University of Southampton

Faculty of Ocean and Earth Sciences

Graduate school of the National Oceanography Centre Southampton

Volatile organic compounds (VOCs) in rivers and estuaries

by

Paul Lawrence Hackett

ORCID ID https://orcid.org/0000-0003-1512-7402

Thesis for the degree of MPhil

October 2020

University of Southampton

Abstract

Faculty of Ocean and Earth Sciences

Graduate school of the National Oceanography Centre Southampton

Thesis for the degree of MPhil

Volatile organic compounds (VOCs) in rivers and estuaries

by

Paul Lawrence Hackett

Volatile Organic Compounds (VOCs) are a set of low molecular weight compounds typically with a low boiling point. They have previously been observed as important in atmospheric and oceanic environments, however, the relative importance of terrestrial input into oceanic systems has previously not been determined. This is partially due to the difficulty analysing these hydrophilic compounds from solution and the nanomolar concentrations they are typically found in.

This thesis reviews current knowledge of VOC concentrations and cycling, where the global knowledge gaps in VOC concentrations are and the relative importance of riverine and estuarine input. Data was gathered using a membrane inlet proton transfer reaction mass spectrometer (MI-PTR/MS) to determine the relative importance of these compounds in the catchment surrounding the Tamar River, in the South West UK. Development work was undertaken to design and validate the use of a membrane inlet mass spectrometer (MIMS) for analysis of isoprene in natural waters, at environmentally relevant concentrations. This was compared with the pre-existing method on the MI-PTR/MS and both were deployed in fieldwork in the Halladale catchment in Scotland, to gain a closer understanding of the importance of humic runoff for these important compounds.

The method developed and data gathered in this research have provided some of the first simultaneous VOC data in riverine and estuarine systems and increased the understanding of these compounds in representative UK onshore water systems.

Table of Contents

Table of Tables

Table of Figures

Table of Figures

Research Thesis: Declaration of Authorship

Print name: Paul Hackett

Title of thesis: Volatile organic compounds (VOCs) in rivers and estuaries

I declare that this thesis and the work presented in it are my own and has been generated by me as the result of my own original research.

I confirm that:

1. This work was done wholly or mainly while in candidature for a research degree at this University;
2. Where any part of this thesis has previously been submitted for a degree or any other qualification at this University or any other institution, this has been clearly stated;
3. Where I have consulted the published work of others, this is always clearly attributed;
4. Where I have quoted from the work of others, the source is always given. With the exception of such quotations, this thesis is entirely my own work;
5. I have acknowledged all main sources of help;
6. Where the thesis is based on work done by myself jointly with others, I have made clear exactly what was done by others and what I have contributed myself;
7. None of this work has been published before submission

Signature: .....Date

Acknowledgements

"To write a thesis, first, begin your acknowledgements"

-Somebody who I forgot to write down the name of, right at the start of this project

In the four years of putting this thesis together, I have had the pleasure of working with, talking to and spending time around a fantastic range of other scientists, plus other humans too. First of all, thanks must go to my supervisory team of Jo Dixon, Rachael Beale and Duncan Purdie. Jo, without your input, feedback and useful comments, this thesis and for that matter, this project would be nowhere. Rachael, your help with methods- be that mine or your own, your lab experience and skills were invaluable to me, and it was a pleasure to work alongside you in Scotland. Duncan, while far away, your feedback, knowledge and advice throughout this project were invaluable.

For the first datachapter, thanks must go to all the people who sampled with, or for me. This includes Vas Kitidis, Glen Tarran, John Stephens and the crew of the Plymouth Quest.I also thank Chris Webb, whose summer dataset was used in the chapter. For the Halladale work, I sampled alongside, and/or gained additional data from the entire LOCATE team, including Amy Pickard, Justyna Olszewska, Bryan Spears, Nancy Dise, Chris Evans, Nathan Callahan, Annette Burden, Jennifer Williamson, Adam Pinder, Chris Barry, Doug Clark, Vas Kitidis, Rachel Beale, Becca May, Stacey Felgate, Dan Mayor, Chiara Borsellino, Richard Sanders, Chris Pearce, Anna Lichtschlag, Peter Williams, Mike Bowes, Pete Gilbert and Stuart Gibb.

Finally, I've been incredibly lucky to have such support from a huge amount of my family and friends. You all know who you are, but at the very least I'd like to thank- from outside PML; Dominique and Neil Hackett, Judith Nicholls, Ry, Steven and Hagrid, Camille, Jen, Matt and Lize, as well as all the others who have kept me sane during the research and writing. Inside PML, my lab buddies Charel and Daniel, gym buddy Saskia, lunchtime walk buddy Zara, quiz buddies Franki and Emily, house buddies Rich and Kieran, pizza buddy Becca, office buddies Yang, Chris, Chris, Rach, Francesco, Patrick, Kevin and Emilie, as well as anyone who made it to a pub on Fridays to keep us all sane. The last 4 years wouldn't have been the same without any of you.

Glossary

AMT	Atlantic Meridional Transect
BEST	Bio-Env Stepwise method *
BVOC	Biogenic Volatile Organic Compound
CDOM	Chromophoric Dissolved Organic Matter
MIMS	Membrane Inlet Mass Spectrometer
MI-PTR/MS	Membrane Inlet Proton Transfer Reaction Mass spectrometer
nMDS	Non metric dimensional scaling *
OVOC	Oxygenated Volatile Organic Compound
PCA	Principal Component Analysis *
VOC	Volatile Organic Compound
WCO	Western Channel Observatory

*See primer manual (Clarke and Gorley 2015a)

Chapter 1 Introduction

1.1 Background

Volatile Organic Compounds (VOCs) are a class of compound with a carbon backbone and a high vapour pressure (Herrmann 2010). This typically leads to compounds being abundant in the atmosphere in varying concentrations and involved in a range of air-sea flux (eg. Carpenter et al. 2012; Yang et al. 2013; Halsey et al. 2017). Atmospheric and marine flux, concentrations and reactions have been studied in a range of systems, from near shore to open ocean (Beale et al. 2013, 2015; Yang et al. 2014) and from atmosphere in both landlocked and marine systems (Greenberg and Zimmerman 1984; Kesselmeier and Staudt 1999; Mao et al. 2006). However, while concentration and, to a lesser extent, riverine-atmosphere exchange, have been examined, the importance of terrestrial water input into marine systems has previously been overlooked. Previously, an annual report on near-shore waters suggested riverine and estuarine input may be important to these near shore coastal waters (Beale et al. 2015).

Two distinguishing categories of VOCs to be considered are Oxygenated VOCs (OVOCs), which contain an oxygen atom and Biogenic VOCs (BVOCs), which are produced by living organisms, primarily plants (van Meeningen et al. 2016) and marine bacteria and phytoplankton (Shaw et al. 2010). Inherently, volatile compounds have lower molecular weight, so only the lightest few members of each particular species are both volatile, and common enough to study. Some compounds, such as methanol, can be considered both OVOCs and BVOCs, as not only oxygenated but also biologically produced (Tie et al. 2003). Examples of four VOCs are shown in Figure 1.1, below. These were selected for their relative abundancy, with some estimations suggesting acetone, acetaldehyde and methanol contributing 85% of the measured organic carbon (without methane) in marine air (Lewis et al. 2005), and isoprene having been regarded as the most abundantly produced BVOC (McGenity et al. 2018). Even the nomenclature has only solidified in the most recent decades, with the definition of OVOC considered simply ‘other’ in 1999 (Kesselmeier and Staudt 1999), but still exemplifying the difference between BVOC and Anthroprogenic VOC’s (AVOCs in that work). For the purposes of this work, as expanded in the glossary, the acronyms for oxygenated and biogenic volatile compounds (OVOCs and BVOCs) shall be used.

VOC production has been identified via photochemical, biogenic and anthropogenic means, however each compound’s varying precursors and formation mechanisms means these are difficult to identify, particularly due to previous research primarily focusing on a small number of

these compounds. Methods to identify multiple compounds, such as proton transfer reaction mass spectrometry, have only recently become available (Beale et al. 2011). It is via these methods that it is now possible to identify a more complete collection of these compounds simultaneously, in a wider range of water environments.

The study of VOCs is important for a wide range of reasons and has been critically understudied due to their relative volatility and the difficulty this leads to in analysis. Volatile carbon atmospherically affects the atmosphere's self-cleaning capacity and the hydroxyl radical (OH) (Read et al. 2012). In marine systems, they are an important carbon source for biota (Dixon and Nightingale 2012), yet the marine budget is less well defined, with no overall understanding of the reactions or complexities of these important compounds.

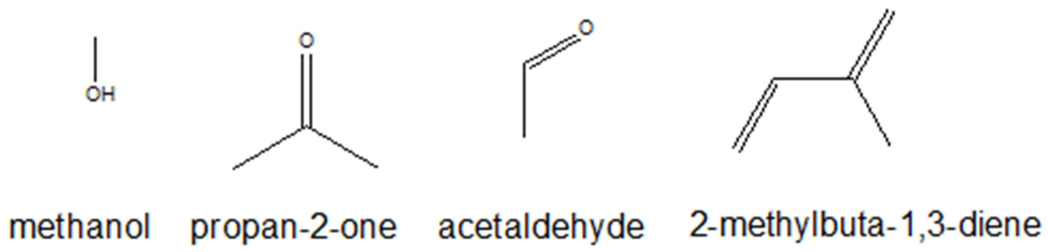


Figure 1.1. A selection of VOCs and their preferred IUPAC names. For this work, propan-2-one shall be identified as acetone, and 2-methylbuta-1,3-diene shall be identified as isoprene.

1.2 Importance of Volatile Organic Compounds

1.2.1 Atmosphere

A volatile compound, by definition, is a compound with relatively high vapour pressure (Warneke et al. 2003; Herrmann 2010; Monson 2010; Beale et al. 2011), and as such, any volatile compound found in abundance is likely to be atmospherically ubiquitous, albeit in varying concentration. While each compound is discussed in more detail below, a range of compounds have common reactions including atmospheric reactivity and production, albeit by varying mechanisms. For example, a number of volatile compounds are produced by biomass growth and then again upon the decay or burning of biomass, for example methanol, acetone and acetaldehyde (Holzinger et al. 1999; Galbally and Kirstine 2002) and isoprene (Broadgate et al. 1997, 2004).

Volatile compounds atmospherically are subject to a wide range of reactions. One of the most studied is the reaction with ozone, leading to the net formation of ozone via the degradation of VOCs in the troposphere, which is highly dependant on a number of factors, including UV, varying reaction pathways and NO_x sinks (Atkinson 2000). The OVOCs studied here (methanol, acetaldehyde and acetone) comprise 85% of the mass of total non methane organic content in air (Lewis et al. 2005) while isoprene is the most abundant biogenic volatile organic compound (BVOC) (McGenity et al. 2018).

1.2.2 Terrestrial

VOC concentrations in terrestrial land have previously mainly been studied in the context of soil, and agriculture. However, like VOCs in the atmosphere, concentrations in soil are also both subject to flux with water and breakdown, albeit typically more via biota. While a major proportion of production is via plants (Kolb 2009; El Khawand et al. 2016), most of this is broken down again, via prokaryotes (Kolb 2009) soil-inhabiting microbial oxidation (Taylor et al. 1980) or other soil respiration (Griebel and Owens 1972). Flux from soil to the atmosphere has been observed both inward (Cleveland and Yavitt 1997) and outward (Kirstine et al. 1998) for isoprene. However, the OVOCs are barely studied, with the premise of each change in conditions can cause a large change in microbiological makeup, and while a small amount of work has been completed, the investigation into these areas is still in its' infancy (Insam and Seewald 2010)

1.2.3 Marine

The importance of VOCs in marine systems has been known since their photochemical production from dissolved organic matter was identified in the late 1980s (Mopper and Stahovec 1986; Keiber et al. 1990). Since the identification of these compounds production, they have been noted as a less-quantified area of the carbon cycle, particularly from photochemical production in both the atmosphere and marine systems and movement of dissolved carbon (DOC) in the marine environment. While the specific marine inputs and production mechanisms vary from compound to compound, the ocean is closely linked to the atmospheric concentrations, either as a significant source or sink (Yang et al. 2013, 2014). While OVOC emission and deposition has been studied in oceanic systems, any deposition or evaporation is less clear in riverine and estuarine systems.

As compounds with bioavailable carbon (Monson 2010), it is perhaps unsurprising that an amount of marine biota, from microbial uptake to plankton has been known to utilise VOCs as a carbon source, either for uptake for energy or assimilation for growth when available, or release volatiles during growth , repair or decay (Lindinger et al. 1998a; Warneke et al. 1999; Millet et al. 2008; Dixon et al. 2011a, 2013b, 2014; Halsey et al. 2017; Sargeant et al. 2018).

1.3 Compounds

1.3.1 Methanol

1.3.1.1 The atmosphere

The atmosphere contains 4 Tg methanol, and sources and sinks 340 and 270 Tg yr^{-1} respectively (Heikes 2002), this totals to 6% of carbon input to atmosphere. The primary sources of atmospheric methanol are thought to be plant growth, *in-situ* atmospheric production and combustion of materials (Jacob et al. 2005), however, it typically has a short atmospheric lifetime, between 5-12 days, indicating loss processes may be fast or varied. Atmospheric production is largely via the methylperoxy radical (CH_3O_2) produced from atmospheric methane (see equations 1+2). This radical scrubs OH ions out of the atmosphere, with methanol a by-product for around 50% of the reactions it undergoes, a major aspect of the atmospheric production of methanol.

Equation 1, production of methylperoxy radical from CH_4

a) $CH_4 + OH \rightarrow CH_3 + H_20$
b) $CH_3 + O_2 \rightarrow CH_3O_2$ (methylperoxy radical)

Equation 2, example production of methanol from methylperoxy radical and perhydroxyl radical (Jacob et al. 2005)

a) $CH_3O_2 + HO_2 \rightarrow CH_3COOH + O2$
b) $CH_3COOH + h\nu \rightarrow CH_3O + OH$

The predominant sink is thought to be via gas phase oxidation via OH (Galbally and Kirstine 2002; Heikes 2002; Jacob et al. 2005) shown in equation 3, although oceanic uptake is also thought to a significant sink, of up to 150 Tg yr^{-1} (Heikes 2002), with debate still ongoing as to whether the ocean is a net sink (Heikes 2002; Beale et al. 2013; Yang et al. 2013, 2014) or source in at least some areas (Singh et al. 2000; Millet et al. 2008). The same mechanism for removal is thought to be present in the aqueous phase (Asmus et al. 1973; Atkinson 1986; Galbally and Kirstine 2002).

Equation 3, removal of atmospheric methanol via hydroxyl radical oxidation

$CH_3OH + OH \rightarrow HCHO + HO_2 + H_2O$

1.3.1.2 Marine

Methanol concentration in the open ocean has been identified in both Atlantic and Pacific oceans, up to several hundred nM (Williams et al. 2004a; Kameyama et al. 2010; Beale et al. 2013; Wohl et al. 2019) although is typically seen at lower levels, of 100-200nM. The highest concentrations of methanol have been identified in remote regions such as mid-Atlantic and the North Pacific, particularly those with low biological productivity and moving to shelf seas or near-shore systems, indicates lower concentrations with an annual study at a river-influenced shelf sea site never reaching 100nM (Beale et al. 2015). However, lower concentrations have also been identified in the Arctic ocean (Wohl et al. 2019), which could suggest either lower production in colder waters, or, less likely, a significant biological methanol sink in these cooler, less biologically active waters. A full summary of published measurements is seen below in Table 2.1.

