459	357	155	244	248	83	23578	483	135	156	95	2582	114	193	79	68	53	23	110	193	341
Tetrachloroethene	81	37	141	1183	487	150	661	258	370	226	424	534	271	251	279	556	435	526	522	20	180	386	264	362
Dibromochloromethane	3510	2917	1105	34978	5496	3990	688	1018	216	1033	87	317	306	866	106	592	5118	3148	1156	302	267	2124	1563	778
Bromoform	78881	84762	47089	708566	130291	122378	16202	56377	5445	123763	1636	6648	2024	15536	60394	1684	262431	130930	31951	4557	6340	865	751	1139
2-chloropropane	7610	277	24	194	7955	2942	4270	50	1797	113	7038	6271	253	7873	7942	12382	12535	9323	15717	1859	2374	26117	10168	9123
1-Bromoethane	57	52	35	27	66	39	24	51	53	65	20	22	60	39	81	60	113	64	50	61	6	73	12	25
1-Bromopropane	8263	12654	26384	11170	39575	7318	7041	717	984	236719	8340	7576	3759	21637	17368	9587	7141	3904	6477	293	2203	12511	4972	3197
2-chlorobutane	524	223	400	720	141	301	235	785	203	1425	853	1315	327	652	637	981	323	516	784	34	521	2594	2211	972
Iodoethane	131	225	165	79	111	54	63	67	144	74	251	290	583	396	619	881	834	871	1266	54	299	691	372	582
1-chlorobutane	580	1522	753	552	858	305	500	935	1160	86	4788	4029	18013	1982	1824	3275	2065	1895	3241	356	1631	10072	5802	5577
2-Iodopropane	514	1474	231	444	380	1879	467	1376	13782	53	5057	7403	13770	4308	58502	5269	4244	4845	2441	76	1054	6719	889	1116
Chloroiodomethane	449	351	100	312	294	500	92	171	120	318	84	75	82	122	107	115	935	173	203	41	12	52	9	11
1-Iodobutane	74	981	46	79	47	99	113	293	344	526	5411	727	510	570	715	750	696	812	909	48	1030	1155	1058	1218
2,3-Dibromopropene	21615	26191	28688	9457	26391	5179	7713	6176	4157	14403	32758	11591	9190	7045	8504	8875	7456	5449	13802	6610	1400	312131	8571	14331
Diiodomethane	8872	7464	419	4302	1169	1184	308	1146	675	477	301	780	1108	651	2371	521	1001	1367	720	18	199	389	72	124
Iodomethane	1476	1022	1583	736	658	367	359	83	344	95	18	272	1237	1434	1571	1145	1081	1670	1248	98	258	801	244	365
Dibromomethane								507	174	889	0	0	219	342	1660	798	2744	2925	1246	401	165	119	98	96
1-bromopentane						1634	286	6479	3871	57877	13057	13687	871	0	478	6030	4834	3822	7227	602	5352	15669	15758	11171
Dimethyl sulphide	11481	5764	11870	2393	6356	993	2541	1980	1634	1682	286	963	78	1119	3897	1274	2119	2327	3151	963	429	2668	842	11179
Dimethyl disulphide	10331	5676	12845	14725	4171	6001	2488	3770	2229	114	976	919	1060	9350	10830	514	4256	3767	1275	512	495	373	59	324
2,4-dimethylfuran	558	641	536	381	441	268	289	247	142	455	143	195	85	144	319	56	265	124	127	36	314	242	70	37
Alkyne unknown								2502	1943	605	634	709	12354	233	630	720	420	309	2509	22	55	742	1577	639
Limonene								10076	9193	147	22401	20219	418	3841	16787	5667	71360	35990	11462	3919	2221	8046	7052	4723
α-pinene								13438	6374	865	42721	153593	2184	13270	14173	15475	22127	52335	58184	2155	15294	97130	257043	81887
Decanal						511	30017	9474	37945	151848	13182	1987	124458	5967	13941	22568	16230	9621	32970	42517	5574	1539594	39916	25185
Hexanal						2282	4256	1559	6628	95215	8890	6531	44471	1040	3608	4137	4432	2855	4671	667	1913	13077	7909	6295
Nonane (C_9)						1363	2385	10062	17020	1564	25039	18231	7058	1586	2445	2488	4153	3327	33571	323	3204	14034	4433	8809
C10 Branched a						48	19217	3242	268	465	44651	0	45795	63	297	503	384	293	1176	0	281	22311	414	1739
C10 Branched b						20	18115	6236	855	35608	8827	0	44416	308	435	367	239	875	5850	0	6075	2047	0	1865
C10 Branched c						35955	47722	11758	1350	40577	100590	1131	29441	387	451	770	514	659	26463	435	730	0	7220	1200
C10 Branched d						7045	17465	21306	7926	0	22213	26224	269745	10151	9073	10151	8511	8538	338	213	12260	0	16280	8683
C10 Branched e						2345	5424	23034	1861	24350	14300	8739	189574	4011	3600	3283	3954	3984	5246	54	3483	0	10089	5578
C10 Branched f						8718	10430	4319	10875	98649	15283	26025	5325	554	5909	18361	5030	5124	26330	1715	4031	48179	19456	16488
Decane (C_{10})						3939	41618	92602	40261	151821	122352	87054	310480	16715	14842	13970	19319	22720	166514	1396	7918	26943	34817	24770
C11 branched a						3685	5252	10681	23161	18203	21385	86027	323425	4146	1373	5174	2275	2979	17268	271	2329	67998	13078	10265
C11 branched b						6894	19634	86269	14008	19106	26346	531278	605854	1781	4508	1709	6145	5854	47714	8317	3939	1787916	11865	27389
C11 branched c						1404	4119	116258	3497	20185	8456	331378	116797	4445	2162	2719	3038	2683	7705	1489	1888	8993	4582	56677
C11 branched d						402	5571	17632	6666	0	2483	50585	100693	2380	1281	1882	3609	3172	14203	661	5210	10048	2972	1799
Undecane (C_{11})						13592	20430	91042	51285	0	23402	166502	90737	22504	25054	18261	29574	41080	17186	2191	8142	33795	0	36676
Benzene						3117	4122	11173	12461	17333	34227	12383	52561	5097	8114	7831	9473	8448	14367	890	3148	17716	7578	12666
Toluene						52576	68200	252485	8278	156711	714961	183416	18	167	0	0	40726	35690	50687	3682	0	0	0	0
Ethylbenzene						17443	22694	59301	46171	78	285187	60302	4282984	18849	27730	12371	189	8427	38547	1029	5310	23494	17992	67704
m-Xylene						61892	82174	205825	152390	319	912820	187056	1640	63472	80974	39374	39235	25960	18452	3506	14858	67520	52957	209446
p-Xylene						25526	29092	71854	44539	155779	279636	63230	1268039	19401	25835	11565	10376	8663	8896	1165	5069	26281	16251	61638
n-propylbenzene						7895	9428	25188	14427	35431	131188	20448	618995	6599	7761	4110	68407	3138	1067764	459	2571	8883	6214	23092
1,3,5-trimethylbenzene						21319	31046	72514	42665	748	384966	62131	2424439	24789	22080	12160	9424	8097	4509	1053	751	24771	22286	69592
1,2,4-trimethylbenzene						10075	12080	27634	12076	487	102615	17695	676670	7245	6915	3496	3569	2752	27560	324	2234	9442	7572	19620
1-ethyl-2-methylbenzene						7062	10142	13864	8743	69897	106008	0	526246	6225	5486	2777	2916	2254	15545	334	1723	4813	4833	14330
1,2,3-trimethylbenzene						29259	37801	66155	43894	30460	369379	0	2571543	27993	28324	17147	15908	12668	23269	1721	7715	30484	19132	64713
1-ethyl-3-methylbenzene						8028	38	11205	7312	4690	111200	157	796971	6168	5814	3021	3141	2325	3381	403	3315	6642	4820	15242
sec-butylbenzene						8028	5768	3677	2339	3101	0	16331	261123	1661	4541	3437	580	594	3809	153	1135	3104	1434	4965
Aromatic unknown 1						1253	890	749	834	708	35763	5765	21333	1788	579	970	327	308	1582	146	417	2253	595	3808
Aromatic unknown 2						1425	1911	2896	1928	22116	27401	3645	36165	268	1124	925	1192	804	1562	98	148	1357	397	214

Appendix 2: Concentration of VOCs [pg L^{-1}] for the time series experiment. (Continuation)