1.3.1.3 Sources and Sinks

The primary source of atmospheric methanol is biogenic in nature (Millet et al. 2008), however, a range of anthropogenic sources such as biomass combustion and urban sources should be noted as well (Jacob et al. 2005). Methanol atmospheric budgets suggest the largest atmospheric source is plant growth, however, these vary significantly in magnitude (Jacob et al. 2005). It is generally thought the direction of flux in the ocean is downward: that is, the uptake of atmospheric methanol into the oceans, however, some models suggest a modest source between 0 to 20 Tg Yr^{-1} (Heikes 2002; Carpenter et al. 2004; Jacob et al. 2005; Lewis et al. 2005; Sinha et al. 2006; Read et al. 2012; Yang et al. 2013; Wohl et al. 2019). Furthermore, wet deposition from rainfall

has been suggested as a significant source into the ocean (Felix et al. 2014). A significant biological methanol source has also been observed from a wide array of marine phytoplankton (Mincer and Aicher 2016). Once in the marine system, methanol is thought to be predominantly used as a carbon or energy source to biota, with this ratio varying in differing oceanic provinces (Dixon et al. 2013b). However, this is known to vary both in magnitude and ratio closer to shore (Sargeant et al. 2016), with the majority of methanol being dissimilated for energy. There is very little data published upon the feasibility of rivers or estuaries providing a direct methanol source into oceanic environs, with no discernible correlation seen with seasonally varying flow in a near-shore coastal site (Beale et al. 2015). This work suggests rivers may not have a significant source of methanol into near-shore UK shelf seas, however, it is not known if this relationship continues elsewhere.

Table 1.1, A summary of published water VOC concentrations in a range of systems- ordered riverine, estuarine, near shore and open ocean.

Water concentration					
Methanol (nM)	Acetone (nM)	Acetaldehyde (nM)	Isoprene (pM)	Location	Reference
-	53-1400	130-2200	-	Polish river	(Dabrowska and Nawrocki 2013)
-	-	2.0-12	-	River Otha	(Takeda et al. 2006)
-	-	-	100-1400	Colne estuary	(Alvarez et al. 2009)
16-78	2.0-10	4.0-37	-	Near shore UK	(Beale et al. 2015)
-	-	18	-	Near shore Florida	(Mopper and Stahovec 1986)
-	-	2.0-22	-	Hiroshima Bay	(Takeda et al. 2014)
-	2	5.6	-	Black Sea	(Mopper and Kieber 1991)
-	3.0±0.23	1.4±0.08	-	East of the Bahamas	(Zhou and Mopper 1997)
48-361	2.0-24	3.0-9.0	-	Atlantic transect	(Beale et al. 2013)
-	-	-	0.70-54	North Sea	(Broadgate et al. 1997)
-	-	-	0.10-6.3, 0.10-6.6	Atlantic transect, Arctic ocean	(Hackenberg et al. 2017)
160-330	4.4-41	<5.9	36-120	North Pacific	(Kameyama et al. 2010)
-	-	-	0.20-40	Indian Ocean	(Kameyama et al. 2014)
120 ±48	18±8.1	-	-	Atlantic transect	(Williams et al. 2004a)
15±6.0	8.0±2.0	3.8±1.0	0.94±0.24	Arctic Ocean	(Wohl et al. 2019)
Summary (nM)					
-	18-1400	9.0-2200	-	Summary River	
-	-	-	100-1400	Summary Estuary	
9.0- 360	2.0-26	2.0-37	0.10-120	Summary Ocean	

1.3.2 Acetone

1.3.2.1 The atmosphere

Acetone, as one of the most abundant carbonyl compounds in the atmosphere and is an important source of OH ions and a precursor to peroxyactyl nitrate, important to the ozone layer (Singh et al. 1995; Fischer et al. 2012). Acetone has an annual source of 40-60 Tg, comprising of oxidation of propane, biomass burning and anthropogenic (Singh et al. 1994) (in descending order of magnitude). 80% of atmospheric propane is oxidised into acetone, via a reaction chain, an example of which can be seen in equation 4 (Singh et al. 1994).

Equation 4, example reactions of oxidation of propane to acetone (reaction pathway for 80% of propane, other 20% via a different scheme) (Singh et al. 1994).

a) $(CH_3)_2CH_2 + OH + (O_2) \rightarrow CH_3CHO_2CH_3 + H_2O$
b) $CH_3CHO_2CH_3 + NO + (O_2) \rightarrow CH_3COCH_3 + NO_2 + HO_2$

The direction of the flux in regard to oceanic acetone has been proposed at varying sizes and directions, with estimates between -48 Tg yr^{-1} (Marandino et al. 2005) to +13 Tg yr^{-1} (Jacob et al. 2002), but recently the ocean surface is considered to be a sink of acetone in higher latitudes, but a source nearer the tropics (Fischer et al. 2012; Beale et al. 2013; Yang et al. 2014).

1.3.2.2 Marine

Concentrations of acetone in open ocean have been measured consistently in the low nanomolar level, with highest measurements seen in the oceanic gyres in the Atlantic (Beale et al. 2013). In comparison, no such distinction was seen in the Pacific, with oceanic provinces causing little effect (Kameyama et al. 2010). Nearer shore, acetone concentrations remain similar to these open ocean concentrations, which could suggest similar sources and sinks in these environments. In nearer shore waters, it is somewhat easier to complete a seasonal survey, which observed a maxima in summer (Beale et al. 2015). This could suggest some seasonal influence unrelated to volume of runoff- either anthropogenic or biological production. One potential cause of this is increased UV light, which is known to be a source via UV degradation of CDOM, however, this correlation has only been observed in marine systems, not terrestrial runoff (Zhou and Mopper 1997). This summer maxima is perhaps surprising considering the extraordinarily high measurements seen in riverine waters in Poland, however this may have a significant anthropogenic impact (Dabrowska and Nawrocki 2013), and no other riverine concentrations are available for comparison. If accurate, this would suggest winter, with much higher run-off and

river flow, would have higher concentration of acetone than summer in river- influenced systems, however, this does not seem to be the case from the published data available.

1.3.2.3 Sources and Sinks

As discussed above, the primary atmospheric sources are secondary reactions from anthropogenic sources and biota (Fischer et al. 2012). In comparison, atmospheric oxidation and photolysis are generally accepted as the major sink processes, however the direction and magnitude of ocean-atmospheric flux is still discussed (Marandino et al. 2005; Sinha et al. 2006; Fischer et al. 2012; Read et al. 2012; Tanimoto et al. 2014a; Yang et al. 2014). In marine systems, acetone production was thought to predominantly (between 48-100%) be photochemical, although a small biological source from *Vibro* species has also been recorded (Nemecek-Marshall et al. 1995; Dixon et al. 2013a, 2014; Halsey et al. 2017). The most common precursor for acetone is CDOM and unsurprisingly for a photochemical reaction, there is a strong diurnal cycle (Mopper and Stahovec 1986; Keiber et al. 1990; Zhou and Mopper 1997) to this production. This could be linked to light-dependant production from diatoms, previously observed in the North Atlantic (Halsey et al. 2017) or independent from biological sources. Acetone uptake by biota has been identified, particularly in coastal environs (de Bruyn et al. 2013; Dixon et al. 2014), and a further sink from photo degradation is also discussed (Mopper and Stahovec 1986), however no budget has successfully quantified these oceanic concentrations.

1.3.3 Acetaldehyde

1.3.3.1 The atmosphere

Atmospheric acetaldehyde is perhaps the least studied of the three oxygenated compounds in the atmosphere. An estimated 220Tg is emitted annually (Singh et al. 2004), and of that, the source is debated between *in situ* atmospheric production (Millet et al. 2010) and ocean emission (Singh et al. 2004). Atmospherically, the production mechanism is similar to that of acetone, in that propane is a major source (Rosado-Reyes and Francisco 2007) via the Isopropanal pathway- see equation 5.

Equation 5- The isopropanol pathway for acetaldehyde production in the atmosphere. The initial reagent is formed via equation 4a.

a) $CH_3CHO_2CH_3 + HO_2 \rightarrow CH_3CHO_2HCH_3 + O_2$
b) $CH_3CHO_2HCH_3 + h\nu \rightarrow CH_3\,CHOCH_3 + OH$
c) $CH_3\,CHOCH_3 \rightarrow CH_3C(O)H + CH_3$

However, it is generally agreed to have a very short atmospheric lifetime, of under 24 hours. In the atmosphere, acetaldehyde acts as both a source of ozone and peroxyacetal nitrate. A small source is thought to come from the oxidation of isoprene, via methyl vinyl ketone (Atkinson et al. 2006) and ethanol.

1.3.3.2 Marine

Acetaldehyde in the open ocean has been measured at rather low nanomolar concentrations, with the highest open oceanic measurement at 9nM. However, unlike acetone and methanol, drawing closer to the shore appears to increase acetaldehyde concentration, with up to 22nM seen in Hiroshima Bay and 37nM in coastal shelf seas in the South West UK (Takeda et al. 2014; Beale et al. 2015). A seasonal influence was noted in the shelf sea, with increased acetaldehyde found in autumn and winter, which could potentially be linked to increased run-off, or decreased consumption from biota. Moving further upstream, concentrations of up to 2160nM (Dabrowska and Nawrocki 2013) have been identified in riverine systems, however, similar to other compounds discussed here, there is a paucity of measurements across multiple rivers in varying environs.

1.3.3.3 Sources and Sinks

As discussed, the primary atmospheric source is considered to be between *in situ* atmospheric production or oceanic emission and the largest sink has been estimated as gas phase oxidation by the OH ion (Millet et al. 2010). In marine systems, the primary production mechanism is commonly believed to be photochemical, although the involvement of biota or precursors is still discussed (Mopper and Stahovec 1986; Keiber et al. 1990; Mopper and Kieber 1991; de Bruyn et al. 2017). Biological production was thought to be relatively negligible, however a significant phytoplankton source has been observed producing acetaldehyde in a light-dependant reaction (Halsey et al. 2017) and there seems to be no evidence of chemical production in water (de Bruyn et al. 2017). While loss processes are less extensively studied, still a general agreement of the predominant loss to biological sink processes such as microbial oxidation (Dixon et al. 2013a; Beale et al. 2015) and further experiments with filtered seawater suggested this was likely a result of biota larger than 0.2µm in size with a turnover rate of between 185-3000 min (de Bruyn et al. 2017).

1.3.4 Isoprene

1.3.4.1 The atmosphere

Isoprene, like the other compounds discussed here, provides a sink for hydroxyl (OH) radicals and ozone (Broadgate et al. 1997) and itself comprises approximately 1/3 of the biogenic volatile compounds in the atmosphere (Steinke et al. 2018). Modelling suggests a total atmospheric emission of up to 600 Tg carbon annually of isoprene (Guenther et al. 2006; Pfister et al. 2008) and it is thought to be the most abundant biogenic volatile organic compound (BVOC) with a similar magnitude to all others combined (McGenity et al. 2018). Oceanic isoprene emission has been observed from some environments such as a Norwegian fjord (Sinha et al. 2006), as well as further offshore in the North Sea and southern oceans (Broadgate et al. 1997).

1.3.4.2 Marine

Isoprene concentrations are typically seen as an order of magnitude lower than oxygenated volatiles in ocean water. In open ocean, the highest recorded is still under 0.05nM (Kameyama et al. 2014). Highest isoprene concentrations appear to be in the summer months in near shore environments- up to 0.06nM, with significantly less activity in the winter (Broadgate et al. 1997). Estuarine concentrations in the Colne Estuary reach 1.4 nM, the highest recorded marine concentration (Alvarez et al. 2009). This suggests estuaries may be a significant source of Isoprene to the marine system, be it via riverine input or estuarine production, however this has yet to be examined in other estuaries. A faster isoprene degradation rate was observed higher upstream in the estuarine system, suggesting increased biological activity from runoff, a potentially favoured source of carbon, or even a preference for less saline conditions (Alvarez et al. 2009).

1.3.4.3 Sources and Sinks

Isoprene has extensive atmospheric biogenic sources, from bacterial to foliage (Fall and Copley 2000; Müller et al. 2008), however known significant sinks include the soil and bacterial degradation (McGenity et al. 2018). In marine systems, this is no different, with photochemical isoprene production on the surface (Ciuraru et al. 2015), phytoplankton in the water column (Shaw et al. 2003) and intertidal communities in the benthos (Exton et al. 2012) and sediment (Alvarez et al. 2009). The marine source depends on if a top down or bottom up method is used as an estimate and this varies significantly, between 0.32 and 11.6 Tg C yr^{-1} (Luo and Yu 2010). Isoprene has both a source and sink in estuarine waters, with one study observing consistent concentrations of isoprene over 800 days (Alvarez et al. 2009). Correlation has been observed with photosynthetic activity, using chlorophyll a as a proxy (Palmer and Shaw 2005; McGenity et al. 2018), and this suggests the oceanic sources are predominantly biological in nature.

1.4 Scope, Aims and Objectives

1.4.1 Knowledge gap and scope

As discussed above, while an amount of research has been completed in marine systems, there exists a dearth of knowledge of OVOC concentrations in terrestrially controlled water such as rivers and estuaries- as shown in table 1.1, and the scant measurements that exist show great variation and inconsistent analytes. Previous studies in the last two decades have indicated a natural next step would be to increase research into terrestrial inputs, exchange processes on a local and global scale, influence of urban or natural environs and biogenic sources (Kesselmeier and Staudt 1999; Seco et al. 2007; Millet et al. 2008; Takeda et al. 2014) or the input of a VOC from an unknown source into nearshore waters (Takeda et al. 2014; Beale et al. 2015). This work will aim to provide data, methodologies and propose solutions to a number of these questions, specifically those addressed in 1.4.2.

1.4.2 Aims and Objectives

The overarching aim of this thesis research is to determine the influence of land type, season and salinity upon the concentration and influence of OVOCs in terrestrial water to near-shore marine systems.

To address these aims, three specific objectives were identified, namely:

1. To develop a new, reliable **method for determining Isoprene** in natural waters at environmentally relevant concentrations
2. To examine the **seasonal variation** of OVOC concentration across a range of riverine, estuarine and marine sites in South West UK
3. The **influence** of highly Humic/Peaty soils upon the concentration of VOCs in runoff

Objective 1 was addressed first with laboratory tests, including comparison of calibration, field data and detection optimisation of the MIMS for detection of Isoprene, and then continued in field testing

To achieve objective 2 required a seasonal study of OVOCs across a range of sites in South west UK, with water from both surface and at depth where possible.

Objectives 1 and 3 were realised during a 2 week fieldwork trip to Northern Scotland, as part of the Land Ocean CArbon TransfEr (LOCATE) (National Oceanography Centre 2020) fieldwork,

where surface samples from a wide range of run-off environments were analysed for both OVOCs and Isoprene, via both PTR-MS and MIMS.

Chapter 2 Methods

2.1 Introduction to Methods

2.1.1 VOC analysis

A volatile compound in a water-based matrix has an inherent difficulty to accurately detect: that is, the high solubility and reactivity of these compounds. This can cause difficulty in separating solute from solvent and previous studies have shown a tendency for the analyte to adsorb to the surface of analytical equipment and be lost. This typically depends on material and temperature. When compared, stainless steel tubing significantly reduced the instrumental response for methanol and silicone effectively adsorbed completely, leaving the signal negligible (Beale 2011a). Therefore, for any work with these compounds, care is to be taken with materials used to ensure an accurate measurement.