Compound	06/02/2005	07/02/2005	07/03/2005	08/03/2005	09/03/2005	14/03/2005	15/03/2005	16/03/2005	17/03/2005	21/03/2005	22/03/2005	23/03/2005	29/03/2005	04/04/2005	05/04/2005	06/04/2005	13/04/2005	14/04/2005	15/04/2005	18/04/2005	19/04/2005	26/04/2005	28/04/2005	29/04/2005
1,1-dichloroethene	31	18	323	71	208	30	24	46	39	142	35	92	92	49	101	54	84	95	35	106	53	131	112	95
Dichloromethane	4001	4317	4369	5661	5799	1390	708	857	614	1376	1331	1228	1228	1364	2296	1960	5221	4731	6329	7389	5124	6355	5249	651
Cis-1,2-dichloroethene	138	92	943	607	870	160	183	211	176	325	204	212	212	1356	540	2444	287	166	225	179	187	405	181	122
Chloroform	24584	22061	5075	5204	5908	2759	1740	2444	2334	5688	5373	5937	5937	5128	11115	7612	8607	8165	11962	14956	10793	14969	16525	550
1,1,1-trichloroethane	171	110	765	162	394	149	78	121	71	162	70	134	134	128	284	211	205	69	178	185	152	142	110	25
Carbon tetrachloride	494	264	2487	1523	2316	452	240	418	475	491	348	254	254	301	905	304	399	403	563	883	507	656	717	675
1,2-dichloroethane	250	183	1123	699	926	278	172	219	228	384	192	181	181	227	562	187	270	211	271	321	331	501	334	278
Trichloroethene	277	381	815	323	740	120	141	861	203	1702	337	108	108	338	628	180	450	242	208	361	648	834	738	645
Bromodichloromethane	25	76	2605	3718	1767	167	247	737	82	7475	3205	2113	2113	39	151	628	129	683	74	103	526	179	55	770
cis-1,3-Dichloropropene	36	44	223	132	165	40	51	44	32	112	65	49	49	30	115	71	23	40	38	43	91	87	98	126
trans-1,3-Dichloropropene	18	13	114	289	158	36	55	39	48	81	28	70	70	16	68	45	73	41	25	60	24	51	39	71
1,1,2-trichloroethane	89	51	469	1227	500	277	172	151	205	654	188	341	341	190	748	284	386	213	110	108	256	358	197	104
Tetrachloroethene	370	333	930	771	1124	469	328	384	388	722	411	491	491	569	1268	605	458	385	465	648	787	1329	1028	743
Dibromochloromethane	759	644	353	13041	4416	1160	2167	1477	211	42913	11939	8980	8980	379	468	4442	1484	5675	842	916	812	964	1010	4909
Bromoform	918	841	1239	109648	45922	37494	66863	9672	1894	906965	151170	225107	225107	1912	5936	197339	1481	131505	1714	3043	4604	4080	3464	126288
2-chloropropane	6817	7110	19179	16062	19313	2053	1517	1865	1906	3710	2069	1852	1852	1634	3641	1972	4961	3756	6276	6064	7877	8875	4700	3169
1-Bromoethane	39	8	192	113	504	59	19	29	22	100	38	30	30	23	104	105	77	64	37	80	50	140	111	65
1-Bromopropane	3152	3176	9064	7814	2474	953	380	78	91	528	224	635	635	721	2659	776	235	597	3855	4622	1769	344	1931	499
2-chlorobutane	1132	906	3714	2572	3536	1322	429	1304	1039	1549	111	1577	1577	1278	5096	1369	5738	1953	2741	3835	2052	4052	2066	717
Iodoethane	595	574	532	1027	1000	292	175	117	166	544	342	373	373	307	507	552	729	804	1019	1340	1143	1393	1685	609
1-chlorobutane	5186	5055	21576	9869	12929	3709	1348	2748	3155	3651	2843	3838	3838	4420	13792	4452	9156	7314	10123	13564	28639	14383	8426	413
2-Iodopropane	1122	723	2951	2636	3194	696	361	169	65	2158	738	570	570	364	699	922	1033	1506	941	942	1211	2599	725	1353
Chloroiodomethane	17	23	244	589	405	104	73	29	44	511	175	165	165	18	128	268	150	187	79	97	131	204	266	1000
1-Iodobutane	1231	1099	522	535	704	1037	742	907	959	1812	1962	2364	2364	1831	2028	2368	2307	2284	2502	2791	2392	3296	3326	480
2,3-Dibromopropene	10745	4699	18375	15184	17232	3364	2775	2888	4644	11430	5017	2949	2949	2982	6342	3408	7634	888	3963	4426	45725	12011	7841	5912
Diiodomethane	58	44	267	944	574	592	454	139	77	3532	1008	589	589	241	1033	889	61	679	207	405	140	280	1220	3930
Iodomethane	322	233	1707	1527	3295	382	326	230	307	3672	297	358	358	273	412	320	683	426	253	432	572	1110	1713	11351
Dibromomethane	99	49	549	6897	3830	930	960	11	88	19044	2953	3690	118	39	49	3454	93	4155	127	160	310	221	244	1364
1-bromopentane	9543	4142	422	10212	8065	1447	3096	941	948	14015	4374	5638	3200	1705	2651	4358	3988	6525	4302	4380	21270	5674	2858	7812
Dimethyl sulphide	1592	1233	4512	10047	12075	2723	1793	1653	1386	24730	5957	7889	7889	1868	4457	5517	2874	4929	4751	7621	5197	12336	7438	348
Dimethyl disulphide	71	19	456	203	2001	1023	686	209	161	159939	8183	32847	32847	1100	2404	6490	988	8748	1288	1449	2834	1656	3584	10794
2,4-dimethylfuran	54	257	407	480	651	228	173	421	130	543	244	258	258	141	691	366	197	180	229	118	287	421	114	43546
Alkyne unknown	617	663	512	366	726	260	256	112	424	1990	741	793	793	2217	5408	1440	1651	19525	1288	2289	1691	4370	2319	3523
Limonene	324	3568	9470	33986	13219	412	13965	8905	8746	207299	33783	46306	46306	7079	14167	43382	5910	4650	3703	4914	3984	7675	5850	18324
α-pinene	64018	54441	97429	45103	119025	77694	109799	1626	2006	189510	150068	177697	177697	111313	271879	184728	93371	96207	79985	92620	52776	159289	80643	23139
Decanal	55671	16833	62037	36730	73509	2438	10094	24703	9695	20465	18060	3725	3725	847	17689	6690	5143	3432	13009	35508	45355	13765	24755	8321
Hexanal	3163	2029	60850	44045	49039	7722	5879	8592	9465	22625	7456	6558	5456	3753	10466	5673	10448	7878	5789	7602	7170	15058	8181	22816
Nonane (C_9)	5795	1757	23010	8342	11015	14202	4817	4816	13955	11666	6681	9092	7058	4310	11596	56450	5872	30263	6742	6652	40046	11740	4200	3542
C10 Branched a	0	180	0	0	9672	0	0	0	661	0	0	6161	0	0	0	5226	0	1310	425	0	4991	0	0	6882
C10 Branched b	0	170	0	0	0	0	0	0	2221	0	0	1069	0	0	0	2136	589	2442	177	0	7535	0	0	2891
C10 Branched c	228	680	38984	15073	8972	0	212	3071	523	965	526	524	374	1525	98010	5342	956	4563	381	0	8749	877	5118	13378
C10 Branched d	4132	997	132312	14548	34047	12982	7648	10179	7723	9756	14267	11123	6566	6501	14064	13945	6221	9134	3908	12048	6720	24503	14688	1357
C10 Branched e	4750	1896	206953	15743	22804	14136	5436	5245	11580	20487	9597	8819	6656	8459	13329	8957	5212	8672	7430	8723	8952	14981	10811	8457
C10 Branched f	14065	7812	33146	93734	0	0	2817	0	997	4145	2580	4293	4360	7794	4955	3577	8098	4447	5974	4028	1658	5682	4212	14931
Decane (C_{10})	15740	17108	146237	24022	32734	31743	20015	33436	32478	43139	23884	32658	37862	31306	54051	88237	28129	44876	28680	16811	62752	35264	10386	342
C11 branched a	21326	1541	246981	0	4900	2918	695	3805	0	7320	4697	3718	2725	0	0	16617	0	2220	0	2444	53271	3838	6949	12980
C11 branched b	8508	12055	15487	16423	49631	6796	2725	5117	43661	31889	10447	9771	9771	5668	12543	38908	9785	9435	6405	4113	19667	14407	6266	62154
C11 branched c	4455	3390	6354	3683	24810	6018	3034	3927	9471	4996	3160	36321	36321	3821	4492	20671	9462	68779	4161	2235	7938	3889	981	6936
C11 branched d	3362	3374	9783	9777	9430	6431	7970	14464	3560	4935	3872	30515	30515	3252	4455	18002	48632	28618	1643	2280	78721	7580	7055	1100
Undecane (C_{11})	18901	8849	81704	48880	60109	51913	822	35956	57248	39033	58709	47997	47997	37229	42835	66105	47452	38332	23440	22663	55319	34099	17944	751
Benzene	12456	7158	36012	19039	25788	10408	7441	21020	8883	336843	12020	9252	9252	14002	31548	11555	12098	8078	8553	12273	28732	19319	9267	1684
Toluene	0	0	131080	90541	102707	29986	20665	8318	59960	402841	118673	64110	64110	109259	178814	90615	82772	45086	41443	56040	1108561	178511	83596	366
Ethylbenzene	21531	11342	19646	15141	16685	9146	6834	5635	14533	116180	34536	16352	16352	32898	51581	22326	23128	54553	9857	12520	499226	48787	17978	4272
m-Xylene	63041	35448	52897	41770	44461	24385	19741	16401	41924	338130	102617	48366	48366	94758	144549	62618	65463	34410	25767	33279	1428336	133083	45997	9767
p-Xylene	19681	10249	16293	12337	12993	7348	6269	4834	13851	100235	30408	14355	14355	27791	43587	20936	20205	12966	7961	9663	439849	39194	14300	3518
n-propylbenzene	9092	4484	4595	14391	5375	2777	2083	2878	4589	29109	9604	4432	4432	16450	12970	10761	6954	5490	3625	4201	227323	14167	4516	2994
1,3,5-trimethylbenzene	23003	11749	13606	17756	12690	10443	9948	8763	13853	103730	34415	14492	14492	31489	42320	28847	21283	13197	10371	12651	580551	44827	12283	0
1,2,4-trimethylbenzene	6571	3488	3809	6430	3910	6952	5519	3935	4137	33111	10477	4996	4996	8667	12312	11629	5381	4886	3913	4572	151841	11959	3225	0
1-ethyl-2-methylbenzene	4555	3036	323	2866	3243	2234	1999	1884	3691	23733	7828	4355	4355	6951	9184	8167	4548	4091	2196	2345	116369	9890	2675	294
1,2,3-trimethylbenzene	22469	16244	16645	13001	17649	12140	10328	9788	18143	98157	35656	17607	17607	28431	43737	41324	24232	17909	10093	13568	479118	43186	15122	8187
1-ethyl-3-methylbenzene	5120	3186	2147	2866	2783	1802	2153	2238	3994	16350	6904	3183	3183	6196	10310	12781	3833	4471	1717	700	145208	8791	2394	11424
sec-butylbenzene	1650	965	1490	1233	299	594	721	389	1183	4452	2680	909	909	1617	1928	3692	1228	1409	596	2181	48107	2628	683	3173
Aromatic unknown 1	1261	392	2606	255	904	215	395	138	1219	114	1109	103	103	630	10310	1032	364	483	191	678	16379	1128	78	2788
Aromatic unknown 2	177	681	4167	95	1038	540	675	313	202	4920	1519	2805	2805	2159	4440	5536	992	1608	705	506	32513	2196	854	570

Appendix 2: Concentration of VOCs [pg L^{-1}] for the time series experiment. (Continuation)

Compound	03/05/2005	04/05/2005	06/05/2005	08/05/2005	10/05/2005	12/05/2005	14/05/2005	16/05/2005	18/05/2005	20/05/2005	22/05/2005	24/05/2005	26/05/2005	28/05/2005	30/05/2005	01/06/2005	03/06/2005	05/06/2005	07/06/2005	09/06/2005	11/06/2005	13/06/2005	15/06/2005
1,1-dichloroethene	270	97	69	69	46	16	28	26	154	165	97	45	106	32	78	38	95	93	83	75	191	10	99
Dichloromethane	19265	10004	7811	11668	6617	3730	18060	11428	38337	15073	11768	4117	13294	4192	9336	8718	4538	7715	3828	5821	10526	8595	7862
Cis-1,2-dichloroethene	2389	2176	173	190	100	12	228	143	516	298	189	56	1649	31	26	1070	113	105	68	24	82	9	35
Chloroform	37854	18821	15198	26455	15003	14587	39717	25829	61921	34574	25132	15839	37914	19311	28505	24173	27951	26340	27567	27207	40321	22052	28573
1,1,1-trichloroethane	366	88	91	131	140	36	192	29	297	176	87	42	134	24	65	101	79	65	122	67	184	65	89
Carbon tetrachloride	988	360	271	556	274	284	626	434	1045	665	365	228	492	314	377	182	372	264	526	319	555	191	364
1,2-dichloroethane	525	199	145	256	97	147	261	174	571	355	214	52	157	152	257	190	69	246	67	192	367	126	74
Trichloroethene	527	357	323	199	188	187	311	284	951	464	311	177	252	183	231	228	196	221	325	287	618	195	211
Bromodichloromethane	175	89	58	26455	33	67	279	57	169	140	110	71	80	75	195	126	72	42	151	98	60	72	97
cis-1,3-Dichloropropene	39	16	25	35	15	22	52	42	50	34	127	25	44	27	27	37	100	37	36	22	132	8	18
trans-1,3-Dichloropropene	91	23	82	23	15	40	19	13	49	32	47	34	50	21	34	18	24	31	74	25	38	50	44
1,1,2-trichloroethane	3043	258	182	176	32	64	34	116	428	233	50	44	90	25	68	78	107	46	43	48	346	126	166
Tetrachloroethene	757	389	320	539	2505	408	860	464	1411	10586	15253	17194	15137	12375	10789	7888	8320	4892	6022	6183	7173	2274	2524
Dibromochloromethane	4119	1648	1480	2077	1009	1091	2829	1871	5402	33387	2095	1273	2540	1318	1927	1565	2063	1782	1858	1781	2669	1808	2088
Bromoform	2910	1935	1385	3214	1007	3566	3517	1960	3425	4234	3295	3141	3910	2391	2959	2180	2871	2048	4471	4154	7251	2476	4018
2-chloropropane	16685	3576	4955	3329	2960	1207	4522	4741	11967	10540	6938	3018	4844	1365	4158	3188	2340	3046	2053	161	9123	3137	3579
1-Bromoethane	49	14	14	56	21	5	58	18	59	38	37	79	56	71	66	29	76	33	51	92	79	21	24
1-Bromopropane	1475	450	232	521	254	180	614	346	1821	733	469	106	367	151	245	177	295	208	224	1101	550	253	232
2-chlorobutane	9210	3397	2784	5038	2651	620	4822	3240	16160	6939	3033	762	1684	838	1697	1213	1264	1838	934	1166	3605	873	1840
Iodoethane	3494	2068	1729	2952	1674	1697	4837	3081	4864	3260	2721	1648	4140	2590	3537	2849	3078	2883	3187	3035	4117	2248	3012
1-chlorobutane	44881	16854	13307	25731	12931	3547	21385	14855	75592	35206	17891	3818	15231	3667	8068	6635	5652	8226	4725	5756	17803	7704	9242
2-Iodopropane	4290	1229	961	1876	909	305	1535	1093	5501	2419	1495	310	1174	318	644	580	563	487	704	492	1401	618	697
Chloroiodomethane	363	91	321	109	61	77	92	61	165	126	81	59	106	62	81	92	123	54	53	51	212	35	16
1-Iodobutane	7795	4614	4239	6172	3073	3108	7875	5248	7901	6685	5737	3390	6260	3705	5167	4024	4372	4283	4224	4246	5878	3708	4254
2,3-Dibromopropene	2693	388	3470	20	588	3845	8006	474	1202	693	805	80	121	76	76	200	102	22	146	35	41	10	45
Diiodomethane	80	72	95	59	33	29	151	14	89	70	36	75	108	814	227	105	150	125	114	102	150	60	67
Iodomethane	657	474	111	329	153	243	211	277	449	421	365	678	696	952	963	675	1966	1805	3447	1907	1629	925	900
Dibromomethane	291	110	91	154	80	155	185	157	386	376	167	169	312	163	165	128	55	76	223	281	344	144	233
1-bromopentane	26880	13639	11122	14315	5930	2326	11032	7407	39798	20120	15360	4145	9306	3251	3289	3636	4047	3852	3838	3190	12246	6541	6090
Dimethyl sulphide	70987	32054	17477	33717	19121	5237	25000	21904	70141	40337	23256	16159	44990	4008	27316	17266	20541	30435	29663	36377	8323	6920	6550
Dimethyl disulphide	3180	1321	914	1214	546	466	849	647	2291	1611	1080	2821	2576	1863	1884	2883	9669	14003	22572	11926	7401	6325	4235
2,4-dimethylfuran	621	68	189	314	157	132	362	388	1063	649	312	187	1592	201	195	341	273	253	257	498	688	218	273
Alkyne unknown	40020	21420	20421	371418	17316	17042	37673	30825	147789	124742	81460	1349	35338	12526	12671	17531	19699	20992	16454	16888	28542	10444	9775
Limonene	49406	5238	4517	5758	2569	755	4728	3274	10347	8084	5676	2441	5649	1639	1658	1516	691	1745	1315	1583	7140	2548	2816
α-pinene	233295	90665	91436	109474	39861	24895	83309	53248	259205	172386	147095	92198	199902	54686	55318	35440	48672	58596	57226	48162	200954	127840	88358
Decanal	12181	22982	6744	2601	1177	175	18720	261	8562	18996	556	191	1537	2134	2158	629	57492	171	1092	1132	44941	267	1895
Hexanal	22503	8693	5827	0	2183	2836	9086	3655	40559	13385	9450	3136	5327	3075	3111	2085	3095	3363	3441	3727	25974	4933	5284
Nonane (C_9)	33140	12135	8052	17067	2608	1011	7388	3708	35763	42681	18533	1805	4336	940	951	2110	1608	1772	1451	1735	9246	4670	3513
C10 Branched a	1477	350	422	393	151	558	989	239	1289	783	1703	428	449	7157	7245	76	243	102	1955	3207	10124	216	128
C10 Branched b	3403	374	579	1165	287	744	606	335	4295	3347	555	4332	861	0	133	118	134	295	473	0	773	311	396
C10 Branched c	6683	573	1165	256	588	7929	9730	618	2348	9412	2125	173	397	135	137	91	3734	206	7117	1889	854	208	216
C10 Branched d	16807	3475	8731	2338	2183	2254	9272	3446	19888	10761	5755	6836	11020	5178	5238	1836	1783	1353	6156	4913	10411	4199	6122
C10 Branched e	4220	12725	18398	115	1435	2269	757	4447	32215	22022	14115	5958	9257	3436	3476	2905	4121	2820	1124	70	20481	4314	7212
C10 Branched f	19488	9795	9062	11963	4141	1918	5987	3466	29272	17527	15097	3325	6657	2206	2232	2028	2931	2714	2398	1699	11038	34179	5209
Decane (C_{10})	112969	41585	40896	43745	15363	6543	20284	108564	94616	64998	40838	11970	23020	7176	7259	7179	10101	8132	8293	7053	32411	13802	20082
C11 branched a	25234	4526	8343	13970	568	11046	3060	39680	37881	710	2120	2326	105	15358	15536	2714	2245	441	1132	647	7606	3048	942
C11 branched b	19581	13686	6451	5768	1906	1628	2062	1834	44360	28577	6266	1896	3177	1247	1262	1029	3433	1407	461	376	15892	2132	2635
C11 branched c	33444	6819	6260	2076	1881	988	3703	776	12403	11250	2410	801	1661	566	572	448	1290	456	1206	1209	7105	805	1161
C11 branched d	27082	10292	6597	5851	2492	854	2796	2368	15658	16417	7749	1739	6975	1145	1158	1477	1662	1094	1569	2696	14266	2205	3602
Undecane (C_{11})	172987	78011	70787	63182	22943	10885	54132	20355	154823	100030	68150	21637	36542	13881	14041	11054	19309	1544	14978	13897	56483	23475	25639
Benzene	27958	8655	6127	11275	4369	4026	10014	12264	25169	12199	12828	3734	11311	5369	5431	19749	12968	15159	11848	16015	40930	12765	8495
Toluene	535733	110409	98809	144822	59555	60663	95461	223409	298048	138330	230826	57167	171087	56802	57458	117683	69621	85911	118105	184310	551656	149398	89628
Ethylbenzene	175334	16300	27547	36776	10462	15598	36373	24352	150105	123626	66079	40824	29611	12230	12370	22586	24082	19689	24341	40830	179342	39352	18747
m-Xylene	493895	30289	88990	123256	33534	37101	25498	51217	83172	114302	220389	43043	41242	32074	32445	83088	41495	53002	91413	140537	590497	144218	71305
p-Xylene	139345	91588	27767	37148	10403	10736	65815	43998	219729	35681	65873	13179	47285	9254	9361	21891	11558	14299	25853	38129	178118	42356	21111
n-propylbenzene	57722	11763	13553	15096	4614	4259	11603	18019	22253	15429	28072	5125	17876	2975	3010	6561	3739	4740	8902	13473	67890	14879	7067
1,3,5-trimethylbenzene	162055	33615	34413	41031	11094	8909	23364	39279	69749	40163	72753	11097	38125	7099	7182	14688	8599	10168	21617	31739	168996	37026	17075
1,2,4-trimethylbenzene	129	9423	9376	15512	3255	2509	6659	10336	20105	11991	19006	3437	10233	2067	2091	4140	2428	2929	6196	9033	47470	10574	5722
1-ethyl-2-methylbenzene	31792	6959	7179	11332	2353	1768	4631	7716	16078	8834	14971	2444	7942	1462	1479	2904	1646	1880	4073	5610	33696	7266	3445
1,2,3-trimethylbenzene	137760	32616	30473	65243	11058	8528	22448	30060	66087	38882	62061	12327	35363	7654	7743	13142	8685	9733	20608	27269	159719	32271	16989
1-ethyl-3-methylbenzene	37705	7722	6877	14050	2094	1180	5930	3847	10402	5917	8964	2024	210	965	977	1682	1221	1661	4103	5297	33266	6277	3443
sec-butylbenzene	11097	2212	2649	3228	653	1572	1771	6003	14085	9148	14105	2656	5150	1359	1374	2602	1552	422	1092	1415	8901	1332	877
Aromatic unknown 1	2215	950	935	2723	245	424	636	705	2043	2665	4282	962	5521	395	400	297	431	245	428	472	3540	702	473
Aromatic unknown 2	8443	1863	2005	3699	539	427	1318	1166	3325	2393	2971	624	35	302	306	1532	56	449	1077	1063	7642	1428	870

Appendix 2: Concentration of VOCs [pg L^{-1}] for the time series experiment. (Continuation)

Compound	17/06/2005	19/06/2005	21/06/2005	23/06/2005	25/06/2005	27/06/2005	29/06/2005	01/07/2005
1,1-dichloroethene	59	117	71	112	32	103	147	22
Dichloromethane	5420	8166	6715	2929	4761	7439	4039	5852
Cis-1,2-dichloroethene	100	75	27	44	24	46	422	69
Chloroform	34120	28319	23292	21192	19094	25938	31198	13043
1,1,1-trichloroethane	119	205	36	105	82	69	94	50
Carbon tetrachloride	429	274	214	354	215	214	548	101
1,2-dichloroethane	87	274	63	29	103	99	169	89
Trichloroethene	232	381	117	298	177	280	543	0
Bromodichloromethane	332	231	34	23	53	146	84	301
cis-1,3-Dichloropropene	59	38	38	87	40	56	115	59
trans-1,3-Dichloropropene	130	32	62	87	9	10	68	30
1,1,2-trichloroethane	89	175	56	34	90	37	356	272
Tetrachloroethene	2170	1103	852	1039	1049	1775	4254	1398
Dibromochloromethane	2447	1847	1517	1521	1348	1777	2510	1395
Bromoform	10478	3877	2752	3154	3223	4089	10549	1977
2-chloropropane	2536	4586	3250	1745	3366	4301	1726	353
1-Bromoethane	216	56	96	48	31	44	270	14
1-Bromopropane	854	421	233	173	711	285	158	1588
2-chlorobutane	1361	1497	937	634	535	1229	1150	1334
Iodoethane	3145	3103	2608	2764	2361	2907	4676	1503
1-chlorobutane	7020	7533	1605	2677	3109	6039	4432	7061
2-Iodopropane	664	782	437	431	373	770	912	895
Chloroiodomethane	47	26	35	65	27	50	121	39
1-Iodobutane	4254	3591	3765	3396	3614	4257	4389	3306
2,3-Dibromopropene	102	54	23	67	200	17	140	255
Diiodomethane	268	97	85	84	161	72	243	47
Iodomethane	724	845	620	971	687	596	1219	315
Dibromomethane	397	244	141	274	131	175	283	112
1-bromopentane	64364	4191	4602	3131	1519	4616	4514	7378
Dimethyl sulphide	3105	6724	4669	2476	4303	11051	4601	3461
Dimethyl disulphide	3232	3253	1666	1688	2534	2449	2518	1030
2,4-dimethylfiran	452	242	195	196	152	237	462	241
Alkyne unknown	5391	20180	17853	10780	4892	5991	5568	11986
Limonene	2131	1674	1106	885	660	1033	1661	2380
α-pinene	64273	54928	38685	52552	32878	29076	41990	51750
Decanal	1492	2118	25805	11857	733	529	35772	926
Hexanal	3179	3419	2028	2539	1545	3300	3228	3833
Nonane (C_9)	3036	7547	1290	1454	613	1860	2062	4088
C10 Branched a	1284	645	110	109	41	400	554	349
C10 Branched b	1140	1133	128	4760	170	275	789	181
C10 Branched c	309	1425	155	7399	576	119	1936	2803
C10 Branched d	6705	3861	3174	3758	6571	4963	2298	7416
C10 Branched e	7131	5524	4812	5012	3871	3027	5298	7378
C10 Branched f	4031	3480	1848	2100	1103	1490	5200	4757
Decane (C_{10})	12876	18424	5556	6599	2334	3006	6772	16053
C11 branched a	27973	3039	290	1685	266	3575	3580	765
C11 branched b	2342	5233	257	974	568	284	1273	3507
C11 branched c	1191	2208	730	566	849	1428	418	1379
C11 branched d	2277	16208	1257	1680	764	959	1000	4513
Undecane (C_{11})	24978	35702	9010	13624	4380	5084	11586	30958
Benzene	6445	26335	6693	3612	6336	8449	4836	5707
Toluene	117607	983527	142904	152919	187478	190554	175452	169402
Ethylbenzene	24099	394823	30999	45591	38741	38057	42465	65056
m-Xylene	80937	1034267	97347	132917	111647	114708	121915	186337
p-Xylene	23934	290613	27134	37765	30101	31248	33252	59778
n-propylbenzene	7716	129903	8639	14564	9531	9429	10943	23181
1,3,5-trimethylbenzene	18470	302290	20321	37354	25244	23722	27166	67486
1,2,4-trimethylbenzene	6370	78376	6076	10074	6660	7162	7686	18329
1-ethyl-2-methylbenzene	3546	52112	3969	6284	4398	4427	5117	12909
1,2,3-trimethylbenzene	17870	245705	18123	33629	21136	22671	24701	57401
1-ethyl-3-methylbenzene	3725	64908	2955	6986	3411	5160	4493	14383
sec-butylbenzene	885	19491	664	1961	857	1264	1122	4016
Aromatic unknown 1	506	6910	346	782	337	649	582	1692
Aromatic unknown 2	970	12013	680	123	1016	1057	1066	3514

Appendix 3. Meteorological and physico-chemical conditions for the time series experiment *.