Previous study has either used a purge and trap method (de Bruyn et al. 2013; Andrews et al. 2015; Mincer and Aicher 2016; Schlundt et al. 2017), various equilibrators (Tanimoto et al. 2014b; Wohl et al. 2019), or various forms of chromatography (Nemecek-Marshall et al. 1995; Beale et al. 2011). All of these methods have their own benefits and drawbacks in terms of accuracy, speed, portability and species detectable, as discussed below in Table 2.1. One significant problem across all these methods was the inability to analyse a number of compounds simultaneously- for example, some analytes required drying via Tenax or a similar absorbant material, which would effectively absorb other analytes (Ketola et al. 2006). Furthermore, for isomeric species such as acetone and propanal, basic mass spectrometry is unable to distinguish between these compounds. The hurdle for effective multiple VOC characterisation was partially negated with the development of the proton transfer reaction mass spectrometer (PTR-MS), which allowed the process of separation via ionisation using a hydronium (H_3O^+) ion. This causes the molecular ion to take on a +1 mass and a positive charge, allowing separation via M/Z. While this method is not effective at separation of isomeric species such as acetone and propanal, it allows common compounds such as methanol and acetaldehyde to be detected quickly and accurately and the concentration of acetone to be inferred, as propanal has been inferred as negligible in marine systems (Beale et al. 2011). It is currently unknown if this is greater or lesser in freshwater, however, as previous work in rivers has suggested propanal and acetone at similar concentrations (Dabrowska and Nawrocki 2013).

For a method to be viable for measuring environmental concentrations, it is important to consider the concentrations expected to determine the sensitivity. As shown below, in Table 2.1, the OVOC compounds studied are typically detected in marine and riverine environments at nanomolar levels. In comparison, isoprene is more typically seen in picomolar concentrations, or potentially

sub-picomolar in remote oceans (Broadgate et al. 1997; Hackenberg et al. 2017), increasing to just over 1nM in estuarine systems (Alvarez et al. 2009). Therefore, the development of a method that can reliably detect in sub-nanomolar levels is essential to ensure measurements are reliable and relevant.

2.2 Methods used to identify VOC concentration

2.2.1 Purge and trap/Gas Chromatographic methods

Traditionally, the use of chromatographic methods to identify VOCs has been the most reliable, accurate and in most cases the only suitable method. Chromatography works off the principal of variable adsorption, where mixed compounds are driven across a column (a stationary phase) by a solvent (the mobile phase). Both of these phases can depend on the analyte and desired detection limit, and VOCs have successfully been quantified with a range of columns (Qin et al. 1997; Zhang et al. 2015).

The sample introduction methodology depends upon the expected concentration, sample medium and instrumental sensitivity, but either a small sample loop will be used to contain and inject a subsample directly into the chromatographic column and detected by a range of instruments, or pre-concentration can be used. Pre-concentration is the process of increasing concentration to a detectable level, typically carried out with a purge and trap system, whereby a sample is purged of the analyte and this is trapped in a medium that can release the analyte when required, such as a cryo-trap (Mendes et al. 2000; Singh et al. 2004).

While ubiquitous, chromatography is typically reasonably slow, often requires pre-concentration, limiting sample throughput and increasing complexity. More modern methods, such as the use of membrane inlets or direct equilibration are available, as discussed below.

2.2.2 Membrane methods

The use of a semi-permeable membrane to separate analytes has been used for a range of analytical equipment. Here, the focus shall be on two particular types: those which require a carrier gas, such as membrane inlet proton transfer reaction mass spectrometry (MI-PTR-MS) (Beale et al. 2011) and those which do not, such as membrane inlet mass spectrometry (MIMS) (Tortell 2005). These have the advantage of a very fast sample turnaround, high accuracy and the possibility of selecting an alternate membrane in material to affect permeability to different compounds (Firpo et al. 2015). However, these methods typically do require some retention time to allow for the analyte to adsorb, diffuse and then pervaporate on the other side of the

membrane, which, while swifter than purge and trap methods, still cause some systems to be too slow for continuous measurement.

2.2.3 Equilibration methods

The introduction of high throughput gas analysis such as the proton transfer reaction mass spectrometer (PTR-MS) has caused the introduction of a third method: equilibration between gas and analyte in a closed system (Kameyama et al. 2014). This has the advantage of being swift, in some cases allowing for underway ship measurements with human input and can be calculated to allow full equilibration using simple compressed air (Wohl et al. 2019). However, methods like this are difficult to set up, require pure or calibration gases and lead to high moisture levels in instruments, causing excess wear or drift.

Table 2.1. A comparison of different methodologies used for analysis of trace gases, along with analysis time and requirements for an analysis.

Method	Users	Requirements	Analysis time per sample
Purge and trap	(de Bruyn et al. 2013; Andrews et al. 2015; Hackenberg et al. 2017)	Heating and cooling elements, carrier gas.	~30 min
Membrane inlet	(Beale et al. 2011; Dixon et al. 2013a; Yang et al. 2014)	Pressurised high purity gas	~30 min
Equilibration- bubble column	(Kameyama et al. 2010; Tanimoto et al. 2014a)	Pressurised carrier and calibration gas	~70 min
Equilibration- showerhead	(Johnson 1999)	Pressurised gas, air standards.	~5 min
Equilibration- Segmented flow	(Wohl et al. 2019)	Pressurised carrier gas	Continuous possible

2.3 OVOCs via PTR-MS

2.3.1 Method

The method used for analysis of VOCs, in this case methanol, acetone and acetaldehyde is a modified version of the research described in Beale et al. (2011). This method has successfully been deployed on long cruises such as the Atlantic Meridional Transect (AMT) (Beale et al. 2013) and also in annual study (Beale et al. 2015) of OVOCs in open ocean and near-shore coastal systems. Samples were taken through immersion of a gastight, lighttight bottle either in the water at a sample site, or in an acid washed stainless steel bucket drawn from the site. They were transported at *in situ* temperature and analysed within 8 hours, as longer term storage can cause sample degradation (Beale 2011a; Dabrowska and Nawrocki 2013; Wohl et al. 2019). By keeping samples in the dark and cool, it is hoped that no photochemical reactions would occur, and only natural biological processes at the same rate as *in situ* would be a factor. While filling bottles, it is important to minimise bubbling, as this is a very efficient way to strip volatile compounds from a sample- in fact, some methods use this mechanism (Kameyama et al. 2010). For analysis samples were transferred with minimal air intrusion into an outer membrane. This method was used without modification for the first work presented here, the seasonal comparison, that is, achieved via flushing the sample in a nitrogen enriched environment, to ensure all gas contamination of the sample was inert. For Chapter 4, below, this was replaced for reduced contamination and increased speed by a pair of 100ml gastight glass syringes, connected directly into the membrane via luer locks. This allowed the sample to have absolutely zero gas contamination and saved a gas cylinder, making the method more applicable for fieldwork.

This sample was pumped at a rate of approx. 4 millilitres per minute, into an outer Fourinated Ethylene Propylene (FEP) tubing, of 3m length, submerged in a 50 °C water bath. Inside this tubing a 0.17mm wall diameter silicon membrane through which built in purifier (BIP) nitrogen was pumped in the opposite direction to the water flow, at 50 ml min^{-1}. It is this carrier gas that was analysed by the Proton Transfer Reaction Mass Spectrometer (PTR-MS), built by Ionicon, Austria. Methanol was detected at M/Z 33, acetone at M/Z 59, and acetaldehyde at M/Z 45, corresponding to the molecular mass of methanol, acetone and acetaldehyde+1 respectively, due to the proton transfer reaction protonating the volatile compound. This is typical of both the analytical methodology (Beale 2011b; Beale et al. 2011), and the PTR-MS (Lindinger et al. 1998b). The internal reaction mechanism from the PTR protonation and soft ionisation can be seen below, in Figure 2.1. Of note is that the protonation of methanol is direct, however both acetone and acetaldehyde is via the addition of a water molecule. As discussed above, a known interference at M/Z 59 using PTR-MS exists between acetone and proponal, isomeric species which both

protonate to mass 59. A number of studies have considered this to be a known uncertainty (Williams et al. 2004b; Marandino et al. 2005), however, this interference was shown to be negligible in comparative work (Beale et al. 2011) and later calculated as well below 10%, with acetone contributing 93-98% of the signal at mass 59 (Beale et al. 2015). Therefore, for the current work it is reasonable to assess the acetone concentration shown in the data as a realistic upper limit.

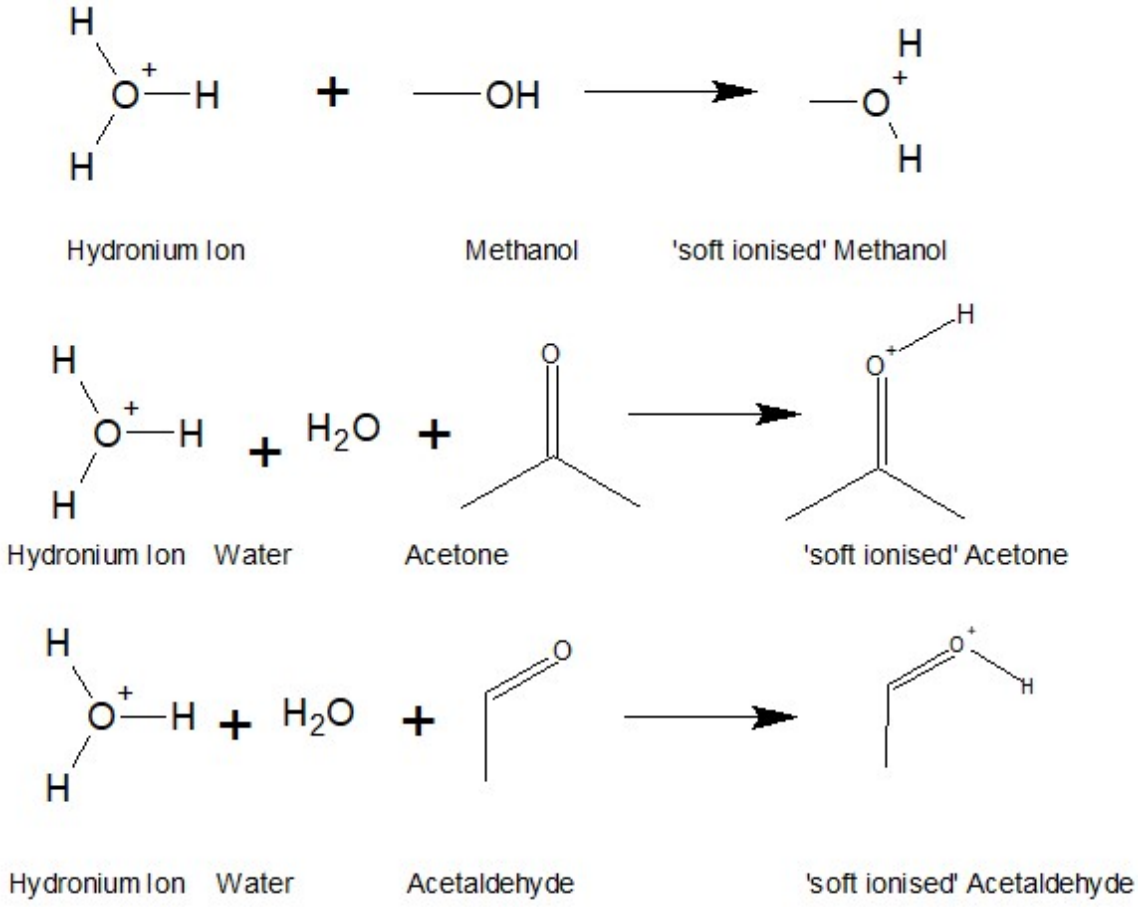


Figure 2.1. A mechanism of protonation and soft ionisation for VOC compounds in the PTR-MS, via the addition of a hydronium ion. All compounds except methanol also require a water molecule, as discussed above

2.3.2 Calibration

Calibration in water was performed via the use of mixed solvent standards made by serial dilution. Methanol was calibrated between 5 and 1000nM, acetone between 0.5 and 100nM and acetaldehyde between 1 and 120nM. For each of these, full examples of these calibration curves can be found in Figure 2.1-2.3, below.