	Meteorological						Physico-chemical			
Date	Air Temperature [° C]	Humidity [%]	Pressure [mBar]	Rain Fall [mm. day^{-1}]	Wind speed [m s^{-1}]	Irradiation [W m^{-2}]	Salinity [PSU]	Seawater Temperature [° C]	Turbidity [TFU]	Tide [m]
06/08/2004	19.43	88.97	1013.3	1.02	3.41	68.76	32.77	17.39	3.78	6
10/08/2004	18.76	95.48	1005.09	0.826	3.09	125.32	32.07	18.36	3.87	5.88
11/08/2004	18.83	95.82	1005.88	0.539	3.02	100.21	31.82	18.53	3.78	3.3
13/08/2004	19.23	93.22	1006.79	0.4	2.18	99.63	31.43	18.3	3.68	5.09
16/08/2004	18.03	93.88	1002.3	1.444	4.75	55.37	30.4	17.97	3.69	8.18
17/08/2004	18.78	89.65	997.39	1.023	3.37	35.7	29.95	17.89	3.54	4.45
19/08/2004	16.75	98.1	993.96	4.441	10.17	53.86	29.91	17.45	3.66	8.02
15/10/2004	9.96	100	995.08	0.24	0.39	25.42	30.89	12.5	285.12	8.84
18/10/2004	9.47	99.93	1005.25	0.113	0.91	62.25	30.27	12.09	437.64	7.42
21/10/2004	10.47	95.22	991.83	0.27	5.93	14.36	29.85	11.59	229.35	3.91
26/10/2004	10.25	92.84	1007.47	0.01	0.89	39.16	29.54	12.03	319.3	1.49
27/10/2004	11.23	87.95	991.22	0.03	3.83	10.69	29.93	11.86	436.71	8.04
12/11/2004	10.49	94.16	1024.32	2.142	6.79	20.92	30.07	11.32	417.66	1.93
15/11/2004	10.24	98.17	1026.94	2.685	6.95	18.39	31.3	10.65	494.3	8.7
18/11/2004	6.61	100	1013.14	1.714	5.48	7.71	30.69	10.88	400.75	7.5
22/11/2004	12.31	99.58	1016.31	3.594	8.38	10.96	30.29	10.09	268.72	2.8
24/11/2004	11.75	99.45	1027.23	1.17	4.1	13.82	30.48	10.48	198.7	3.96
26/11/2004	10.1	99.93	1019.13	0.624	3.6	17.65	30.57	10.63	253.03	6.19
29/11/2004	6.74	89.65	1018.84	0.784	3.25	48.99	30.12	9.54	456.94	8.05
01/12/2004	7.92	96.58	1009.47	0.129	1.29	33.17	30.24	9.34	217.82	6.46
26/01/2005	7.48	95.58	1035.71	0	0.45	29.76	32.64	6.79	394.26	8.27
03/02/2005	9.09	98.52	1036.91	0.02	0.95	41.21	33.08	7.7	1006.07	2.89
04/02/2005	8.71	95.37	1024.99	0.01	4.41	18.37	32.88	7.72	1029.11	3.81
05/02/2005	6.48	99.95	1015	0.33	0.6	35.33	32.91	7.6	2171.59	3
06/02/2005	4.83	100	1020.67	0.05	0.45	49.11	32.76	7.39	1875.68	2.34
07/02/2005	5.28	93.3	1020.51	0.01	2.01	17.72	32.84	7.11	410.63	4.13
07/03/2005	6.58	100	1033.18	0.001	3.61	78.91	29.72	5.16	572.94	4.4
08/03/2005	7.89	100	1034.19	0	3.19	141.48	30.3	5.56	592.34	4.17
09/03/2005	8.32	100	1036.01	0	1.65	99.3	30.11	5.87	670.34	6.2
14/03/2005	6.49	100	1009.37	0.024	8.52	15.98	31.13	5.82	890.02	6.75
15/03/2005	9.66	100	1010.26	0	11.56	8.54	31.46	6.25	864.94	6.06
16/03/2005	10.39	100	1011.77	0.002	11.54	11.68	31.97	6.87	787.95	4.48
17/03/2005	10.25	100	1021.94	0	9.36	20.12	32.5	7.47	680.77	3.84
21/03/2005	15.39	100	1003.96	0.016	7.72	45.54	33.69	8.73	256.64	4.05
22/03/2005	12.35	100	1000.62	0.001	8.86	19.34	33.79	8.8	259.32	6.44
23/03/2005	12.64	100	1010.04	0.01	8.31	57.97	33.91	8.81	258.91	6.19
29/03/2005	12.28	100	1012.94	0	2.33	170.51	30.28	8.35	434.67	8.55
04/04/2005	8.79	100	1020.77	0.001	5.32	102.18	38.36	8.9	222.27	3.16
05/04/2005	9.12	100	1020.34	0.007	8.99	53.97	33.54	8.55	241.17	4.19
06/04/2005	8.55	100	1003.55	0.03	11.35	43.28	33.38	8.5	213.69	5.48

Appendix 3. Meteorological and physico-chemical conditions for the time series experiment *. (Continuation)

	Meteorological						Physico-chemical			
Date	Air Temperature [° C]	Humidity [%]	Pressure [mBar]	Rain Fall [mm. day^{-1}]	Wind speed [m s^{-1}]	Irradiation [W m^{-2}]	Salinity [PSU]	Seawater Temperature [° C]	Turbidity [TFU]	Tide [m]
13/04/2005	8.92	93.49	1006.86	0.006	1.21	124.58	34.47	8.82	327.47	4.74
14/04/2005	7.99	99.43	1000.73	0.01	0.59	148.43	^	8.86	217.97	7.13
15/04/2005	7.16	96.9	1008.92	0.037	2.9	39.63	^	8.76	390.55	4.33
18/04/2005	8.25	97.16	994	0.033	1.91	80.21	32.27	8.14	207.2	4.36
19/04/2005	8.07	96.98	1007.31	0.012	1.4	126.07	32.16	8.17	217.33	4.2
26/04/2005	12.04	92.19	1007.23	0.014	1.19	95.35	30.48	9.26	392.65	8.4
28/04/2005	12.64	92.07	1007.59	0.001	6.74	56.41	34.91	9.54	357.87	7.55
29/04/2005	13.07	87.9	1016.74	0	2.54	289.47	^	9.89	196.92	7.7
03/05/2005	13.11	95.5	1010.11	0.001	2.23	93.26	35.91	10.95	432.58	2.12
04/05/2005	11.96	85.45	1023.66	0.019	0.92	146.9	35.79	10.94	379.4	1.71
06/05/2005	11.14	90.06	1018.1	0.006	2.52	245.11	^	10.59	361.9	0.75
08/05/2005	9.45	83.03	1016.51	0.001	1.3	164.13	37.22	10.35	366.12	8.31
10/05/2005	10.54	77.64	1025.21	0	1.55	285.74	^	10.71	518.4	8.26
12/05/2005	12.25	67.99	1023.31	0	2.76	360.79	36.1	11.31	608.86	7.19
14/05/2005	12.1	74.04	1021.61	0	6.31	365.36	36.49	11.46	217.29	3.85
16/05/2005	11.27	88.73	1019.17	0.001	2.22	88.93	36.98	12.31	389.85	3.22
18/05/2005	10.73	78.95	1017.62	0.001	2.77	115.61	36.65	12.05	464.4	4.39
20/05/2005	13	93.28	1005.12	0	4.65	56.43	36.34	11.89	652.32	3.12
22/05/2005	11.3	96.51	1002.76	0.008	2.37	182.82	30.52	11.55	538.46	3.14
24/05/2005	12.54	99.79	1010.63	0.012	3.66	73.48	30.61	11.43	626.08	2.32
26/05/2005	14.66	89.36	1014.49	0.003	2.65	289.06	33.08	12.08	816.57	7.1
28/05/2005	14.46	89.89	1009.06	0	5.8	57.21	^	12.64	705.52	3.71
30/05/2005	13.66	83.36	1024.17	0.002	0.46	305.29	^	12.83	670.75	2.45
01/06/2005	14.43	98.45	1017.02	0.002	2.49	51.59	36.61	13.3	293.85	2.49
03/06/2005	14.2	94.87	1005.97	0	3.16	122.27	36.22	13.28	218.04	1.77
05/06/2005	14.3	91.58	1016.79	0	1.73	138.03	35.8	13.09	^	4.09
07/06/2005	16.17	80.87	1036.12	0	0.42	241.06	36.11	13.68	214.1	2.31
09/06/2005	16.68	81.69	1033.69	0	0.13	176.72	36.02	14.26	218.68	7.77
11/06/2005	16.61	81.03	1019.5	0	0.64	416	35.89	14.2	216.02	6.09
13/06/2005	11.59	92.49	1008.05	0.007	2.1	87.02	35.33	13.89	213.12	2.39
15/06/2005	15.72	94.5	1007.84	0.001	3	91.5	34.58	13.54	212.8	3.11
17/06/2005	17.72	99.34	1025.5	0.001	3.17	252.56	35.03	14.3	214.56	5.88
19/06/2005	19.68	95.81	1016.86	0	0.66	176.57	35.77	15.26	214.36	2.91
21/06/2005	17.01	90.87	1020.2	0.001	2.84	216.41	35.8	15.3	216.95	6.08
23/06/2005	17.76	87.99	1018.72	0	2.76	412.84	35.6	15.4	216.35	4.42
25/06/2005	18.3	100	1023.61	0.002	6.1	103.63	^	15.5	176.2	5.53
27/06/2005	17.63	100	1025.24	0	4.73	424.64	36.11	16.48	216.87	1.46
29/06/2005	17.54	100	1008.26	0.004	2.62	132.94	36.48	16.86	217.95	7.29
01/07/2005	15.55	100	1012.16	0.007	4.45	144.59	35.95	16.38	218.92	6.75

(*) The data presented correspond to the daily average for each sampling day.
(^) Data not available.

Appendix 4. Concentration of VOCs [pg L^{-1}] for the day and night sampling in the Menai Strait.

Time (hr)	Isoprene	C5	C6-branched	C6 branched	C6 branched	Ciclohexane	C8	1,1-dichloroethene	Dichloromethane	Cis-1.2-dichloroethene	Chloroform	1,1,1-trichloroethane	Carbon tetrachloride	1.2-dichloroethane	Trichloroethene	Bromodichloromethane	1,1,2-trichloroethane	Tetrachloroethene	Dibromochloromethane	Bromoform	2-chloropropane
21:00	53.0	372.0	87.3	15.5	17.0	356.9	35.7	0.0	29.7	5.7	233.1	0.0	2.9	5.4	1.9	1.3	0.9	4.2	2.1	14.1	42.0
23:00	27.9	211.2	50.2	4.3	6.5	138.3	6.1	0.0	19.6	1.5	53.8	0.0	1.8	2.0	0.7	1.4	0.0	1.1	1.6	3.5	18.6
01:00	28.1	206.6	49.4	4.2	5.6	116.1	4.7	0.0	23.4	1.6	60.7	0.4	1.8	2.2	1.1	0.0	0.0	1.0	2.2	2.6	21.4
03:00	19.7	217.0	50.7	3.6	5.0	93.9	3.3	0.0	21.7	0.8	58.6	0.0	1.8	2.0	0.4	0.8	0.0	0.7	1.5	1.4	19.5
05:00	14.5	191.5	44.8	7.6	14.6	79.9	4.0	0.0	16.8	1.0	46.2	0.0	1.4	1.5	0.0	0.0	0.0	0.5	1.4	1.5	13.9
07:00	20.2	238.6	55.7	3.4	5.6	93.5	5.2	0.0	27.8	1.8	82.7	0.0	1.6	2.4	1.1	0.4	0.0	1.3	2.0	3.8	29.0
09:00	57.1	314.3	74.6	7.1	9.0	258.2	9.8	0.0	33.7	3.7	130.3	0.8	2.6	3.8	1.4	0.8	0.0	2.6	1.8	6.1	37.2
11:00	53.1	324.0	78.2	6.5	8.9	274.5	16.9	0.0	34.5	4.4	136.9	0.0	2.7	1.6	0.0	1.2	0.0	3.7	1.6	8.4	44.8
13:00	17.8	178.3	40.6	3.0	4.7	57.5	8.3	0.0	20.2	2.0	84.3	0.3	1.6	2.3	1.4	0.4	0.0	1.1	2.9	3.6	31.9
15:00	58.1	433.4	106.3	9.5	15.0	271.8	14.1	0.0	46.1	5.9	229.6	0.9	2.7	3.6	1.3	0.9	0.0	3.6	2.9	6.0	52.1
17:00	59.7	391.8	96.6	9.5	13.6	298.7	21.4	0.0	34.7	6.1	193.0	0.6	3.0	3.5	1.3	1.3	0.0	4.0	2.2	8.8	49.0
19:00	62.4	336.2	81.5	7.1	10.6	257.0	18.2	0.0	32.9	5.0	175.1	0.0	2.4	3.6	1.8	0.9	0.0	3.4	2.1	8.5	38.0
21:00	52.0	351.4	84.8	4.6	9.8	238.4	15.5	0.0	43.1	4.9	243.4	0.6	2.9	3.8	1.9	1.4	0.0	3.3	2.5	8.9	42.8

Appendix 4. Concentration of VOCs [pg L^{-1}] for the day and night sampling in the Menai Strait. (Continuation)

Time (hr)	1-bromoethane	1-bromopropane	2-chlorobutane	Iodoethane	1-chlorobutane	2-Iodopropane	Chloroiodomethane	1-Iodobutane	2,3-dibromopropene	Diiodomethane	Dimethyl sulphide	Iodomethane	2,4-dimethylfuran	Dimethyl disulphide	Alkyne unknown	a-pinene	Dibromomethane	Limonene	Octanal	Benzene	Ethylbenzene	p-Xylene
21:00	1.0	16.7	14.2	35.9	113.0	10.8	0.0	4.9	0.0	0.0	1845.5	1.8	1.7	3.5	43.7	10.7	2.6	22.9	0.0	183.9	223.8	52.3
23:00	0.3	3.6	5.2	7.6	37.7	4.7	0.0	1.0	0.0	0.0	840.1	1.2	0.7	1.5	10.3	3.6	1.1	17.4	0.0	28.6	64.3	18.0
01:00	0.0	3.7	5.7	9.7	41.0	5.5	0.0	1.2	0.0	0.0	649.9	1.2	0.6	1.4	13.9	3.8	0.9	19.2	0.0	24.6	38.6	11.2
03:00	0.0	3.7	4.1	7.6	25.3	5.2	0.0	0.9	0.0	0.0	538.6	0.6	0.4	1.2	9.7	2.5	0.6	13.8	0.0	19.1	23.4	7.7
05:00	0.0	4.9	4.3	5.4	24.8	3.9	0.0	0.5	0.0	0.0	616.3	0.5	0.0	0.9	7.0	2.4	0.5	14.7	0.0	17.3	24.6	7.2
07:00	0.0	5.4	4.6	11.6	37.5	7.8	0.0	1.6	0.0	0.0	1165.5	0.7	0.8	2.0	13.9	4.2	1.1	36.4	0.0	39.8	69.9	18.9
09:00	0.0	10.1	8.7	18.4	69.0	10.7	0.0	2.9	0.0	0.0	1689.6	1.9	1.2	5.5	19.5	3.0	2.0	16.1	0.0	75.5	99.6	24.7
11:00	0.6	7.9	10.6	21.6	77.8	12.3	0.6	3.5	0.0	0.0	1358.7	1.6	1.4	5.5	29.3	4.4	1.6	26.7	0.0	82.1	120.8	34.2
13:00	0.4	4.1	4.1	12.8	31.9	6.9	0.0	1.7	0.0	0.0	646.5	1.2	0.6	1.3	15.0	2.8	0.7	22.7	0.0	31.7	77.0	21.2
15:00	0.0	9.5	12.3	36.8	106.5	17.1	0.0	6.1	0.0	0.0	1160.0	1.5	1.5	5.5	30.5	4.7	1.7	28.0	0.0	104.2	108.6	27.5
17:00	0.4	9.3	12.8	30.5	103.7	14.9	0.5	5.5	0.0	0.0	1309.2	1.5	1.2	9.8	40.3	5.9	1.7	28.0	0.0	107.7	126.8	33.5
19:00	0.5	8.2	10.2	26.9	84.4	12.6	0.5	4.9	0.0	0.0	1424.2	1.5	1.8	8.2	33.0	5.7	2.0	25.7	0.0	119.9	164.3	39.1
21:00	0.0	3.9	10.7	37.1	78.7	16.2	0.5	6.0	0.0	0.3	1478.7	2.1	1.7	10.3	29.2	4.6	2.1	32.1	0.0	99.5	132.6	35.6

Appendix 5. Pigments (μg L^{-1}), meteorological and physicochemical data for day and night sampling in the Menai Strait.

Time (hr)	Chlorophyll a	Fucoxanthin	Dinoxanthin	B-carotene	cis-fucoxanthin	Chlorophyllade a	Peridinin	Tide (m)	Wind speed (m/s)	Air temperature (C)	Pressure (Bar)	Humidity (%)	Sun light (Lux)	Conductivity (ms cm^{-1})	Water temperature(C)
21:00	4.30	0.92	0.11	0.05	0.26	0.41		6.13	0.00	9.6	1.021	92.00	0	37.02	11.80
23:00	4.33	0.83	0.14		0.26	0.33	0.10	5.52	0.00	9.1	1.020	95.00	0	37.01	11.72
01:00	3.45	0.84	0.16	0.03	0.20	0.20		3.59	0.00	8.0	1.020	95.00	0	36.98	11.64
03:00	3.87	0.89	0.15	0.04	0.23	0.16		2.26	2.08	7.2	1.020	96.00	0	36.96	11.61
05:00	3.80	0.86	0.13	0.03	0.32	0.32	0.12	2.78	0.00	8.1	1.020	95.00	8980	36.94	11.66
07:00	3.74	0.84	0.11	0.13	0.36	0.39		5.08	1.28	15.9	1.021	71.00	44000	37.02	11.79
09:00	4.75	0.90	0.16		0.32			6.34	6.92	16.2	1.021	61.00	76500	37.13	11.85
11:00	3.92	0.85	0.07	0.03	0.24			5.40	5.50	19.5	1.020	49.00	92500	37.23	11.90
13:00	3.05	1.27	0.12	0.06	0.15	0.73		3.33	9.19	18.0	1.020	51.00	87700	37.38	12.06
15:00	1.22	0.61	0.04	0.04	0.09	0.28		1.83	7.33	18.1	1.019	51.00	31800	37.34	11.97
17:00	3.36	0.56	0.15	0.05	0.18	0.60		2.21	5.75	17.7	1.019	49.00	30300	37.33	11.99
19:00	1.73	0.52	0.09	0.08	0.19	0.27	0.19	4.90	3.53	14.4	1.019	57.00	2510	37.37	12.11
21:00	1.25	0.33	0.06	0.03	0.12	0.51		6.43	1.08	12.5	1.019	66.00	0	37.37	12.05

Appendix 6. VOCs produced by macroalgae through the time (pg g^{-1} DW^{-1}).

Time (hr)	Algae type	1,1-dichloroethene	Dichloromethane	Cis-1,2-dichloroethene	Chloroform	1,1,1-trichloroethane	Trichloroethene	Bromodichloromethane	cis-1,3-Dichloropropene	trans-1,3-Dichloropropene	1,1,2-trichloroethane	Tetrachloroethene	Dibromochloromethane	Bromoform	2-chloropropane	1-bromoethane	1-bromopropane	2-chlorobutane	Iodoethane
3 light		0.5	262.5		652.4			24.2			3.4	2.3	443.9	19769.8	104.7	0.0	10.8	64.3	74.9
6 light		0.3	167.3		480.7			56.4			13.7	3.1	744.0	25056.5	78.6	2.9	26.3	29.7	66.9
9 light	AN	1.5	144.0		380.8			72.5			16.4	1.2	970.3	35714.0	76.8	2.8	30.2	27.4	48.5
12 light		1.7	180.5		415.7			74.8			25.1	1.9	914.0	34070.8	75.5	5.6	39.3	29.6	55.5
12 dark		0.2	375.2		876.4			55.2			10.6	1.6	668.5	17690.6	94.8	4.4	88.1	59.0	112.9
3 light		2.3				0.2		12.9		0.8		9.2		4925.4		0.0	0.0		
6 light		1.3				1.3		10.7		0.6		5.9		6017.3		1.0	0.0		
9 light	FV	0.0				1.3		9.3		1.4		3.6		8552.9		0.8	2.7		
12 light		1.9				3.6		10.7		0.5		6.9		6009.1		0.0	15.3		
12 dark		2.7				0.3		6.8		0.4		9.0		2175.0		7.4	25.7		177.5
3 light		1.5					1.0	3.4	0.0	0.7	0.7	57.6		2426.1		0.0	8.0		6.4
6 light		7.7					0.0	22.6	0.5	0.9	0.0	109.3		9024.3		0.0	11.3		0.0
9 light	FS	3.0					0.0	21.7	4.0	2.9	9.1	128.3		13449.6		0.2	18.3		0.0
12 light		1.5					0.7	11.5	0.0	0.0	5.3	77.0		4891.9		1.8	17.5		0.0
12 dark		1.0				1.0	1.4	10.0	1.6	1.0	1.6	73.1		2402.5		3.8	18.0		17.4
3 light		3.0					1.2	5.3				12.5	0.8	3416.9		0.0			22.7
6 light		1.3						13.7				5.9	103.6	10677.4		1.0			27.8
9 light	LD	5.2						16.9				4.9	13.9	10462.2		2.0			0.0
12 light		2.4						19.3				6.7	234.4	15879.6		5.8			117.1
12 dark		20.4	74.6		147.9			0.0			37.2	8.8	0.0	3261.6	127.5		47.1		638.4
3 light		10.8				2.0	132.2	24.1	3.0		0.0	3.5	146.9	24432.0		-0.6	114.3		525.0
6 light		15.4				3.8	128.3	19.6	1.8		0.0	19.7	384.3	39865.5		10.9	67.4		695.5
9 light	UL	26.4				0.0	218.2	64.4	2.2		15.3	0.0	1261.7	91694.5		5.8	112.6		596.7
12 light		21.8				0.0	286.0	136.5	1.7		0.0	0.0	3219.3	177887.3		10.3	277.9		1174.8

12 dark		6.1				4.8	277.3	30.3	3.0		3.6	0.0	-235.1	15262.5		17.1	127.0		2599.8
3 light		6.9		0.7			22.2	77.0	3.8		0.9	1.9	1589.4	97995.4		13.9	5.0	19.5	256.0
6 light		0.0		0.0			18.9	77.6	4.2	3.5			1788.5	114874.8		31.5	109.7		325.0
9 light	EN	3.4		4.9			25.4	114.7	2.3		8.0	2.8	2782.0	168980.3		31.1	146.4		222.2
12 light		15.7		1.4			11.7	137.8	0.8		7.6		2799.5	160610.7		48.7	126.9		234.7
12 dark		0.0	25.4	2.8			75.1	35.7	3.9	0.4	22.4	1.5	519.2	33357.4		51.5	210.7		1677.1
3 light		0.0						2.3			0.4			683.9					0.0
6 light		2.4						0.0			3.8			974.2					51.9
9 light	PP	5.6						2.4			7.4			2808.9					14.6
12 light		4.6						0.0			7.1			2162.5					60.8
12 dark		16.8			302.8		7.7	3.7			27.2	7.2	43.8	494.8	109.7	6.1			204.7
3 light		9.9				2.0		0.6	1.1			2.4	100.1	16658.2					
6 light		6.5				3.3		0.4				18.1	352.3	36543.3					
9 light	GF	16.0				2.8		0.3	0.4				1116.1	81114.3					
12 light		31.1				0.6		13.9	6.2					1170.2					
12 dark		8.3				0.0				2.2				109.9					

Appendix 6. VOCs produced by macroalgae through the time (pg g^{-1} DW^{-1}). (Continuation)