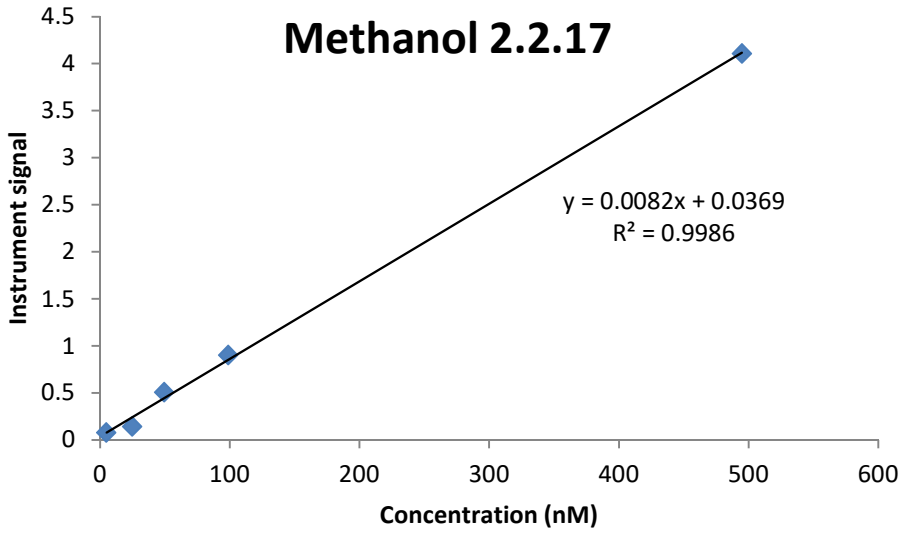


Figure 2.2. A typical methanol calibration on PTR-MS

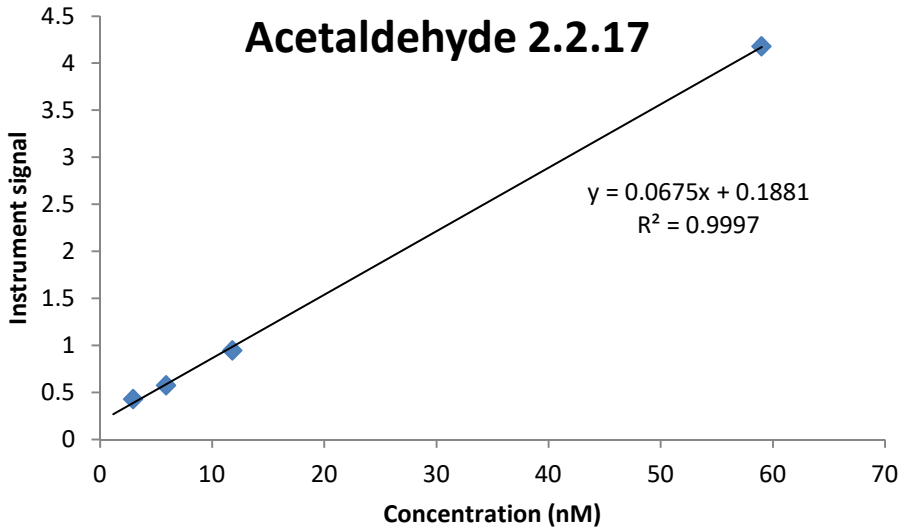


Figure 2.3. A typical acetaldehyde calibration on PTR-MS

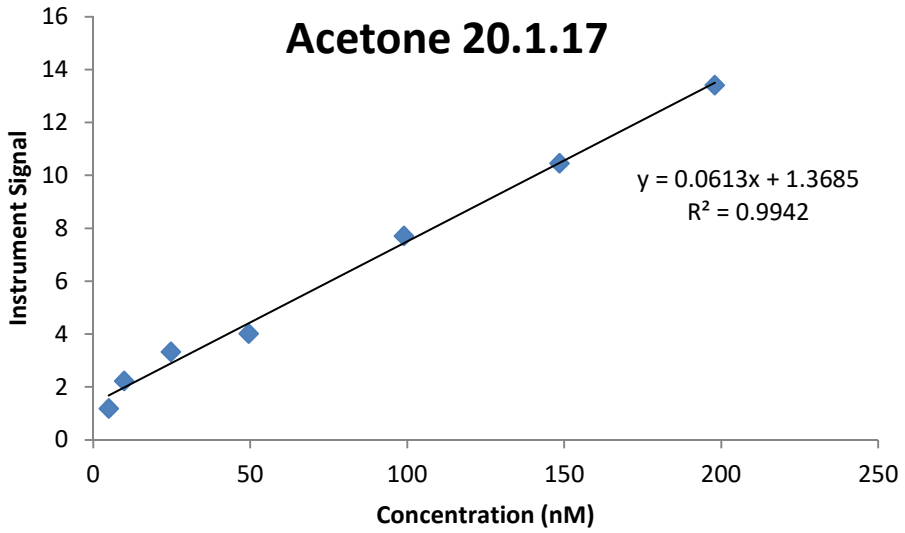


Figure 2.4. A typical acetone calibration on PTR-MS

2.4 Isoprene via MIMS

2.4.1 Existing isoprene analysis methodology

The study of isoprene in the past has been dominated by the use of gas chromatography, typically with a pre concentration method (Broadgate et al. 1997; Shaw et al. 2003; Alvarez et al. 2009; Exton et al. 2010). This method typically requires an incubation of a number of hours, a timed purge, followed by a cryogenic gas trap, which, while precise down to parts per billion by volume, is labour intensive, costly and slow (Exton et al. 2010). A possible update to this method is the use of an automated method for this process, while removing the labour required, for example, the fully automated system described in Andrews et al (Andrews et al. 2015; Hackenberg et al. 2017). However, this does nothing to reduce the gas requirement, nor speed the process with a 50 minute temporal resolution.

Newer developments in the use of the isoprene-ozone reaction coupled with a photomultiplier to identify the chemiluminescence have also been produced (Hills and Zimmerman 1990; Guenther and Hills 1998). This has the advantage of speed, with multiple datapoints per second possible on some equipment (Exton et al. 2010). However, this method also requires the use of high pressure gases and ozone, along with a calibrated light source (Exton et al. 2010).

Isoprene has a much lower solubility in comparison to the other materials- it is only sparingly soluble in water, although miscible with other volatile solvents such as ethanol (Lide and Baysinger 2005). For isoprene standard production, it was found inaccurate to pipette in a similar manner to other VOCs, due to the tendency to provide sufficient vapour pressure to eject from

the pipette with no external stimuli. The measurement of a larger volume and dilution of this, as used for acetaldehyde, was found to also prove problematic, due to 1mL isoprene being insoluble in 1L water. The solution used was the production of a gastight primary isoprene standard in ethanol, which was capable of secondary dilution and was able to be stored for several months.

The use of a membrane inlet mass spectometer (MIMS) for dissolved gas measurements has proved useful in high frequency, high precision measurements, with no requirement for pre-concentration, pressurised gases or complicated procedures. However, while this method has been utilised for a range of dissolved gases, for example CO2 and dimethylsulfide (Tortell 2005), the same cannot be said for isoprene.

2.4.2 Method Development aims

The aim of this method development was to investigate and examine the utility of a new method to examine isoprene at environmentally relevant concentrations, without use of pressurised gases or purge and trapping. The use of a membrane inlet mass spectrometer (MIMS) to analyse gaseous compounds has previously been investigated, with up to 14 VOCs investigated simultaneously in lab air (Ketola et al. 2002) and a range of dissolved gases in seawater (Tortell 2005), while methanol has also proved detectable down to 2ppm via this method in both air and water with a suitable membrane (Allen et al. 2001). The aim of my research is to investigate the use of a MIMS to measure isoprene at environmentally relevant concentrations, and to deploy this system for investigation of the effect of peat moors upon dissolved volatile compounds in northern Scotland.

2.4.3 Method development

Standards used to develop the method were prepared from Isoprene serial dilution in crimp top vials, to ensure no loss. The primary standard was prepared gravimetrically in ethanol, to ensure both longevity (Orr and Leverne Williams 1951) and to use a solvent suitable for larger amounts of isoprene than water (isoprene is only very sparingly soluble in water, under 1ml/litre miscibility). Pure isoprene tends to self-polymerise, therefore stabilised (99.98%) isoprene was used (Orr and Leverne Williams 1951). This was then diluted into a secondary standard in water, again in a crimp-sealed vial. To prepare working standards, volumes of this secondary standard were injected into 100ml gastight syringes of ultrapure MQ water. For standards lower than 1nM, a 10nM standard was produced and diluted again in airtight connecting gastight syringes with luer locks. The working aqueous standards were prepared in gastight syringes, with volumes of a

primary (isoprene in ethanol) or secondary standard injected using a microsyringe (Hamilton Microliter), and then left for 30 minutes for the standard to sufficiently mix.

A Membrane Inlet Mass Spectrometer (HPR- 20, MIMS, Hiden Analytical, Warrington, UK) with a circular membrane cell (approx. 3cm diameter, circular, for a total membrane area of approx. 8cm^2 (Tortell 2005). The membrane selected for this was a Polydimethylsiloxane (PDMS) membrane in the thinnest commercially available thickness, 125 µm, as thinner membranes would not maintain a vacuum but would also be unlikely to have a consistent thickness (Pers.Comm, P.White, 2017). Isoprene was detected at M/Z 69, for the isoprene molecular Ion, and M/Z 41, for the carbenium ion, (Schwarz et al. 2009), as shown below in Figure 2.5. Fragmentation studies show that the M/Z 41 ion is the most prevalent ion fragmented from isoprene and therefore is likely to have the greatest signal to noise ratio (Schwarz et al. 2009).

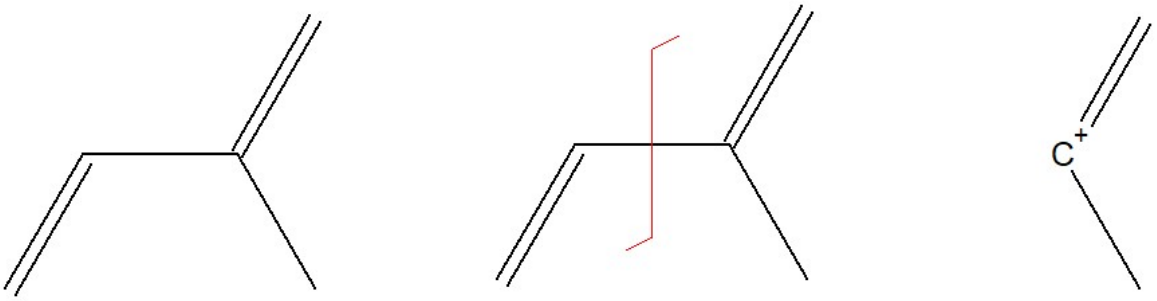


Figure 2.5. Diagrammatic representation of Isoprene fragmentation in MIMS. Left: Isoprene molecule complete and unfragmented. Middle: red highlight showing the particular bond fragmented. Right: the result of the fragmentation the Carbenium ion, which is detected at at M/Z 41.

The MIMS functions with a membrane separating the sample and vacuum of the mass spectrometer. Selecting a thin, semi-permeable membrane to allow some molecules through to be selectively permeated and therefore analysed. The PDMS membrane was placed in an 8cm^2 circular cell on one side of which the sample was pumped across vertically, to ensure no bubble retention (Tortell 2005). A sketch diagram of this system is in Figure 2.6. Once inside the MIMS, a filament produces an electron beam across the incoming flow, which ionises the gas, meaning it can be separated with a quadrupole mass spectrometer set with the electron multipler at 885 V with a dwell time of 1s per analyte and the ionisation current at 50 µA, to cause as little fragmentation as possible.

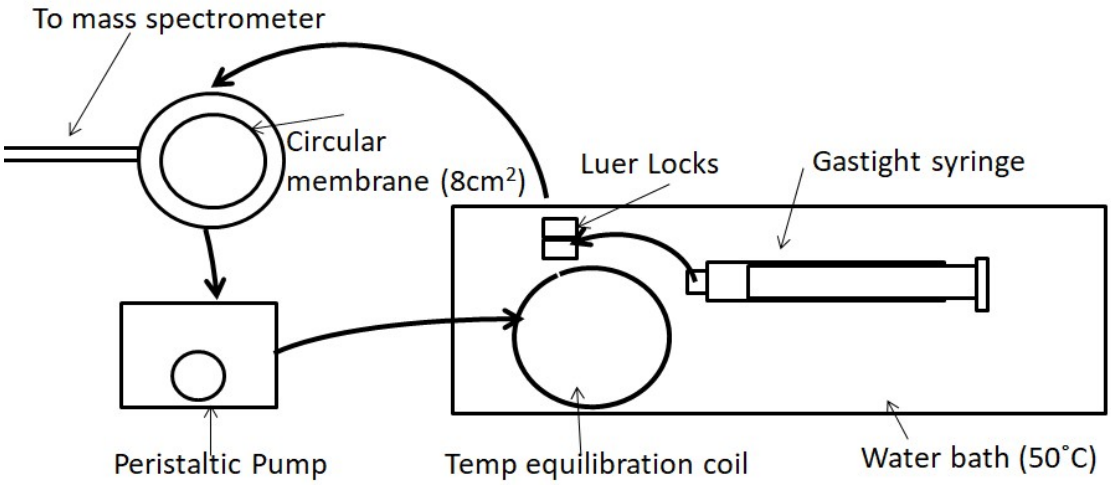


Figure 2.6. A labelled sketch diagram of Membrane inlet sample introduction, showing how a sealed system at a steady temperature was created and maintained during analysis.

Samples were obtained in a similar manner to OVOCs, as above. An acid-washed, gastight bottle was completely submerged in water and allowed to fill with minimal bubbling, to ensure no scrubbing effect takes place. This was kept *in situ* temperature in the dark until analysis, which was completed as expediently as possible, in all cases within 8 hours of sample collection, as discussed above. Previous work has suggested isoprene loss in seawater is close to 0.8pmol L^{-1} in 20 hours, therefore running same-day analysis in the same manner as OVOCs seemed prudent (Broadgate et al. 1997). For analysis, the sample was transferred via Tygon tubing into gastight syringes. This was replicated twice, such that in total three replicates of each sample were available for statistical work. In the preceding 10 minutes before analysis, these syringes were placed in a hot water bath heated to 50°C, which was the shortest reasonable time required to reliably reach this temperature. At the start of the analysis cycle, the sample was pumped into the closed loop, as shown in Figure 2.6, and then were recirculated for the length of the analysis. Between samples, the membrane was rinsed with ultrapure water.

Temperature has previously been found to have a significant effect on volatile compound analysis including DMS and methanol (Bell et al. 2007). To control for this variability, it was decided to keep the temperature of the sample steady with use of a water bath. A comparison was undertaken between iced water at below 5 °C and a hot water bath set at 50 °C. Of these, the most stable and largest signal was found at 50 °C and thus this was decided as the temperature used for analysis. To ensure the sample was kept at this point, a length of Tygon tubing was added to the sample loop, to ensure the sample was predominantly in the hot water bath. This increased the inner volume of the recirculating system to around 80mL. As there is a risk of this increased

temperature affecting any biological process, the sample was placed in the hot water bath as late as possible to still reach the analysis temperature.

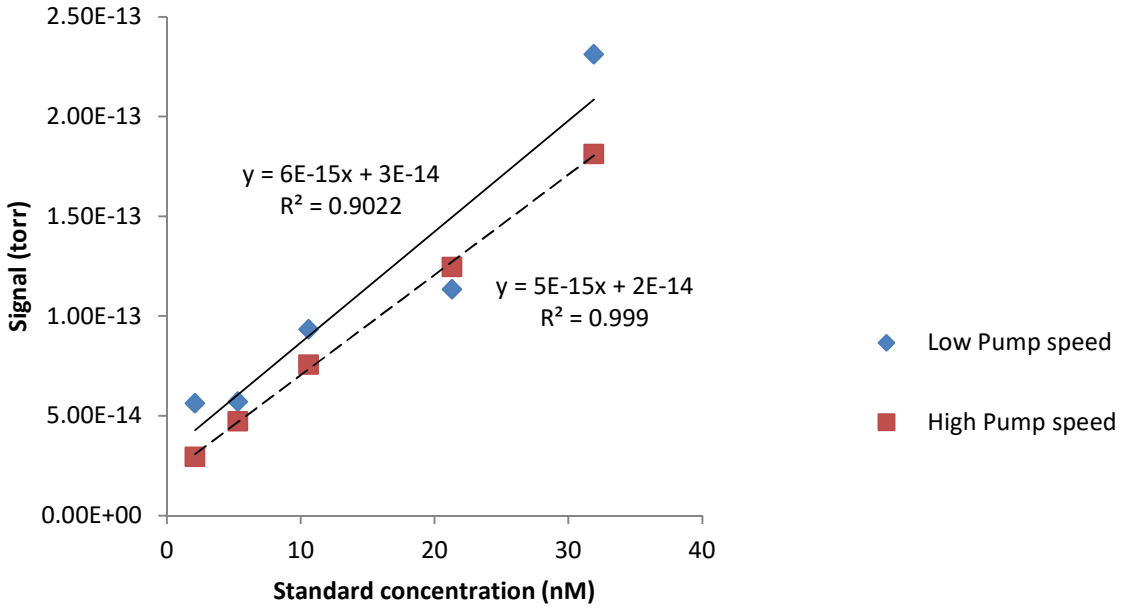


Figure 2.7. Comparison of MIMS signal stability with varying pump speed- 30RPM compared to 90RPM (approx. 1l per min compared to 3l per min)

The flow rate of sample across the membrane is known to have a significant affect upon the gas transfer across the membrane, with higher flow rate thought to promote gas transmission (Tortell 2005). Therefore, experiments were carried out to investigate the optimal flow that could be completed without excess turbulence. The highest and most consistent stable signal was found to be at a pump speed of 90RPM, corresponding to a flow of around 3L per minute (Figure 2.7). Therefore, it is this setting that was used for the sample analysis in the Halladale campaign. A further advantage of this high flow rate was the system became stable after a relatively short time- 5 minutes- leaving a 5 minute analytical run and meaning each sample analysis can complete in only 10 minutes total time, allowing a higher throughput than the OVOC via PTR-MS system by a considerable margin, as shown below in Figure 2.12

2.4.4 Method validation

Method validation is crucial in the development of any new method, to ensure effectiveness and confidence in the method and to determine linear range and detection limits. To determine this, the isoprene via MIMS method was tested for linearity, precision, stability and if there's any carry-over in between samples and standards. Furthermore, where possible, it has been compared to the PTR-MS analysis method, which has previously reliably detected volatile compounds in marine and riverine waters.

2.4.4.1 Linearity

Linearity is a determination if an increase of analyte will linearly increase the signal output on a detector. This can be used to determine the relevant range of concentrations a method can successfully determine. In this case, a priority is lower concentrations, as isoprene is expected to be in the picomolar concentration.