Time (hr)	Algae type	1-chlorobutane	2-iodopropane	Chloroiodomethane	1-Iodobutane	2,3-Dibromopropene	Diiodomethane	Dibromomethane	1-bromopentane	Iodomethane	Dimethyl sulphide	Dimethyl disulphide	2,4-dimethylfuran	Hexanal	Decanal	Alkyne unknown	a-pinene	Nonane	Decane	Undecane
3 light		301.0	47.2	2.8	155.0	42.3	123.1	320.4	264.2	2.7	90.6	70.2		46.0	406.1	34.5	4740.4			551.7
6 light		169.4	88.0	3.0	112.7	9.8	36.5	678.4	212.7	10.8	25.6	67.5		17.0	936.0	29.2	5640.2			230.2
9 light	AN	134.8	71.7	2.1	84.0	34.5	35.6	613.9	201.6	10.5	13.3	73.3		25.1	608.4	30.4	8044.5			289.1
12 light		169.0	131.0	2.6	107.2	33.3	31.4	847.2	329.3	13.4	34.8	236.1		8.2	685.4	37.2	8182.4			744.1
12 dark		303.9	528.9	0.0	159.0	34.4	8.0	465.9	441.4	23.7	469.1	220.9		32.0	501.7	32.3	4414.8			253.7
3 light			86.0	5.0		1.8	89.9	267.9		10.1	56.2	56.5	0.0			56.6	907.7			
6 light			61.0	1.5		4.0	124.1	230.4		8.2	37.2	1.6	0.0			78.0	1049.0			
9 light	FV		152.9	0.0		1.0	33.0	235.6		14.5	70.3	10.6	0.8			18.7	1348.9			
12 light			39.3	0.0		11.2	70.3	193.9		12.1	12.3	3.5	1.3			25.6	1029.8			
12 dark			904.6	0.0	140.7	3.5	26.2	180.1	131.3	88.2	422.7	5.1	6.1			42.5	387.2			
3 light			123.6			0.3	16.2	64.1	46.6	31.0	218.5	0.0			311.3	23.0			285.1	
6 light			163.0			4.2	25.0	188.0	170.7	61.4	410.6	76.1			8808.0	60.4			190.4	
9 light	FS		293.5			3.5	53.3	327.0	0.0	88.2	523.1	137.6			3904.1	58.1			269.9	
12 light			346.0			1.2	16.9	134.0	19.7	94.6	309.1	144.8			1319.7	44.6			195.7	
12 dark			500.7			0.2	0.0	112.7	0.0	122.1	414.3	47.7			986.0	44.5			194.8	
3 light			37.8	45.4	1.7	0.0	14713.6	366.7	11.9	215.3			0.0		1983.1	14.5	45.8	52.4	323.3	371.7
6 light			30.6	102.9	0.0	25.0	26686.5	773.9	184.5	401.1			0.0		300.0	1.0		19.2	172.7	182.6
9 light	LD		42.8	161.1	0.0	0.0	36896.3	882.6	0.0	292.4	89.3		13.4		180.5	11.7		0.0	0.0	0.0
12 light			149.4	354.3	0.0	51.8	48950.7	1489.0	0.0	322.6	10.9		7.4		2511.4	0.0		0.0	0.0	0.0
12 dark			1817.2	65.5	130.6	2.7	9074.1	467.2	42.4	2426.5	654.8	5.3	18.5		0.0	3.6		915.0	206.4	0.0
3 light			866.6	0.0		81.6	1011.5	420.4	2157.1	36.7	25032.9	15267.2	678.1		12009.3	162.6				
6 light			624.1	27.8		1.7	2438.6	753.6	870.1	166.9	8125.2	11525.1	775.1		935.6	174.8				
9 light	UL		1058.3	67.0		52.1	4787.2	2206.2	1187.3	361.2	32577.2	55335.9	1226.6		0.0	217.2				
12 light			1362.5	121.1		16.1	7353.2	4507.1	2516.7	446.3	22782.2	56210.1	1608.0		20.7	251.6				
12 dark			4245.0	17.1		61.4	748.0	695.8	851.8	717.0	80136.2	164209.2	1503.3		0.0	215.9				

3 light		292.9	62.2	167.9	0.0	2452.6	4453.4	2817.5	101.5	682.4	310.2	114.3	810.0	1551.5		220.1	60.2	655.9
6 light		310.4	75.7	291.6	150.0	3993.4	5969.2	2448.0	66.3	1015.4	173.0	99.3	3898.1	32.6		311.8	110.1	717.8
9 light	EN	245.0	116.8	211.8	434.2	5287.8	8104.8	2055.2	108.5	1401.5	330.6	125.0	10263.5	33.2		480.6	458.7	915.7
12 light		307.9	141.4	195.6	16.7	6430.9	9252.3	0.0	86.8	1870.6	194.1	112.6	129.7	25.3		221.3	0.0	0.0
12 dark		1375.5	32.5	1436.7	79.1	1274.5	4674.5	8220.9	1179.4	37822.0	23201.2	495.7	0.0	29.4		710.3	0.0	270.4
3 light			0.6			24.7	24.7	0.0	27.7	15.1	23.6	12.7	0.0	17.7		20.2		10.8
6 light			4.7			33.8	23.7	0.0	20.9	19.6	113.2	17.6	2121.1	45.7		43.1		123.7
9 light	PP		2.0			81.1	84.7	408.4	56.1	27.4	306.7	35.7	10866.7	47.8		121.5		203.9
12 light			7.7			67.5	76.7	266.9	11.8	5.7	74.5	34.2	2145.4	43.9		17.6		32.9
12 dark			1.6	58.5	57.6	12.2	17.3	161.8	4.4	114.4	44.4	31.6	0.0	63.6	22.0	1543.2	220.7	777.0
3 light						689.6	11.0		14.3	83.2	42.8		1564.6	109.5			217.6	
6 light						2235.4	12.4		14.1	76.7	86.9		1870.2	158.9			14.9	
9 light	GF					4234.8	35.4		81.7	142.1	595.4		12.2	189.3			164.0	
12 light						65.2	54.5		96.7	2197.7	483.8		822.9	61.9			337.3	
12 dark						14.1	14.9		152.7	5848.7	1075.2	0.9	6384.8	153.9		882.9	718.3	

Appendix 7. VOCs produced by macroalgae under desiccation (pg g^{-1} DW^{-1}).

Time (hr)	Algae type	Dichloromethane	Cis-1.2-dichloroethene	Chloroform	1.2-dichloroethane	Tetrachloroethene	2-chloropropane	2-chlorobutane	1-chlorobutane	Bromodichloromethane	Dibromochloromethane	Chloroiodomethane	1-Bromopropane	Bromoform	Dibromomethane	1-Bromoethane	1-bromopentane	Iodoethane	2-Iodopropane	1-Iodobutane	Diiodomethane
0		3124	146	7256	33	123	860	245	1657	126	107	11	534	15002	2133	84	1259	1013	1004	176	68
2	AN	2814	159	6776	30	85	1311	250	1880	173	146	20	482	14863	1508	60	431	981	934	204	202
4		2758	166	6295	34	41	1860	257	2183	230	191	83	466	14871	1116	38	921	1029	914	279	468
6		1767	83	5274	36	24	1557	221	1851	261	260	165	291	5957	502	34	538	957	521	246	1592
0		5595	336	19830	132	84	76	5512	2784	38	618	18	2706	69	681	300	1010	1094	3110	157	647
2	FV	5763	305	18368	0	115	77	6293	4692	93	521	64	4458	70	907	914	1354	2573	2821	508	555
4		4351	276	13543	102	62	66	4378	3768	106	392	184	4517	46	565	773	801	952	2230	750	561
6		4333	227	12842	0	66	48	3561	3530	182	356	82	2962	32	496	391	736	1325	2174	530	424
0		3538	220	9664	60	40	2214	426	3581	380	0	26	1782	25	313	275	773	1466	78	327	530
2	FS	4920	557	18321	77	73	4157	570	4813	597	38	75	2679	47	557	630	1048	2589	580	841	1187
4		3842	247	11786	77	49	2965	1048	3626	404	42	0	1638	29	389	491	713	1822	647	394	827
6		3918	136	10744	48	28	1878	426	3289	379	75	0	1045	0	476	397	732	1668	693	291	563
0		10132	548	32266	216	153	81	161	9669	903	53	126	15253	4549	1370	370	3169	1962	6184	1338	1480
2	EN	8231	384	24147	317	113	79	75	6390	589	70	122	10858	3028	972	211	2556	1227	4091	664	1950
4		7130	430	23050	256	103	94	86	5960	630	80	125	10456	2776	856	199	2120	1145	4232	850	1820
6		6425	485	22430	137	109	110	154	5653	764	0	131	10238	2283	750	185	1718	1055	4383	1358	1889
0		24466	1042	75275	642	289	183	241	2785	1540	0		158	3255	364	2287	5352	4013	11419	2956	739
2	UL	19263	857	52056	410	259	725	182	2145	1749	114		326	5791	408	1849	5838	2813	11198	1954	897
4		16674	688	44567	460	164	1241	138	2942	1356	115		737	5441	356	1759	5819	2612	18547	1293	589
6		16294	920	44481	383	237	4019	167	2087	1494	0		2328	4019	209	1739	4692	2645	51400	1869	543
0		14842	873	51823	224	188	116	67	209	137	1102	1182	172	7819	5140	1789	4155	10276	2380	3825	63709
2	LA	8752	447	25414	252	89	64	89	90	205	844	4457	354	5177	6826	1191	4213	33424	1122	5709	108784
4		7330	363	17476	169	77	218	205	83	52	815	4235	488	3930	3429	824	3092	68695	1008	6861	126170
6		6463	305	12535	93	93	80	293	92	246	1483	1393	909	3734	1255	335	7096	227780	2034	11164	54496

Appendix 7. VOCs produced by macroalgae under desiccation (pg g^{-1} DW^{-1}). (Continuation)

Time (hr)	Algae type	Iodomethane	Dimethyl sulphide	Dimethyl disulphide	Isoprene	a-Pinene	Limonene	Pentane (C5)	C6 branched	Hydrocarbon 1	Hydrocarbon 2	Ciclohexane	Octane (C8)	Undecane (C11)	Nonane (C9)	Decane (C10)	Octanal	Hexanal	Heptanal
0		153	4021	17	303	43	337	8601	2065	166	325	1025	448	1640	325	203	223	363	128
2	AN	143	3543	18	273	56	362	9634	2311	158	262	761	370	1209	257	378	360	333	311
4		119	2084	26	230	68	376	9180	2161	189	296	812	228	667	158	769	2514	297	594
6		184	107719	15	168	141	1073	11573	2642	170	219	607	306	477	260	6437	7218	493	1264
0		289	3695	90	1032	349	1624	22782	5303	375	524	1199	752	5026	838	1029	316	1050	1236
2	FV	474	7334	72	1136	455	1497	25346	6164	452	721	1879	752	7377	501	7683	36955	1311	5862
4		417	7463	67	880	198	1681	29018	6936	475	649	1904	638	4389	549	6480	14475	1358	6191
6		246	12292	9	813	116	916	28510	6807	431	570	1568	210	2441	231	5437	17963	466	2556
0		176	10372	36	665	189	1236	17441	4060	287	401	918	575	3848	642	788	242	804	946
2	FS	348	4763	30	886	390	2350	19626	4773	350	558	1528	582	5712	387	4173	28614	1015	6559
4		386	7527	40	807	385	1813	25838	6176	423	578	1695	568	3908	489	3198	12889	1209	6497
6		416	6013	0	702	178	1350	28373	6774	429	568	1560	209	2508	230	4102	17877	464	2950
0		1220	8239	131	7146	415	3013	47577	12034	1076	1430	3191	1209	3808	1558	2099	511	2603	2757
2	EN	887	23162	175	4654	416	2558	51104	12447	934	1123	2717	643	1966	1131	2015	893	1223	3190
4		989	37560	250	3978	389	3520	42217	9802	783	963	2281	679	2233	957	1902	1811	1732	3154
6		1382	47068	357	3510	345	4610	28373	6753	583	808	2163	745	4435	747	1871	2629	2148	3190
0		2099	9462	298	7385	857	5494	127389	31906	2484	3316	6807	2365	7693	3215	3430	1319	3141	3565
2	UL	2770	189438	1715	4883	709	5448	117815	27756	1980	2788	6065	1956	6682	1725	2775	4752	2843	3909
4		2395	497738	549	3367	477	4355	100655	24060	1489	2361	7098	1625	4775	979	4721	28094	3082	7241
6		2398	469032	364	3155	431	5097	75123	17739	1517	1913	4831	1642	5412	757	3846	13096	5441	8960
0		7001	3914	63	1784	639	3043	75260	18351	1568	2191	4658	2095	5797	1420	4615	1329	2260	1842
2	LA	6389	2573	50	627	721	2053	56422	13596	1039	1302	3172	1255	4062	437	2976	4685	7348	3618
4		11664	4221	66	636	342	2076	40806	9950	723	970	2824	1226	3150	490	3473	11175	28401	6703
6		11320	17243	138	994	365	2660	19700	5051	349	570	2113	1238	3794	631	3434	18306	170441	5645

Appendix 8. Meteorological and physico-chemical conditions for the cruise to Liverpool Bay, Irish Sea.

Sample origin	Station	Date	Time (summer)	Depth	Tide as Mersey	Coordinates	Coordinates	Salinity	Water T (surface)	Air T	Wind Speed	Wind Direction	Humidity	Solar Irradiation	Pressure
				m	m	° North	° West	PSU	°C	°C	$m.s^{-1}$	°	%	$W.m^{-2}$	mBar
River Mersey	M1	25/03/2006	14:40	11.80	2.78	53°26.585 'N	003°01.828'W	nd	5.7	11.6	9.4	177	100	71	998
River Mersey	M2	25/03/2006	15:53	9.80	3.67	53°21.108 'N	002°57.410'W	nd	6.2	11.0	7.6	136	100	36	997
River Mersey	M3	26/03/2006	10:40	16.60	7.52	53°29.035 'N	003°04.567'W	nd	5.8	2.4	8.9	212	100	151	999
Seawater Replicate 1	2	25/03/2006	10:25	17.90	5.17	53°23.702 'N	003°43.909'W	nd	6.2	9.7	5.1	230	100	274	nd
Seawater Replicate 2	2	30/03/2006	09:10	21.90	3.80	53°23.754 'N	003°43.400'W	32.4	8.3	10.8	26.2	60	98	78	968
Seawater Replicate 3	2	31/03/2006	13:30	25.40	9.96	53°23.693 'N	003°43.877'W	32.8	7.6	10.1	8.6	53	43	197	1000
Seawater	13	25/03/2006	11:45	21.10	3.90	53°29.266 'N	003°30.495'W	nd	6.4	9.1	6.0	240	100	275	nd
Seawater	9	26/03/2006	12:40	31.90	5.07	53°32.081 'N	003°17.026'W	nd	6.5	10.4	7.0	191	100	446	999
Seawater	1	26/03/2006	14:55	21.50	2.61	53°23.396 'N	004°01.899'W	nd	6.7	11.7	7.4	212	100	86	997
Seawater	3	27/03/2006	14:20	7.80	3.89	53°23.997 'N	003°25.81'W	31.6	7	10.5	14.8	96	87	488	986
Seawater	4	27/03/2006	16:08	11.60	1.76	53°26.862 'N	003°12.349'W	31.2	7.3	10.8	11.7	145	84	300	986
Seawater	5	28/03/2006	11:27	11.20	9.38	53°26.809 'N	003°7.953'W	32.0	7	8.5	9.1	145	87	65	988
Seawater	10	29/03/2006	15:27	35.50	4.37	53°40.065 'N	003°30.863'W	33.1	7.5	7.2	3.6	235	87	868	1003
Seawater	5	29/03/2006	11:53	10.70	9.90	53°32.718 'N	003°08.385'W	31.1	7.3	6.8	4.0	245	89	265	1003
Seawater	7	29/03/2006	13:11	13.90	8.96	53°37.564 'N	003°08.217'W	31.2	6.9	7.0	3.8	280	81	253	1003
Seawater	11	31/03/2006	08:03	28.60	0.38	53°37.361 'N	003°26.412'W	32.8	7.4	8.4	13.0	86	60	47	999
Seawater	8	31/03/2006	09:15	14.50	2.14	53°40.385 'N	003°12.065'W	30.7	7.1	8.2	11.8	79	47	462	999
Seawater	14	31/03/2006	12:28	46.70	9.72	53°31.728 'N	003°44.208'W	33.8	7.9	9.6	4.7	26	48	680	1000
Profile 0 m	12	29/03/2006	19:56	31.30	1.29	53°32.007 'N	003°26.946'W	32.8	7.3	8.2	5.1	263	80	2	999
Profile 10.1 m	12	29/03/2006	18:36	26.90	0.20	53°31.964 'N	003°26.083'W	32.6	7.3	7.9	5.1	300	92	37	1000
Profile 29.4 m	12	29/03/2006	17:20	31.00	1.42	53°32.111 'N	003°26.283'W	32.9	7.4	7.2	7.7	22	81	130	1001
Day/nigh	15	30/03/2006	12:00	14.80	8.68	53°18.906 'N	003°42.937'W	31.9	8.9	11.4	10.9	331	98	144	989
Day/nigh	15	30/03/2006	15:00	11.14	4.44	53°18.908 'N	003°42.984'W	31.8	8.8	12.6	10.9	39	94	137	990
Day/nigh	15	30/03/2006	18:00	6.20	0.50	53°18.911 'N	003°42.945'W	31.6	9.1	11.9	9.9	331	84	71	991
Day/nigh	15	30/03/2006	21:00	8.10	3.83	53°18.844 'N	003°42.908'W	32.1	14.8	11.5	13.6	253	100	2	991
Day/nigh	15	30/03/2006	00:00	14.00	8.30	53°18.887 'N	003°42.986'W	32.0	8.5	11.3	5.0	336	100	2	992
Day/nigh	15	31/03/2006	05:00	7.57	2.04	53°18.907 'N	003°42.928'W	nd	9.7	10.4	15.8	49	90	1	995

nd: no data

Appendix 9. Concentration of pigments [μg L^{-1}] for the cruise to Liverpool Bay, Irish Sea.

Station	Chlorophillade *a*	Peridinin	19'-butanoyloxyfucoxanthin	Fucoxanthin	19'-hexanoyloxyfucothanthin	cis-fucoxanthin	cis-19'-hexanoyloxyfucothanthin	Diadinoxanthin	Alloxanthin	Diatoxanthin	Chlorophyll *b*	Chlorophyll allomer	Chlorophyll *a*	Phaeophytin *a*	β-carotene
M1	0.14	nd	0.77	0.07	nd	nd	nd	0.13	0.02	nd	nd	0.10	2.45	0.23	0.03
M2	0.26	nd	1.15	0.12	0.20	nd	nd	0.13	nd	0.08	0.06	0.14	2.44	nd	0.02
M3	0.49	nd	1.87	0.19	nd	nd	0.23	nd	nd	nd	nd	nd	4.28	0.19	0.04
1	nd	nd	1.28	0.22	0.42	nd	0.20	0.09	nd	nd	0.26	0.18	4.77	nd	0.06
2 (Replicate)	0.11	nd	2.09	0.35	0.66	0.35	nd	0.08	nd	nd	0.25	0.26	6.32	nd	0.07
2 (Replicate)	0.13	nd	1.72	0.18	0.23	nd	0.69	0.14	nd	nd	0.19	0.46	5.63	nd	0.06
2 (Replicate)	0.99	nd	2.17	0.37	0.73	nd	nd	0.17	nd	0.11	0.19	0.42	5.92	nd	0.06
3	0.31	nd	1.77	0.25	0.44	nd	0.25	0.08	nd	nd	0.07	0.33	3.89	nd	0.03
4	nd	nd	0.77	0.12	0.14	nd	nd	nd	nd	nd	nd	nd	1.50	nd	0.07
5	0.12	nd	1.04	0.11	nd	nd	nd	0.06	nd	nd	0.10	0.41	3.36	nd	0.05
6	0.18	nd	1.48	0.26	0.19	nd	nd	0.12	nd	0.07	0.25	0.12	3.26	nd	0.02
7	nd	nd	1.14	0.10	0.38	nd	nd	0.13	nd	0.03	0.22	nd	3.96	nd	0.03
8	0.23	nd	1.93	0.20	0.40	nd	0.63	0.15	nd	0.04	0.12	0.46	6.43	nd	0.07
9	nd	nd	0.74	0.17	0.11	nd	0.22	0.11	nd	nd	0.30	0.30	3.61	nd	0.05
10	0.10	nd	0.77	0.14	0.47	nd	0.13	0.14	nd	nd	0.33	0.19	3.87	nd	0.06
11	0.15	nd	1.06	0.10	nd	nd	0.38	0.08	nd	0.11	0.16	0.22	3.39	nd	0.04
12 (profile-surface)	nd	nd	1.08	0.14	0.11	nd	0.48	0.12	nd	0.22	0.37	0.21	4.96	nd	0.08
12 (profile-middle)	0.14	nd	0.48	0.06	nd	nd	0.10	0.08	nd	nd	0.12	0.12	2.03	nd	0.02
12 (profile-bottom)	nd	nd	0.67	0.06	nd	nd	nd	0.04	nd	0.11	0.18	0.21	2.87	nd	0.03
13	nd	nd	0.69	0.09	nd	nd	nd	0.05	nd	0.10	0.14	0.16	2.61	nd	0.03
13	nd	nd	0.66	0.11	0.23	nd	0.14	0.04	nd	0.18	0.24	0.18	3.41	nd	0.03
14	nd	nd	0.48	0.05	nd	nd	nd	nd	nd	0.06	nd	nd	1.88	nd	0.03
15 (Day/night)	0.12	nd	1.45	0.18	nd	0.08	0.47	0.14	nd	0.01	0.08	0.37	4.25	nd	0.03
15 (Day/night)	0.21	nd	1.88	0.24	nd	0.14	0.50	0.14	nd	0.03	0.16	0.26	5.92	nd	0.05
15 (Day/night)	0.77	nd	4.42	0.72	nd	nd	0.54	0.05	nd	nd	0.30	0.82	8.91	nd	0.10
15 (Day/night)	0.35	0.10	1.66	0.19	nd	0.14	0.42	0.13	nd	0.06	0.07	0.23	3.20	nd	0.03
15 (Day/night)	0.13	0.07	1.90	0.19	nd	0.05	0.57	0.15	nd	0.04	0.16	0.37	5.14	nd	0.05
15 (Day/night)	1.46	0.18	3.37	0.68	nd	0.06	0.51	0.08	nd	nd	0.17	0.50	6.14	nd	0.06

nd: no detected

Appendix 10. Concentration of VOCs [ng L^{-1}] for the cruise to Liverpool Bay, Irish Sea.