Isoprene was detected comparatively both at M/Z 69 (the molecular ion) and at M/Z 41 (the most common ion from fragmentation) on the MIMS. Comparison of the calibrations showed M/Z 41 presenting much improved repeatability compared to M/Z 69. As Isoprene is typically found in these lower concentrations (< 1nM) environmentally, a further calibration was completed to ensure linearity below 1nM. In both cases, an R^2 in excess of 0.98 was obtained for mass 41. Therefore, this mass was used for further analysis.

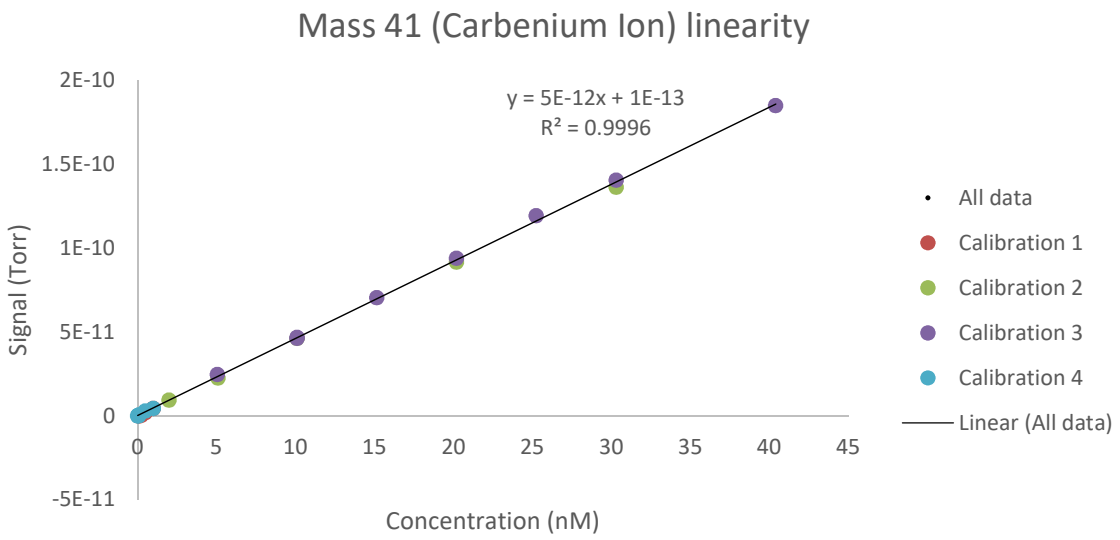


Figure 2.8. Mass 41 MIMS calibrations showing linearity over the range 0.01-40nM

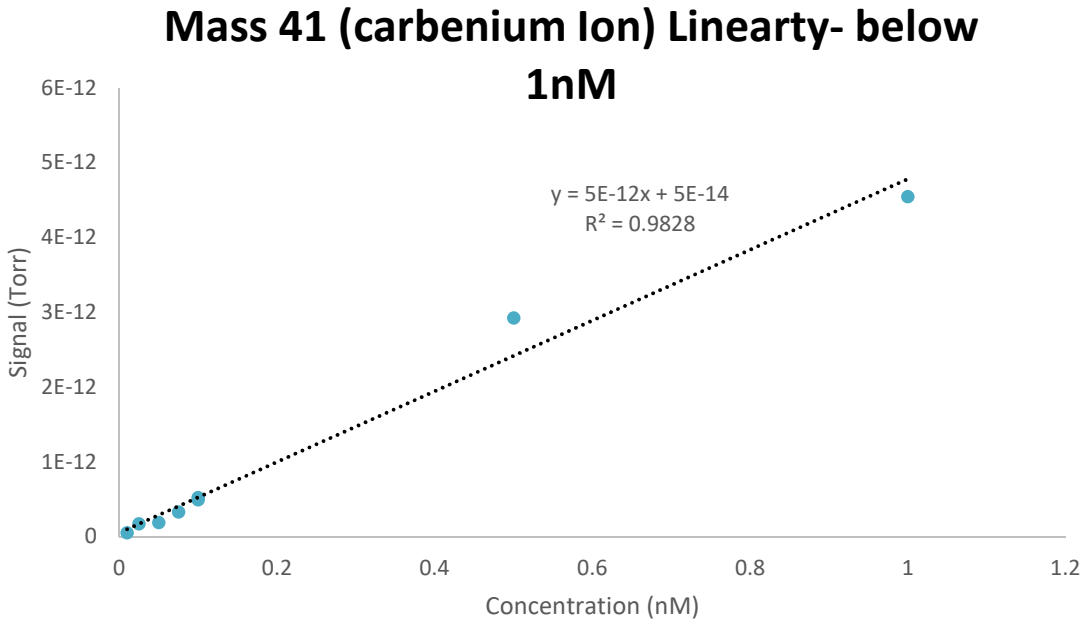


Figure 2.9. Comparison of M/Z 41 and 69 linearity between 2 and 30nM

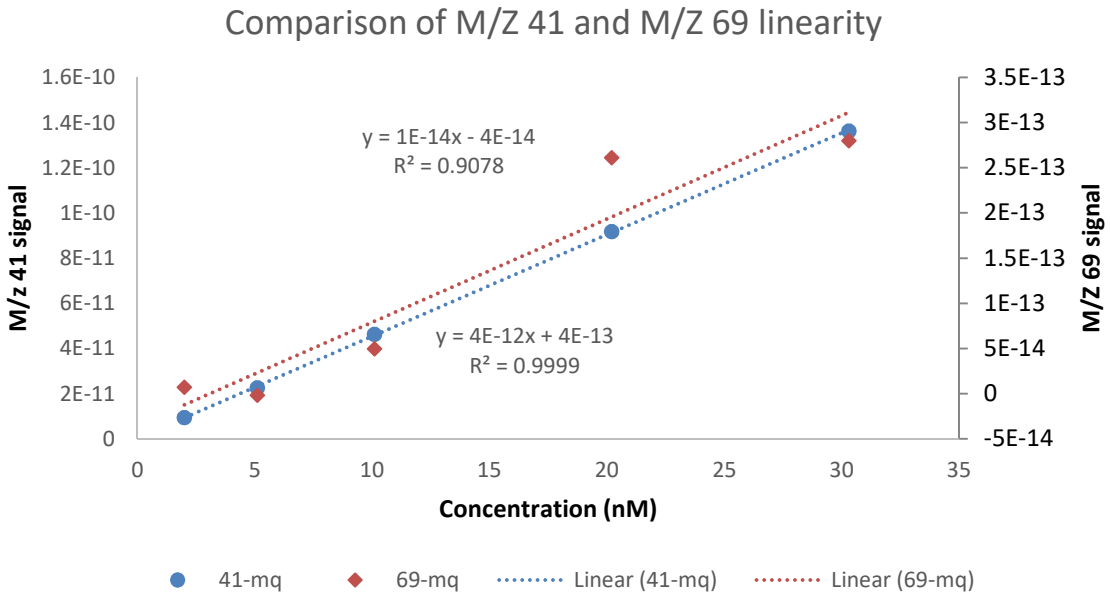


Figure 2.10. Lower concentration calibration of MIMS detection of Isoprene showing continued linearity below 1nM for both mass 41 and 69

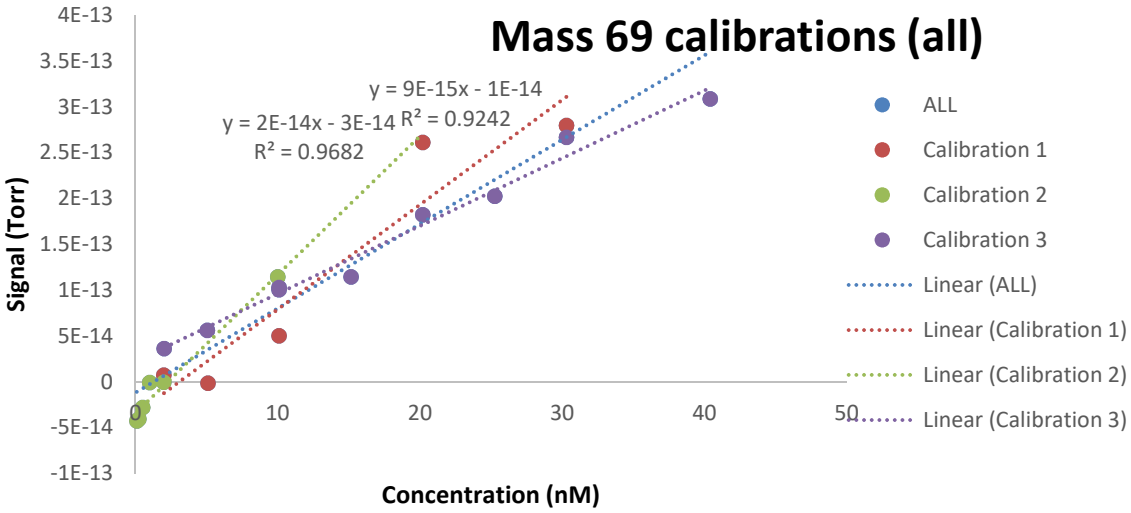


Figure 2.11. Combined MIMS calibrations at M/Z 69, showing consistency compared to M/Z 41, above

2.4.4.2 Precision

Precision is a measure of the reproducibility, and was assessed by repeatedly analysing the same standard. A standard deviation was calculated from a known standard analysed

repeatedly. For this experiment, a 0.1nM standard was mixed repeatedly (n=6), and ran one after the other. As shown below in Figure 2.12, while there was some variation between the standards, a 7.3% standard deviation was calculated. This is likely due to minor turbulence in the system, or possibly random variation within a sample run, as shown in Figure. 2.12.

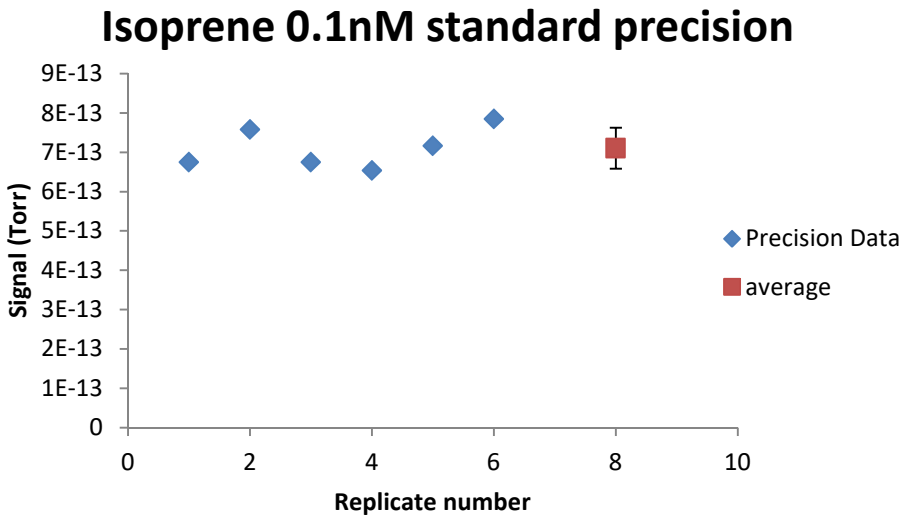


Figure 2.12. A measure of precision of repeated standards at 0.1nM, including standard deviation on repeated analysis (n=6). Measurements taken at at M/Z 41 on MIMS.

2.4.4.3 Accuracy

Accuracy is a measure of the closeness to the true value of the analytes to the value measured in this method. Isoprene in water as a standard is unavailable and if it were, its reliability would be questionable due to isoprene's high volatility and low miscibility with water. Therefore, accuracy was determined by repeated calibrations on standards mixed independently- from a master solution which was also remixed to determine consistency. A cross calibration was also considered with the PTR-MS to determine standard quality, however, the preparation of standards prevented this across the full linear range of the MIMS, as discussed below in 2.4.5.

2.4.4.4 Stability

Stability of the Isoprene signal was assessed with an extended analytical run of 0.1nM standard. This was maintained for the typical length of three analytical runs, to investigate stability. As shown below in Figure 2.8, after around 4 minutes the signal remained steady, and this remained

for the length of the analysis. This assessment suggests a 5 minute wait for signal stability is suitable time before analysis.

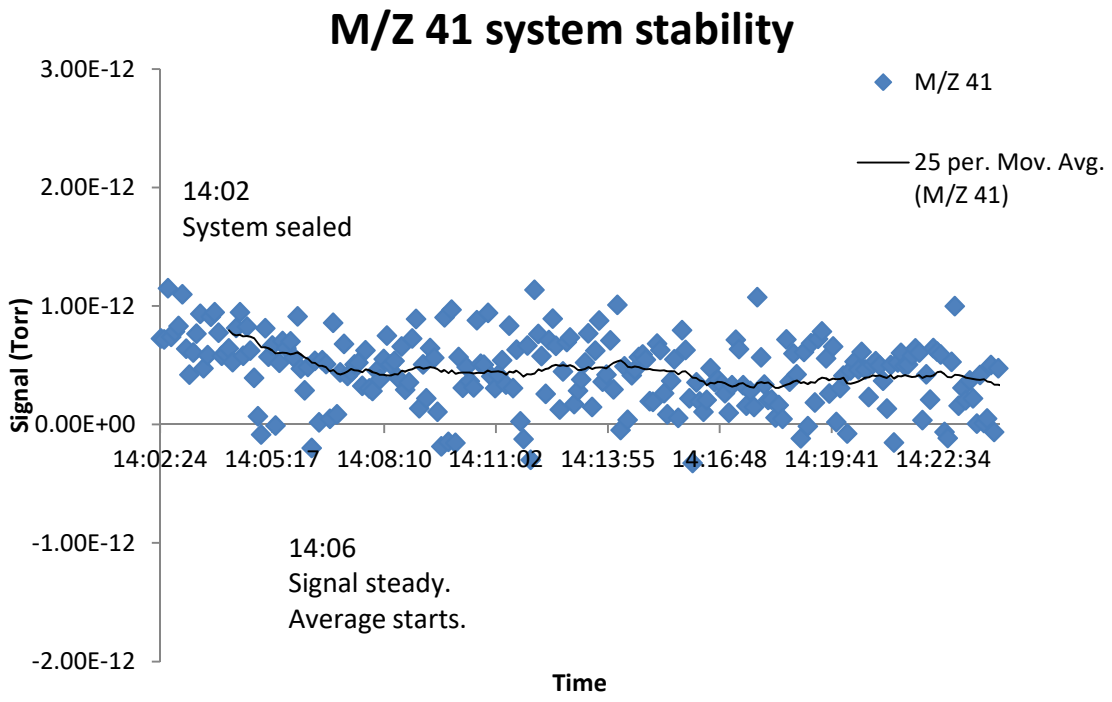


Figure 2.13. A signal/time graph to indicate system stability determined with extended sample run, starting at 14.02 and running to 14.24. The signal, and therefore the system stabilises in approx. 4 min, indicated by the levelling of the moving average, as shown by the black line.

2.4.4.5 Carry-over

To investigate if the system experienced any carry-over, or a 'memory' effect, this test was carried out to ensure a high concentration sample did not have an effect upon the systems response to a less concentrated sample next in sequence. This was done by comparing the signal from a MQ blank before and after a standard run, as shown below in Figure 2.9. The average signal at M/Z 41 was $3.48x10^{-11}$, $3.54x10^{-11}$ and $3.46x10^{-11}$ Torr respectively, suggesting a calibration had no carry over. This was also proven by repeated 10nM standard during and after the calibration, $8.22x10^{-11}$ and $8.09x10^{-11}$ Torr respectively. This suggests the system is not liable for carry-over between samples under 40nM.

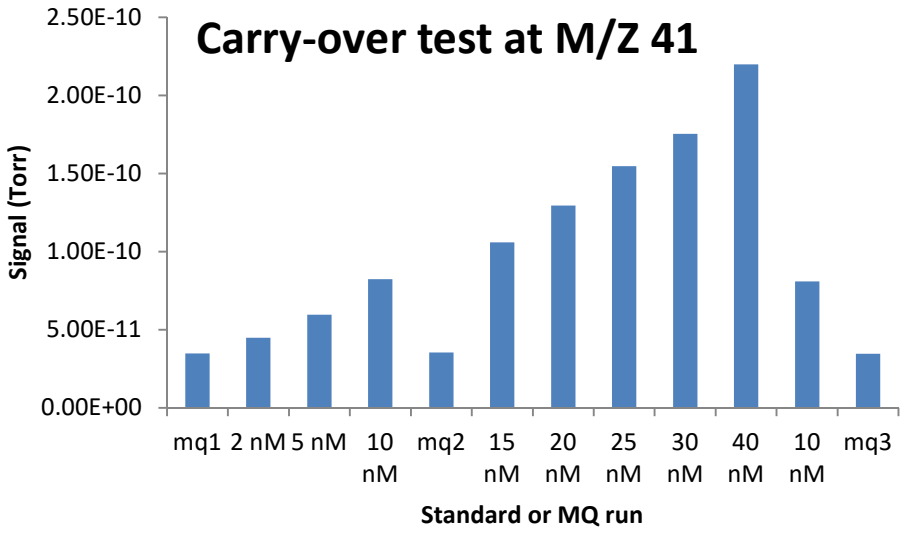


Figure 2.14. Test of the system carry-over via calibration and comparison of the relative accuracy on higher and lower concentration standards. This investigation was completed with the signal at M/Z 41.

2.4.4.6 Limit of Detection

Limit of detection was calculated from 3x the blank signal standard deviation, which was 0.07nM (Long and Winefordner 1983). The system was left running for an extended period with MQ water and the signal divided into 5 minute chunks. These simulated runs were averaged and the standard deviation between these was calculated. Full data from this is shown in Table 2.1, along with the standard deviation concentration for both 3x and 10x standard deviation of blank values. Considering ultrapure MQ water typically has some solvent contamination, the average was subtracted and the LOD calculated from 3x the standard deviation from 0. This signal resulted into a LOD of 0.07nM. This is higher than the lowest calibration point (0.01nM on Figure 2.2) however

still close to previously measured environmental concentrations. Samples below this were considered below the limit of detection and not considered in analysis.

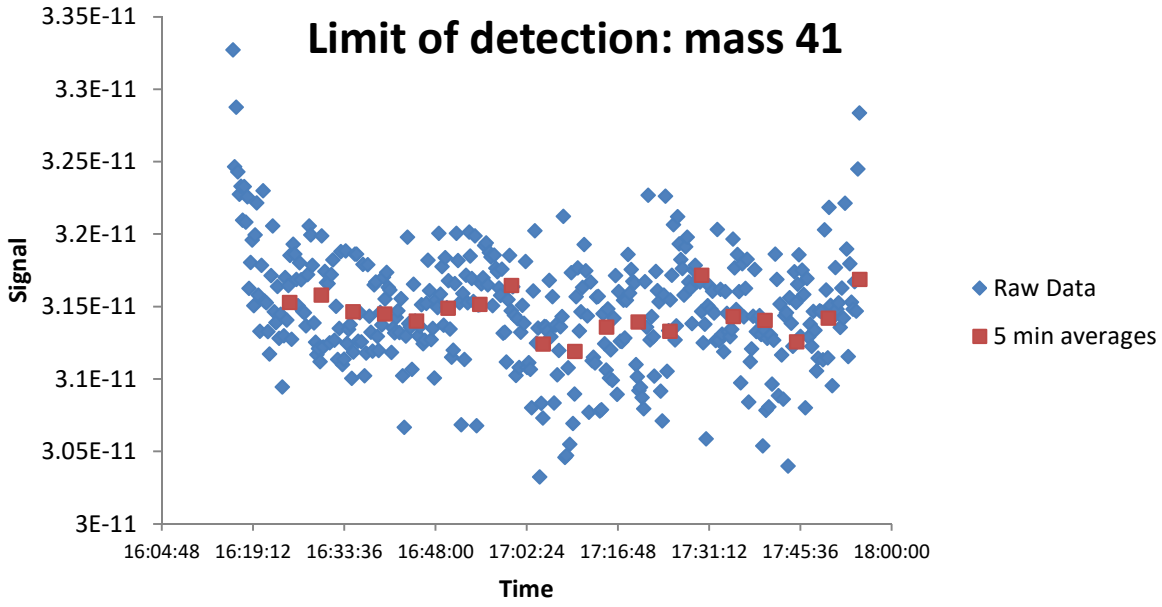


Figure 2.15. Extended analysis of ultrapure water blank measurement, to determine LOD, as shown in table 2.2. Blue diamonds indicate individual measurements (n=397), while red squares are 5 minute averages (n=19). Note Y axis contracted.

Table 2.2. Numerical analysis on the Extended analytical run carried out to determine LOD at M/Z 41, with 19 repeats of the same blank signal, with standard deviation on the signal and calculated LOD (3x standard deviation +average blank).

Analytical run finish time	Average signal (Torr)
16:25:00	3.15283E-11
16:30:00	3.15804E-11
16:35:00	3.14659E-11
16:40:00	3.14489E-11
16:45:00	3.14002E-11
16:50:00	3.14889E-11
16:55:00	3.15161E-11
17:00:00	3.16464E-11
17:05:00	3.12413E-11
17:10:00	3.11921E-11
17:15:00	3.13591E-11
17:20:00	3.13943E-11
17:25:00	3.13301E-11
17:30:00	3.17175E-11
17:35:00	3.14314E-11
17:40:00	3.14055E-11
17:45:00	3.12571E-11
17:50:00	3.14204E-11
17:55:00	3.16893E-11
count	19
Standard deviation	1.44385E-13
3x standard deviation	4.33156E-13

Calculated concentration (nM)
0.00928
0.0721

2.4.5 Comparison with PTR-MS

To compare the MIMS with a previously published method for volatiles, the MI-PTR-MS, a calibration was completed using the same standards at the same time. Unfortunately, the residual ethanol in the isoprene standard led to the highest possible standard being 1nM, due to the possibility of saturating the membrane at mass 45 for ethanol. These graphs are shown below, for both mass 41 and 69, as shown in Figure 2.16 below. As a result of this, the comparison between the two instruments was reduced to comparative calibrations, seen below for MI-PTR-MS and in

figure 2.8 for MIMS. As shown with the intercept location, it would prove difficult to prove significance at lower concentrations for PTR-MS.

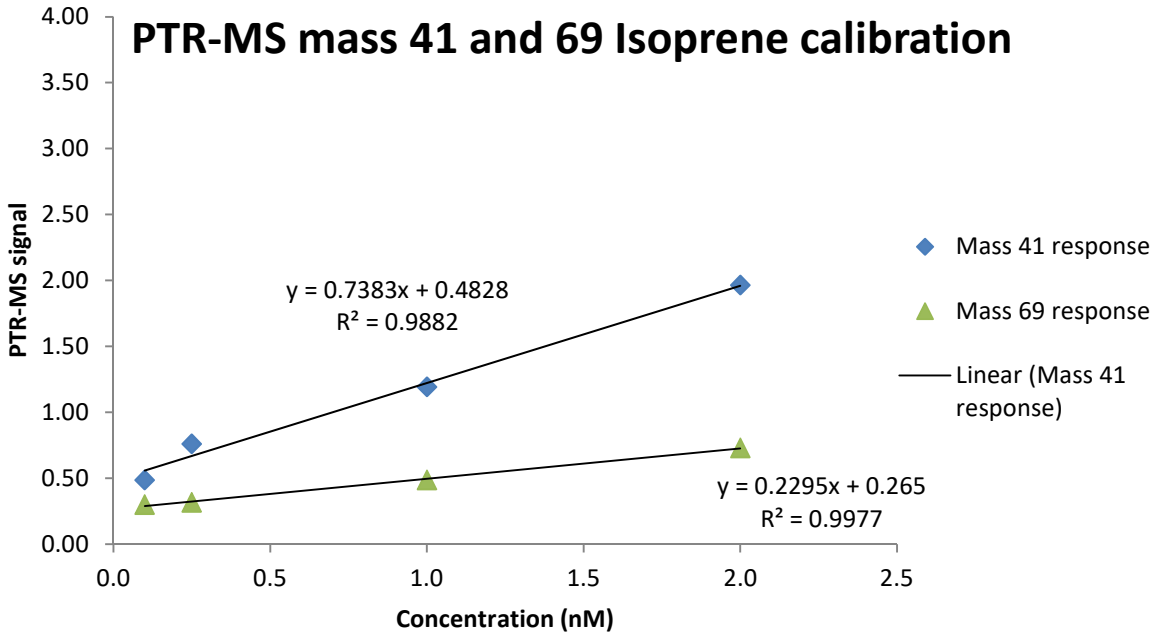


Figure 2.16. Calibration comparison between Ions 41 and 69 on the PTR-MS between 0.1 and 2nM.

From this work, it is clear the MIMS has a much steeper calibration curve at lower concentrations, suggesting the readings from the MIMS would have a much lower variability. Furthermore, the MIMS method is significantly faster than the PTR-MS, allowing a higher sample throughput and the possibility of use underway on a vessel.

2.4.6 Method development conclusions

The primary aim of this section, as discussed in 2.4.2, was the development of a new methodology for analysis of isoprene at environmentally relevant concentrations. As discussed in preceding sections, while a number of methods for detection of isoprene have been utilised, there is no equipment that is able to detect samples at a high resolution, requires no bottled gases and is still able to detect at environmentally relavant picomolar concentrations using off the shelf equipment and membranes. While this is a step forward in the determination of isoprene, it is hoped that this method can also be utilised on a range of other volatile compounds with further development, and potentially increase the available dataset. Further developments could include an increase in the membrane surface area- hollow fibre membranes are already in use for dissolved gas analysis (Sims et al. 2017), and theoretically could increase sensitivity by orders of magnitude.

2.5 Auxiliary methods

Determination of VOC concentrations alone leaves a great range of environmental attributes potentially ignored. To fully understand any processes behind VOC cycling, an array of other variables should be determined. These were decided primarily with relevance to the VOCs, environment, or general importance. CDOM is known as a VOC precursor, so it was important to determine within the same samples as VOCs were measured, while a project aiming to provide conclusions in estuaries should always determine salinity alongside temperature and pH. Furthermore, other water quality measurements such as turbidity, nutrients and dissolved oxygen were taken, due to their relative ease by commercially available sensors and importance to understanding of the bigger picture

2.5.1 CDOM via UV-vis spectrophotometry

Chromophoric Dissolved Organic Matter (CDOM) was detected by a Cary 60 UV/Visible spectrophometer, using method from Kitidis (Kitidis et al. 2006). Samples were filtered with a syringe and inline filter of 0.45 µm pore size, directly into a quartz cuvette which was rinsed in triplicate with ultrapure water before each analysis. The spectrophotometer was set to scan from 800nm to 200nm which covers ultraviolet and all visible light and the data analysed with a single exponential model (Kitidis et al. 2006) and slope ratio was calculated using the method of Helms (2008) as well as the ratio, to determine molecular mass of the corresponding CDOM.

2.5.2 Auxiliary nutrients and salinity

During winter simultaneous measurements of temperature, salinity, dissolved oxygen, total dissolved solids and pH were made *in situ* using a YSI ProDSS 4-port multi-probe (www.YSI.com/ProDSS) and associated sensors. For riverine samples (zero salinity) the optical dissolved oxygen and pH probes were also exchanged for nitrate and ammonium sensors. The multi-probe was calibrated using pH standards of 7 and 10, a redox standard of 250 mV and NO_3- and NH_4+ standards of 1 and 100 ppm respectively, as per the manufacturer's guidelines. All the standards were obtained from Xylem analytics UK. (http://www.xylemanalytics.co.uk/index, accessed 20/10/17). For samples at L4, nitrate and ammonium were completed using standardised methods for the Western Channel Observatory, specifically copper/cadmium column for nitrates and indophenol blue for ammonium. For more details, see https://westernchannelobservatory.org.uk/documents/pml-wco_nutrient_protocols.pdf .

2.6 Method- Conclusions

The detection of volatile compounds in water has been radically altered in the last few decades with development of faster, more accurate and more versatile instrumentation. Two techniques discussed here, proton transfer reaction mass spectrometry and membrane inlet mass spectrometry, have proven potential to vastly improve knowledge of volatile compounds in environmental matrices, however, development, improvement and addition to these methods is still ongoing. This section has demonstrated the reliability of these methods shown, as well as comprehensively proving their suitability for analysis at environmentally relevant concentrations. However, for further testing, use of these methods in an real-world analysis problem would be required. This suitability for extraction and determination of volatile compounds in natural waters will be determined in South West UK (Chapter 4) and the Halladale catchment in northern Scotland (Chapter 5).

Chapter 3 Volatile organics: from Catchment to Coast

3.1 Introduction and Aims

As discussed in chapter 2, the suitability of the PTR-MS method for analysing VOCs in near-shore systems has been determined and it is hoped to be able to use this existing method to gather data in riverine and estuarine systems. There are relatively few measurements of OVOCs in rivers and estuaries and no simultaneous measurements- that is, multiple compounds analysed together. Furthermore, there is very little understanding of sources and interactions of these compounds in brackish and fresh waters. Therefore, the use of this method to analyse a range of sites in a typical marine system, involving a full salinity gradient, a range of runoff sources and ideally, some manner of previous published VOC measurements. Luckily, an ideal catchment was available: the catchment area around Plymouth, UK, and associated inputs influencing suite L4.

Plymouth Sound in southwest England receives inputs from the Tamar and Plym estuaries (Morris et al. 1982). The Tamar and its tributaries have a catchment area of 1500 km^2 (Butler and Tibbitts 1972), while the Plym has a catchment of 150 km^2 (Uncles et al. 2015). The catchment from the Tamar and Plym encompasses farmland to the north and Dartmoor to the north east. Dartmoor is a National Park comprised of mainly peatlands overlying granite (Fyfe et al. 2014). Closer to the estuarine mouth, both the Tamar and Plym are surrounded by more industrial and residential land. Land use in southwest England is dominated by farming (Jarvie et al. 2008) and the Tamar's catchment is estimated as 95% agricultural; arable and pasture (Mighanetara et al. 2009). In total, the flow of riverine water into Plymouth Sound averages 36.5 m^3s^{-1} (Uncles et al. 2015). A number of smaller rivers including the Yealm, Erme and the Dart cluster around Plymouth and together these contribute a yearly average of 29.2 m^3s^{-1} of freshwater (Uncles et al. 2015). The Yealm and Erme primarily consolidate runoff from farmland for the majority of their length. In comparison, the Dart and its two tributaries, the East Dart and West Dart, flow through Dartmoor for much of their length. Dartmoor peatlands are known to contain carbon, however, the amount of carbon stored is not well understood (Fyfe et al. 2014). Highly humic peat bogs have previously been identified as a significant source of bioavailable dissolved organic carbon (Rathgeb et al. 2017), which could be a primary source of OVOCs to inland rivers and estuaries (Hope et al. 1997). The Tamar and Plym discharge into Plymouth Sound and can influence the long-term time series station L4 (Smyth et al., 2015), which is approximately 10 km offshore to the south of Plymouth and is part of the Western Channel Observatory (WCO).
(https://westernchannelobservatory.org.uk/)

This chapter aims to present the first comprehensive assessment of the distributions of methanol, acetone and acetaldehyde in catchment and estuarine waters influencing the marine coastal station L4. Comparing summer (May-July 2016) and winter (January-March 2017) distributions of VOCs and evaluating the significance of terrestrial catchments as primary sources of OVOCs to receiving coastal waters.