Station	Dichloromethane	Cis-1,2-dichloroethene	Chloroform	1,1,1-trichloroethane	Carbon tetrachloride	1,2-dichloroethane	Trichloroethene	Bromodichloromethane	Tetrachloroethene	Dibromochloromethane	Bromoform	2-chloropropane	1-Bromoethane	1-Bromopropane	2-chlorobutane	Iodoethane	1-chlorobutane	2-Iodopropane
M1	6.5	6.2	12.5	1.1	4.7	4.1	34.8	0.8	29.4	0.6	0.9	7.4	0.0	0.0	3.5	0.3	3.3	0.0
M2	11.3	4.6	30.3	2.5	11.4	10.5	44.0	1.7	45.5	0.7	1.1	29.9	0.2	0.0	2.8	0.3	6.5	0.0
M3	5.0	3.0	8.6	0.8	4.1	2.1	18.7	0.5	15.1	0.0	3.1	99.9	0.0	0.0	4.1	0.4	2.7	0.0
1	1.7	0.0	5.2	0.0	2.7	1.0	3.3	0.0	2.2	0.0	0.0	28.2	0.0	0.0	2.0	0.0	0.0	0.0
2 (Replicate)	2.1	0.4	3.2	24.3	1.9	2.1	0.0	0.0	3.4	0.0	2.2	0.0	0.0	0.0	8.8	1.0	35.9	306.5
2 (Replicate)	304.9	14.2	1352.8	0.1	1.2	0.7	1.3	0.0	1.5	14.0	0.0	28.3	1.4	18.2	28.9	183.1	336.6	38.1
2 (Replicate)	0.8	0.2	4.6	0.0	0.5	0.2	0.0	0.0	0.2	0.0	0.0	2.3	0.0	0.0	0.7	0.2	1.5	0.6
3	3.6	1.7	8.7	0.0	4.1	2.2	4.4	0.0	4.6	0.0	0.0	43.8	0.0	0.0	5.4	0.7	0.0	0.0
4	2.9	0.5	2.0	0.0	1.4	0.6	2.7	0.0	0.8	0.0	0.0	30.6	0.0	0.0	3.8	0.0	0.0	0.0
5	292.4	8.9	546.9	0.0	2.1	1.4	14.1	0.0	4.6	7.7	0.0	40.9	0.0	6.5	40.2	79.2	321.5	62.5
6	248.0	9.8	794.7	0.0	1.3	1.0	5.8	0.0	27.1	7.4	1.6	33.6	0.7	23.2	18.4	107.4	318.2	55.3
7	271.6	6.3	422.1	0.0	1.3	0.9	4.3	0.0	5.9	8.8	4.3	28.0	1.0	3.0	13.2	76.4	199.3	35.1
8	48.3	4.3	168.1	0.0	0.3	0.6	0.6	0.0	0.8	3.0	0.0	2.9	0.7	0.7	1.9	9.5	87.9	11.3
9	1.9	0.3	3.0	0.0	1.8	1.0	6.1	0.0	2.2	0.0	0.0	17.9	0.0	0.0	2.0	0.0	0.0	0.0
10	2.6	0.4	9.2	0.7	2.2	0.7	2.0	0.0	1.3	0.0	0.4	8.5	0.0	0.0	1.1	0.9	1.4	0.0
11	78.9	3.7	294.2	0.0	0.7	1.2	0.5	0.0	1.2	2.8	0.1	0.0	0.2	5.7	11.6	18.0	115.7	18.5
12 (profile-surface)	234.8	20.7	1045.0	0.0	0.7	0.5	1.0	0	1.0	10.1	0.0	45.9	0.6	12.4	28.2	102.0	319.0	37.0
12 (profile-middle)	37.2	18.2	249.1	5.2	21.1	13.3	20.6	0.0	17.1	0.0	8.6	108.1	0.0	0.0	32.0	16.9	102.2	15.7
12 (profile-bottom)	500.4	34.2	2754.8	0.0	3.7	4.0	6.1	0.0	4.8	26.3	2.2	43.4	1.1	33.1	120.0	220.8	1146.2	127.2
13	1.6	0.8	2.8	0.0	1.1	0.9	1.3	0.0	1.6	0.0	0.4	0.0	0.0	0.0	3.0	0.0	0.0	0.0
14	1.0	0.0	2.8	0.0	0.7	0.5	0.3	0.0	0.0	0.0	0.0	2.3	0.0	0.0	0.8	0.3	1.7	0.0

Appendix 10. Concentration of VOCs [ng L^{-1}] for the cruise to Liverpool Bay, Irish Sea. (Continuation)

Station	1-Iodobutane	Iodomethane	1-bromopentane	Dimethyl sulphide	Benzene	Toluene	Ethylbenzene	m-Xylene	p-Xylene	n-propylbenzene	1,3,5-trimethylbenzene	1,2,4-trimethylbenzene	1-ethyl-2-methylbenzene	1,2,3-trimethylbenzene	1-ethyl-3-methylbenzene	sec-butylbenzene	aromatic unknown	Isoprene
M1	0.0	0.2	0.0	4.4	19.5	55.0	18.5	41.7	20.0	14.2	33.8	21.7	17.5	79.5	23.4	12.0	5.9	1.8
M2	0.0	0.2	7.5	3.7	25.3	24.6	17.9	31.8	20.3	8.7	30.4	29.1	7.5	60.4	0.0	0.0	0.0	3.4
M3	0.0	0.2	5.3	4.2	23.4	58.9	33.8	102.7	44.1	21.3	66.9	28.1	19.4	89.0	30.0	17.0	14.4	7.8
1	0.0	0.0	0.0	5.8	42.9	37.2	16.9	40.3	38.0	13.0	28.2	31.8	6.2	35.4	0.0	0.0	0.0	3.1
2 (Replicate)	0.0	0.5	15.8	13.1	141.7	104.9	114.9	332.6	133.3	60.8	75.3	2854.2	87.7	413.2	19.8	31.0	18.5	6.6
2 (Replicate)	30.0	1.5	83.0	5.0	25.7	169.5	16.9	32.5	14.3	9.2	16.1	8.6	4.6	37.3	3.6	0.0	3.2	2.5
2 (Replicate)	0.0	0.0	0.0	2.0	3.9	3.6	2.5	4.3	1.6	0.4	1.4	0.9	0.6	2.4	0.2	0.0	0.1	1.1
3	0.0	0.7	0.0	18.8	86.2	79.6	119.6	173.5	100.1	33.6	101.8	69.6	34.5	203.2	0.0	42.8	0.0	14.2
4	0.0	0.4	0.0	3.1	19.9	12.1	10.5	13.4	6.8	0.0	12.1	7.1	0.0	0.0	0.0	0.0	0.0	1.9
5	38.7	0.9	90.6	13.5	56.0	138.5	42.4	77.4	34.2	8.8	59.9	29.7	13.8	76.4	0.0	0.0	0.0	4.0
6	32.8	1.5	82.8	3.8	28.5	172.0	31.7	82.5	33.4	17.5	29.0	20.4	9.1	44.2	14.1	8.0	6.3	4.8
7	30.2	1.2	68.9	4.0	18.6	143.5	26.9	56.5	23.0	9.4	23.1	10.8	8.5	34.0	14.8	0.0	3.7	2.7
8	1.3	0.0	34.2	1.7	5.5	31.5	5.6	8.1	3.1	1.8	3.7	2.3	1.3	6.8	1.0	0.0	0.0	0.6
9	0.1	0.0	0.0	6.2	34.8	41.3	15.6	37.9	17.4	8.5	43.9	24.0	0.0	29.3	0.0	0.0	0.0	2.7
10	0.0	0.0	0.0	4.3	26.1	27.5	18.4	39.4	17.7	9.3	15.2	6.9	6.0	23.3	0.0	0.0	1.6	1.9
11	1.4	0.0	31.4	2.6	6.9	31.5	6.2	11.1	4.2	2.2	3.3	1.5	0.8	6.4	1.0	0.0	0.3	1.0
12 (profile-surface)	13.3	0.9	72.3	4.0	17.9	98.5	12.2	24.4	8.9	3.8	9.7	4.1	3.8	14.5	2.6	0.8	0.9	1.9
12 (profile-middle)	2.0	2.1	0.0	119.1	354.1	447.4	378.6	977.1	409.6	184.4	332.1	114.7	132.6	516.0	99.1	31.9	41.8	51.5
12 (profile-bottom)	31.4	1.9	253.5	29.9	89.0	355.3	78.6	73.2	0.0	30.1	53.0	24.3	15.2	104.8	14.2	0.0	10.2	14.9
13	0.0	0.0	0.0	5.0	28.8	49.1	24.8	85.1	58.7	11.1	56.3	29.3	14.0	79.5	8.8	0.0	7.2	3.3
14	0.0	0.0	0.0	1.9	7.9	6.7	8.1	20.5	8.5	1.8	5.5	3.1	1.5	8.3	1.1	0.0	0.0	1.0

Appendix 10. Concentration of VOCs [ng L^{-1}] for the cruise to Liverpool Bay, Irish Sea. (Continuation)

Station	C_5 branched 1	C_5 branched 2	C_5	C_6 Bra-1	Ciclohexane	Alkyne unknown	C_8	C_9	C_{10} Bra-1	C_{10} Bra-2	C_{10} Bra-3	C_{10}	C_{11} Bra-1	C_{11} Bra-2	C_{11} Bra-3	C_{11} Bra-4	C_{11}	Hexanal	Heptanal	Octanal	□pinene	Limonene
M1	0.0	0.0	6.8	0.0	6.3	0.0	8.8	19.4	13.1	138.4	35.9	57.6	62.6	22.1	13.1	30.8	75.1	17.6	0.0	198.5	16.8	50.4
M2	0.0	0.0	0.0	0.0	8.2	2.9	11.7	0.0	0.0	32.4	0.0	24.7	60.7	13.2	6.5	6.6	95.1	15.0	13.7	38.8	29.8	41.0
M3	0.0	0.0	3.6	27.3	9.7	0.0	30.1	41.1	5.8	16.2	0.0	80.3	17.2	79.4	50.5	37.7	47.8	17.9	25.5	0.0	34.5	54.1
1	1.6	0.0	3.8	3.3	2.9	1.8	7.9	0.0	0.0	0.0	0.0	40.5	0.0	2.8	1.3	4.5	68.3	11.4	22.5	101.4	16.4	25.5
2 (Replicate)	281.9	0.0	0.0	255.5	77.2	5.6	108.8	15764.9	427.0	0.0	276.3	7429.2	772.4	4096.5	2170.3	899.7	1016.2	526.6	0.0	332.7	38.5	164.9
2 (Replicate)	16.9	19.0	624.7	154.6	37.3	1.0	9.7	15.2	0.0	62.4	41.8	60.9	28.5	2.6	6.0	0.0	97.3	9.7	0.0	54.7	13.1	57.9
2 (Replicate)	0.0	0.0	8.8	2.5	1.4	0.2	1.5	0.0	0.0	4.3	0.0	7.7	5.4	0.5	0.9	18.2	8.1	2.7	0.0	24.8	1.0	5.0
3	0.0	0.0	17.2	5.2	10.0	0.0	36.8	36.4	52.8	75.9	0.0	149.8	0.0	59.1	266.6	41.5	219.1	46.5	63.0	0.0	104.0	96.2
4	0.0	0.0	0.0	0.0	8.1	0.0	3.7	7.4	6.6	0.0	63.4	0.0	0.0	11.0	23.5	22.1	81.7	6.0	30.8	0.0	16.9	26.7
5	25.0	38.7	1068.8	289.6	799.4	0.0	19.5	36.1	0.0	0.0	69.8	71.9	0.0	94.2	41.0	59.2	82.7	46.9	21.4	0.0	62.1	128.6
6	26.5	28.9	784.7	199.2	479.4	0.7	25.1	14.6	8.4	13.9	23.0	26.6	8.3	5.4	12.0	12.1	26.7	3.2	0.0	0.0	18.7	60.1
7	11.5	18.5	477.1	122.0	314.3	0.0	20.8	0.0	13.6	12.7	36.3	50.3	2.2	0.0	0.0	0.0	0.0	2.2	14.9	0.0	14.8	68.1
8	2.3	4.2	74.3	21.2	93.2	0.2	3.8	0.0	1.7	5.4	1.9	29.1	7.1	9.4	33.4	10.4	47.7	4.4	0.0	31.2	2.5	14.5
9	0.0	0.0	7.4	1.8	3.7	0.0	7.3	8.4	0.0	14.5	0.0	16.5	0.0	0.0	0.0	11.6	33.3	14.8	13.2	60.0	30.1	43.8
10	0.0	0.0	21.6	6.9	11.7	0.4	8.6	0.0	14.7	14.7	0.0	30.7	2.5	0.0	0.0	0.0	27.7	10.8	0.0	39.4	7.2	72.9
11	6.1	7.3	166.3	44.7	144.7	0.3	2.9	0.0	2.1	5.7	9.6	28.9	81.7	2.8	16.8	23.9	30.4	5.2	0.0	49.2	3.0	16.7
12 (profile-surface)	18.0	19.7	457.2	125.2	508.7	1.2	6.3	0.0	0.0	0.4	25.8	58.6	2.9	6.9	5.5	6.5	62.8	4.9	5.0	9.6	7.6	27.6
12 (profile-middle)	0.0	8.1	410.3	74.3	275.0	217.7	162.1	731.2	0.0	318.5	310.6	708.6	274.3	0.0	1112.7	0.0	858.1	110.1	0.0	1043.2	76.7	516.0
12 (profile-bottom)	51.6	56.1	1444.7	394.9	2128.0	4.1	24.5	64.8	27.4	45.7	84.1	209.3	404.5	0.0	0.0	0.0	355.4	38.9	0.0	28.2	45.1	176.7
13	0.0	0.0	0.0	0.0	5.2	13.6	0.0	1363.7	198.5	0.0	61.0	0.0	0.0	0.0	0.0	274.2	186.8	61.4	38.7	43.4	12.2	49.0