3.2 Sampling

Sampling took place during summer 2016 (May-July) and the subsequent winter 2017 (January-March). Summer sampling and analysis was completed by Christopher Webb, while I completed the winter sampling, analysis and data/manuscript preparation- see acknowledgements for further detail of those who assisted in both summer and winter sample gathering. The major rivers and tributaries influencing water in Plymouth Sound were sampled in addition to station L4 (Site 11, Figure 3.1.)

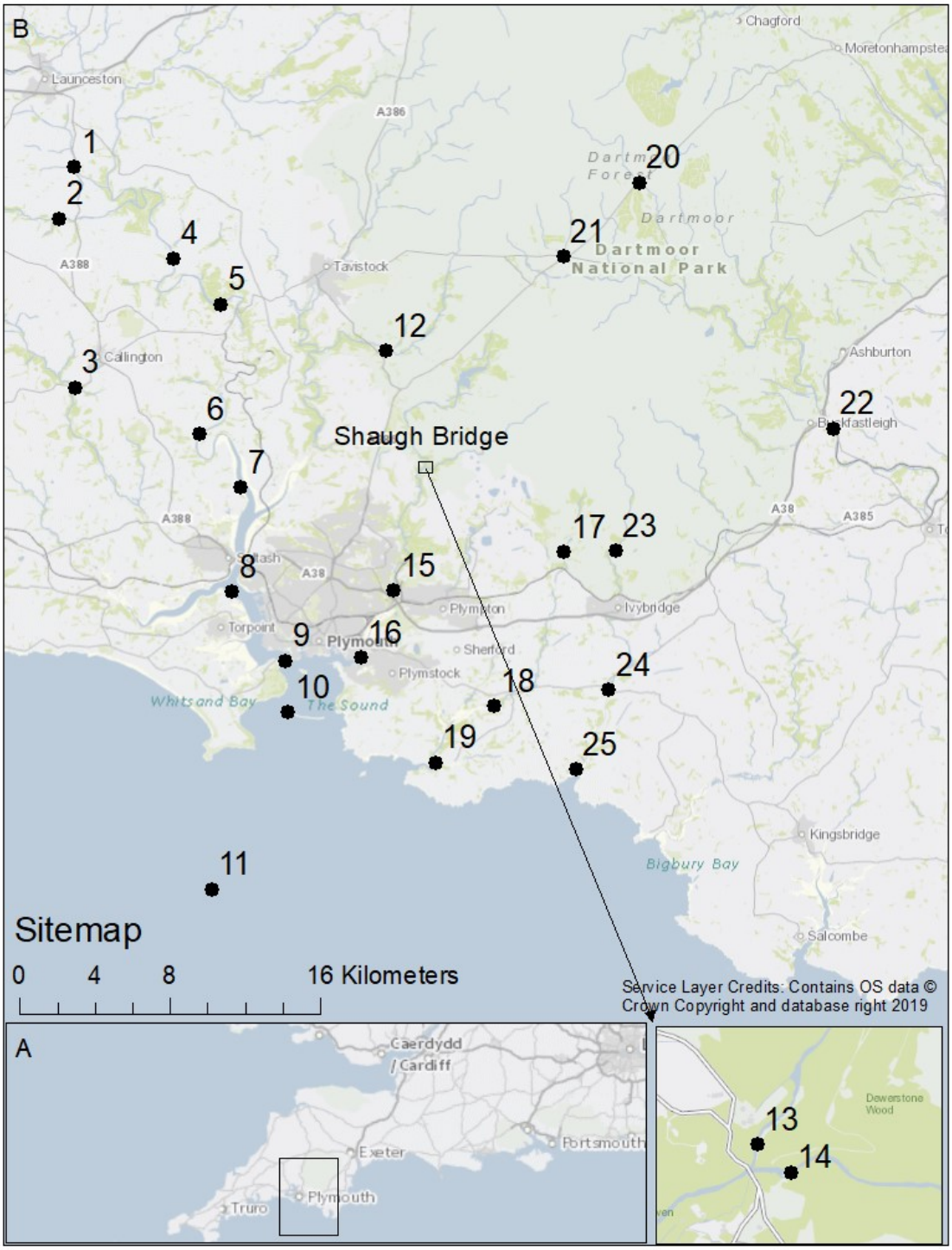


Figure 3.1. A) Map of South West UK, with main study area highlighted. B) Plymouth and the local area, with sample sites numbered. C) Inset of Shaugh Bridge sample site showing river confluence

Water was typically sampled between 8-11am and the samples were kept in the dark and at *in situ* temperature prior to returning to the lab. Surface river and estuarine samples were obtained by lowering an acid-washed and rinsed stainless steel bucket from a bridge or pontoon with a rope. Typically the bucket was rinsed with sample water three times before the sample was taken.

Triplicate samples for OVOC analysis (methanol, acetone and acetaldehyde) were collected by immersing opaque glass bottles (volume of 330 ml) in the bucket and letting them slowly fill without bubbling. The bottles were filled to overflow and secured with gas-tight stoppers to eliminate headspace. Samples from station L4 were obtained using a niskin bottle fitted with Tygon tubing (as described in Beale 2011). All water samples for OVOCs were analysed on the day of sample collection. The time between collection and analysis was typically 2-4 hours. During winter simultaneous measurements of temperature, salinity, dissolved oxygen (optical sensor), total dissolved solids and pH were made *in situ* using a YSI ProDSS 4-port multi-probe (www.YSI.com/ProDSS). For riverine samples (zero salinity) the optical dissolved oxygen and pH probes were also exchanged for nitrate and ammonium sensors. The multi-probe was calibrated using pH standards of 7 and 10, a redox standard of 250 mV, and NO3 and NH4 standards of 1 and 100 ppm respectively. All the standards were obtained from Xylem analytics UK. (http://www.xylemanalytics.co.uk/index, accessed 20/10/17). For samples at L4, nitrate and ammonia were completed using standardised methods for the Western Channel Observatory, specifically copper/cadmium reduction column for nitrates (Brewer and Riley 1965) and indophenol blue for ammonia (Mantoura and Woodward 1983). For more detail, see https://westernchannelobservatory.org.uk/documents/pml-wco_nutrient_protocols.pdf . The salinity data taken was used to define site type between rivers (0 PSU), estuaries (0-33 PSU) and marine (>33 PSU).

Methanol, acetaldehyde and acetone water concentrations were quantified using a membrane inlet (MI) proton transfer reaction mass spectrometer (PTR-MS, Ionicon, Austria), as discussed in section 2.3.

Analysis for CDOM was undertaken using a spectrophotometric method (VWR UV- 3100-PC spectrophotometer, Penn. USA) and a quartz cuvette as outlined in (Kitidis et al. 2006; Helms et al. 2008). As detailed in section 2.5.1, sub-samples (100 mls) taken from the stainless steel bucket were filtered using a glass syringe and in-line filter (Whatman puradisc FP30 0.45 µm pore size) into a glass bottle. The quartz cuvette was rinsed with Milli-Q water in triplicate, followed by the sample in duplicate, either poured in or directly filtered into the cuvette. The spectrophotometer was set to scan from wavelengths of 800nm to 200nm. This data was exported and analysed using single exponential model (Kitidis et al. 2006) to calculate $\alpha 300$ and $\alpha 350$, indications of CDOM absorbance at 300 and 350nm. These wavelengths were selected as standard wavelengths for reporting photochemistry in natural waters representing the daily UV dose typically used for calculating CDOM e.g. (De Bruyn et al. 2011). Analysis was completed within 4 hours of sampling, to ensure sample stability. Helms SR, was also calculated (winter only), which gives an indication

of the source of the CDOM i.e. a lower SR indicating a more marine source, with higher SR in freshwater, suggesting terrestrially derived CDOM (Helms et al. 2008).

Table 3.1. Summary of sampling sites, dates and primary runoff. Total n=56. nd=not determined

Name	Classification	Number	Dominant runoff influence		Date(s) sampled	Salinity (psu) (respectively to date)	*In-situ* Temperature (°C) (respectively to date)
Lowley Bridge	river	Tamar	1	Arable	6/2/17, 1/7/16	0, nd	6.8, nd
River Inny	river	Tamar	2	Arable	6/2/17, 1/7/16	0, nd	7.1, nd
Lynher	river	Tamar	3	Arable	8/2/17, 7/7/16	0, nd	7.4, nd
Horsebridge	river	Tamar	4	Arable	6/2/17, 1/7/16	0, nd	6.1, nd
Gunnislake	river	Tamar	5	Arable	8/2/17, 14/2/17, 21/3/17	0, 0, 0	6.4, 7.1, 9.3
Halton Quay	estuary	Tamar	6	Arable	6/2/17, 20/3/17	1.0, 10.8	6.8, 10.7
Cargreen	estuary	Tamar	7	Arable	8/2/17, 20/3/17, 26,7,16	6.2, 22.5, nd	7.4, 10.8, nd
Tamar 6	estuary	Tamar	8	Arable	26,7,16	nd	nd
Devils Point	estuary	Tamar	9	Arable	6/3/17, 26,7,16	27.0, nd	9.0, nd
Breakwater	marine	coastal	10	-	6/3/17, 26,7,16	33.4, nd	Nd, nd
L4	marine	coastal	11	-	16/1/17, 6/3/17, 12/7/16	35.0, 35.1, 35.1, [(a)]	10.6, 9.7, 14.6 [(a)]
Horrabridge Walkham	river	Walkham	12	Moor	30/1/17, 7/7/16	0, nd	8.3, nd
Shaugh Bridge	river	Meavy	13	Moor	18/1/17, 20/7/16	0, nd	7., nd
Shaugh Bridge	river	Plym	14	Moor	30/1/17, 20/7/16	0, nd	8.1, nd
Marsh Mills	estuary	Plym	15	Moor	13/3/17, 22/6/16	0, nd	6.0, nd
Oreston	estuary	Plym	16	Moor	13/3/17	22.0	6.0
Cornwood	river	Yealm	17	Moor	18/1/17, 20/7/16	0, nd	7., nd
Puslinch Bridge	river	Yealm	18	Arable	1/3/17, 8/3/17	0, 0	8.0, 8.8
Yealm Pontoon	marine	Yealm	19	Arable	1/3/17, 8/3/17, 30/6/16	34.3, 16.6, nd	9.7, 9.5, nd
Postbridge	river	East Dart	20	Moor	30/1/17, 7/7/16	0, nd	6.9, nd
Two Bridges	river	West Dart	21	Moor	30/1/17, 7/7/16	0, nd	6.9, nd
Dart	river	Dart	22	Moor	14/2/17, 6/3/17, 21/3/17	0, 0, 0	7.3, 6.6, 8.5
Harford Bridge	river	Erme	23	Moor	18/1/17, 20/7/16	0, nd	6.8, nd
Erme	river	Erme	24	Moor	27/2/17, 29/6/16	0, nd	Nd, nd
Mothecombe	estuary	Erme	25	Arable	27/2/17	32.5	nd

Multivariate analysis was completed using Primer-7 (Clarke and Gorley 2015a) software. Data was pre-treated as follows. First, data was imported into Primer, after which data were treated in accordance to analysis. No overall transformation took place, as the data was determined not to require this as most datasets remained within a small number of orders of magnitude. For analysis that requires full datasets, such as Principal component analysis (PCA) data were run through the "missing" function, for where data was unavailable, which inserts values using a expectation-maximisation algorithm. Where a dependant variable had more than 4 missing values, the variable was discarded instead.

Of the two forms of multivariate analysis primarily used in this paper- PCA and non-Metric Dimensional Scaling (nMDS), PCA required the data to be normalised using the normalise function, which fits all data to a Gaussian bell curve with mean of 0 and standard deviation of 1. This allows statistical analysis such that analysis would not favour one variable over another (Clarke and Warwick 1994) This allowed different variables in a dataset to be analysed with comparable, dimensionless scales. It is noted that this is considered the preferred choice for environmental data analysis with multivariate statistics, as such to allow a common scale (Clarke and Warwick 1994) . For the PCA analysis (Figure 3.5) separate analyses were run for each OVOC, to distinguish differences between available correlations and principal components. PCA analysis results is provided in decimal proportion of the total observed variance by that particular principal component (Clarke and Warwick 1994). The PCA routine was used to identify the driving variables for differences between samples and to visually examine the data for any grouping (Figures 3.4 and 3.5).

The other technique, nMDS requires a resemblance matrix between sites. For this technique, the data was not normalised, as this could affect the final analysis. Where VOCs were not detected, the result was considered to be a concentration of 0. The resemblance selected was Euclidean distance, recommended for environmental variables such as those in this paper (Clarke and Warwick 1994). The nMDS analysis routine was run, and a type 1 SIMPROF test (permuting variables) was used to identify potential correlations and groupings within the data. This process involved randomising the labels on the variables (permuting them) to identify if patterns remained when the category structure presented was removed. This statistic was selected to identify if samples such as season, runoff type or salinity could be significantly statistically separated.

For BEST (BIO-ENV) analysis, the same resemblance matrices were analysed with Spearman rank correlation to identify which variables explain resemblances seen. This was completed through a full search of between 1 to 5 variables, where 5 variables were available, as they were measured in summer and winter- the three VOCs, rainfall and air temprature. These were often used in conjunction with an Analysis of Similarities (ANOSIM) test, which permuted the variable or property for analysis within all samples, to distinguish the likelihood of any correlation being statistically significant (Clarke and Warwick 1994). Again, this test allowed identification of any groupings by application of random permutations to ascertain if any pattern could be attributed to chance.

3.3 Results

3.3.1 Environmental variables

Air temperature ranged between 8-13 ˚C (winter) and 13-20˚C (summer) during the study. *In-situ* water temperatures during winter ranged between 6-11˚C. Winter pH measurements suggested that rivers were the most acidic (5.5-8.3, n=20), followed by estuaries (7.2-8.0, n=9) and marine waters (7.9-8.0, n=3). Nitrate (NO3) and ammonia (NH4+) concentrations were measured during winter in rivers and ranged between 0.15-5.8 mg L^{-1} and 0.03-1.7 mg L^{-1} respectively. Wintertime dissolved oxygen varied between 10-12 mg L^{-1}, 8.6-12mg L^{-1}, and 8.4-8.9 mg L^{-1} for the riverine, estuarine and marine waters respectively. The absorption coefficient for CDOM at 300 nM (α300 m^{-1}) ranged from 2.9-52 m^{-1} in riverine waters, 2.6-20.0 m^{-1} in estuarine waters and 0.9-4.6 m^{-1} in marine waters. The highest α300 (up to 52 m^{-1}) was found in rivers draining the peatlands of Dartmoor (notably at stations 21 and 14, Figure 3.1). This contrasts sharply to the marine waters of the Yealm pontoon (station 19, Figure 3.2) which demonstrated the lowest α300 of 0.95 in winter . Intermediate values of CDOM ranging between 2.6-20 were found in estuarine waters. The Helms SR, calculated as described in section 2.5.1 showed values between 0.59-0.91 (n=16), 0.68-1.8 (n=9) and 1.0-1.9 (n=3) for river, estuary and marine stations respectively. These are shown in full in Table 3.2

3.3.2 OVOC distributions

Methanol concentrations across all waters ranged from <27-65nM and 27-152 nM for summer and winter respectively. The highest methanol concentrations were determined in surface waters during winter at the marine station L4 and at 2 locations in the Tamar (estuarine station 6 and

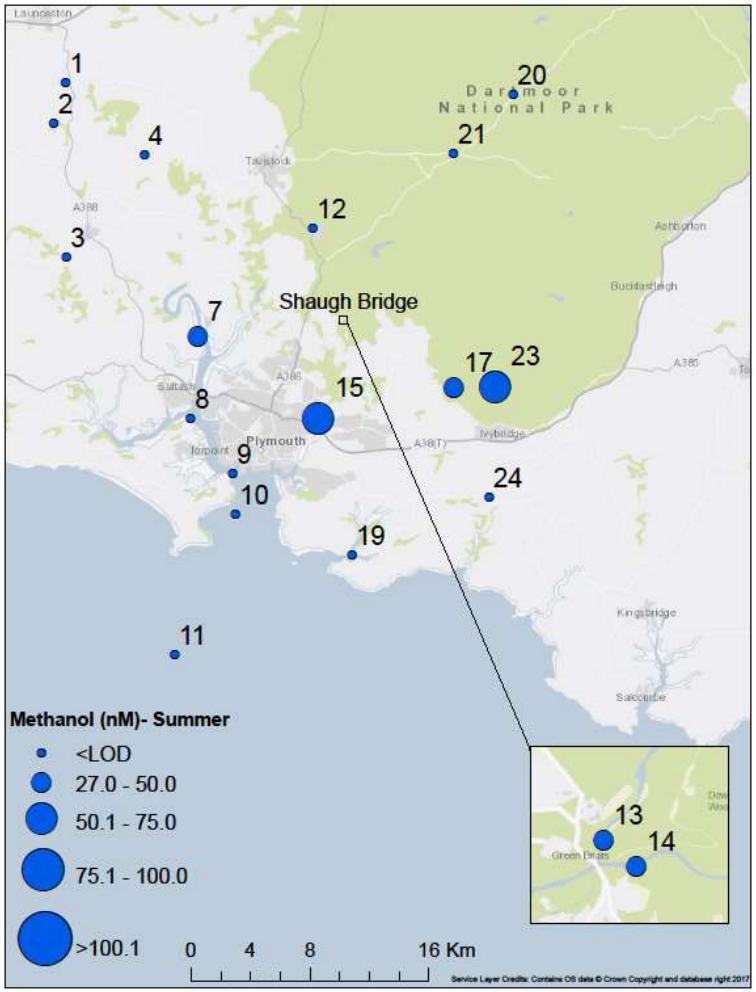
river station 4, see Table 1 and Figure 3.2a & b). A cluster of higher methanol concentrations (46 ± 13 nM, n=5) were evident around the south of Dartmoor in summer (stations 13-15, 17 and 23, Figure 3.2a). Methanol has a relatively high limit of detection compared to the carbonyl compounds which resulted in 68-75% of the samples being below the LOD (27nM). The average concentration of methanol during the summer was 44.7 ±12.3nM (n=6) which was significantly lower than the winter mean of 81.2 ± 40.8nM (n=9) when a student's t-test was applied at the 95% confidence level (n=15, $t=2.5$ $p<0.05$).

Table 3.2, Data summary table for VOCs and auxiliary measurements in both seasons for the study, where nd= not determined. n=56

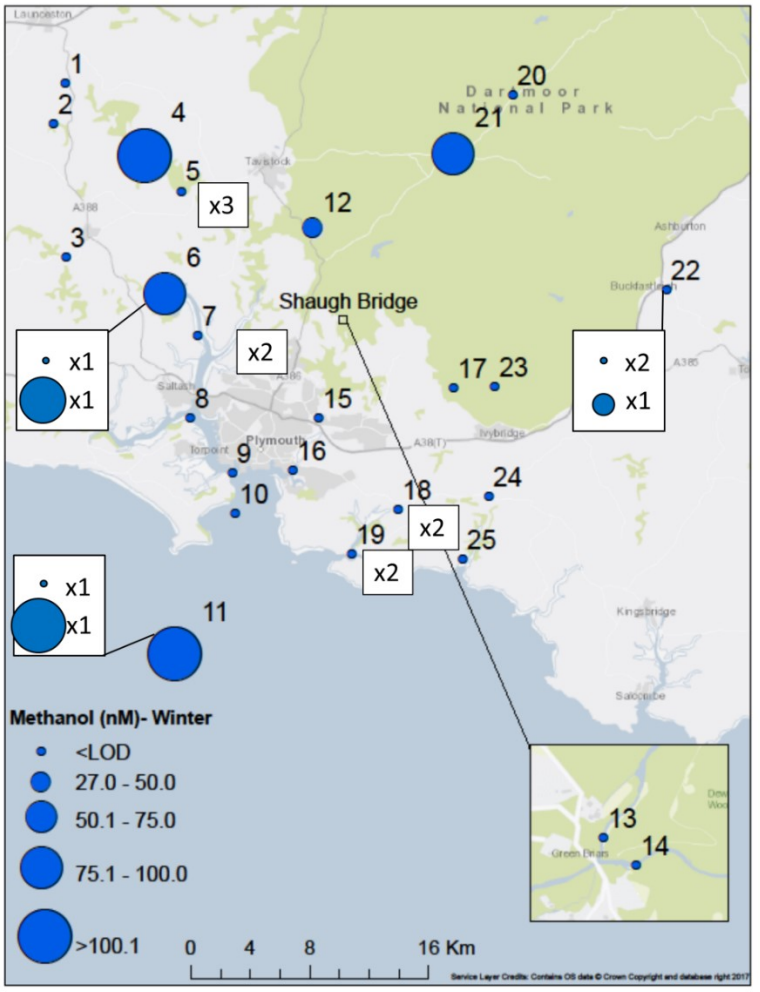
Measurement	River	Estuary	Marine
Salinity			
Summer	nd	nd	nd
Winter	0	0-32	33-35
Water temp (˚C)			
Summer	nd	nd	nd
Winter	6.1-9.3	6.0-11	9.7*
Air Temp (˚C)			
Summer	13-20	13-17	13-15
Winter	8-13	9.0-12	9.0-11
pH			
Summer	nd	nd	nd
Winter	5.5-8.3	7.2-8.0	7.9-8.0
Optical dissolved Oxygen (mg L^{-1})			
Summer			
Winter	nd	nd	nd
	10-12	8.6-12	8.4-8.9
NH_4 (mg L^{-1})			
Summer	nd	nd	nd
Winter	0.03-1.7	nd	48-63
NO_3 (mg L^{-1})			
Summer	nd	nd	nd
Winter	0.15-5.8	nd	59-61
CDOM 300 (nm^{-1})			
Summer	4.9-46	2.6-20	0.95-4.6
Winter	2.9-52	9.2-19	1.3
CDOM 350 (nm^{-1})			
Summer	nd	nd	nd
Winter	1.4-27	0.8-9.8	0.53-3.3
Helms SR (slope ratio)			
Summer	nd	nd	nd
Winter	0.59-0.91	0.68-1.8	1.0-1.9
Rainfall[a] (mm)			
Summer	2.0-17	6.0-54	6.0
Winter	16-71	5.0-70	16-60
Methanol (nM)			
Summer	<27-52	<27-65	<27
Winter	<27-120	<27-90	<27-152
Acetone (nM)			
Summer	0.3-14	3.0-13	2.1-2.8
Winter	0.8-8.7	1.1-7.7	0.5-5.8
Acetaldehyde (nM)			
Summer	6.0-28	7.9-22	4.7-7.4
Winter	2.0-14	4.0-16	1.7-7.3

Figure 3.2. a/b) Summer/winter methanol concentrations, c/d) Summer/winter acetone concentrations, e/f) Summer/winter acetaldehyde concentrations

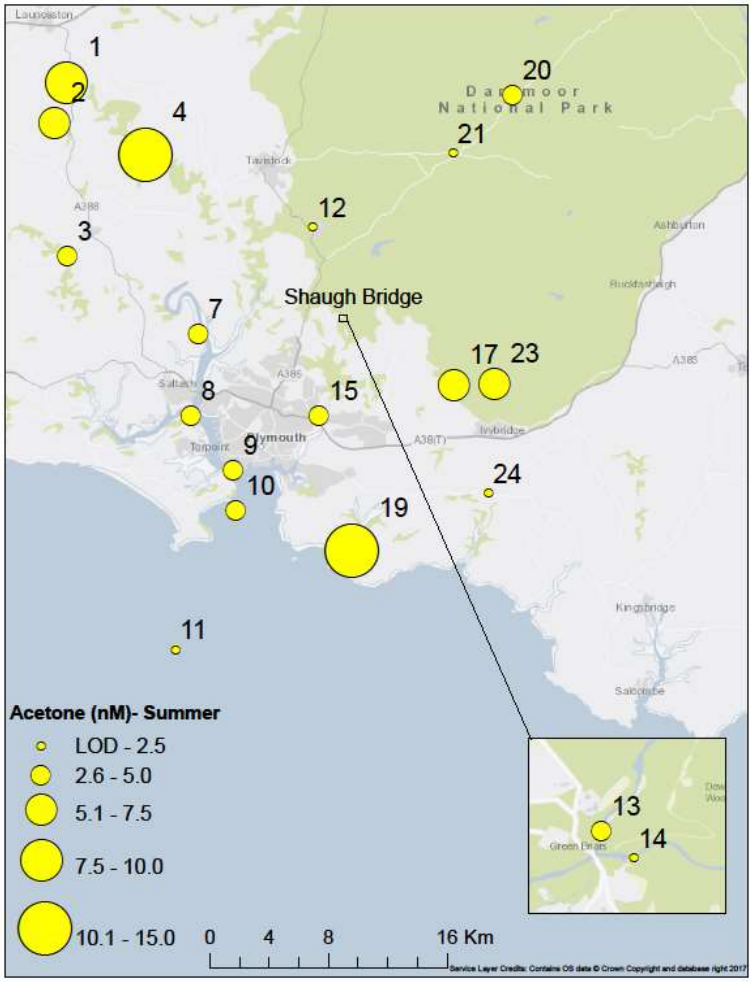
(a) Summer methanol concentrations (22.6.16-26.7.16)



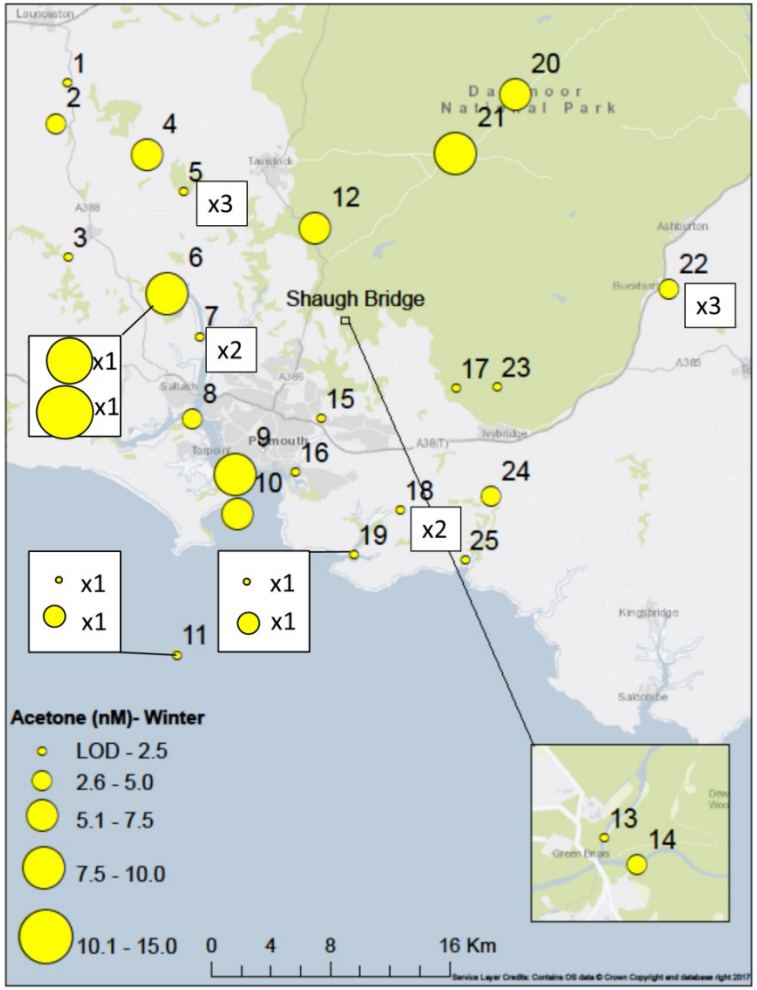
(b) Winter methanol concentrations (18.1.17-21.3.17)



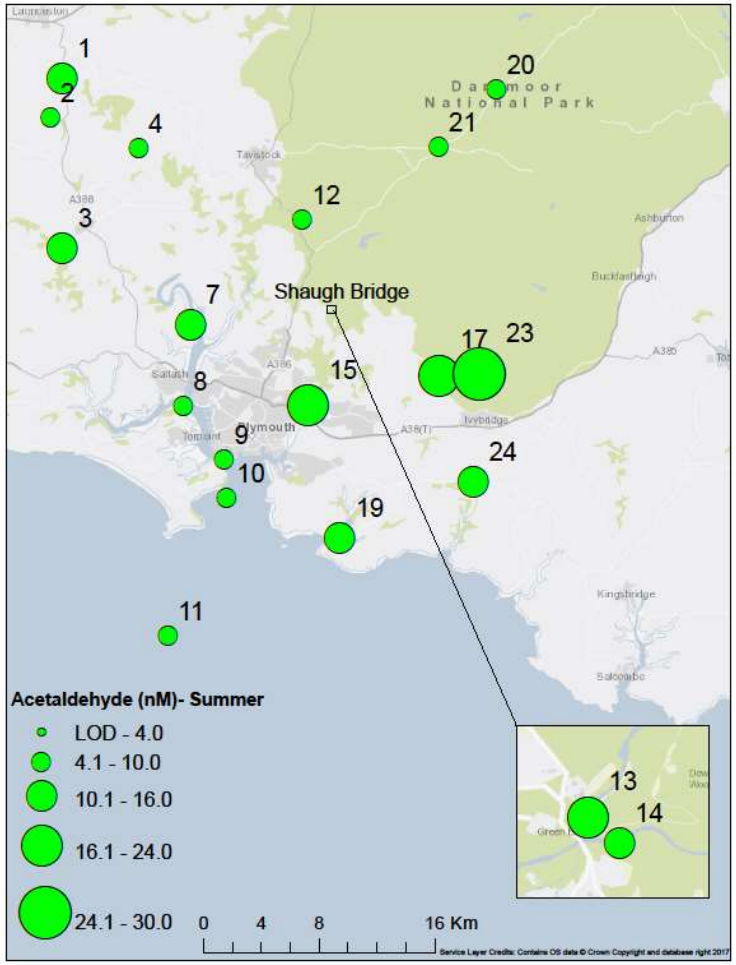
(c) Summer acetone concentrations (22.6.16-26.7.16)



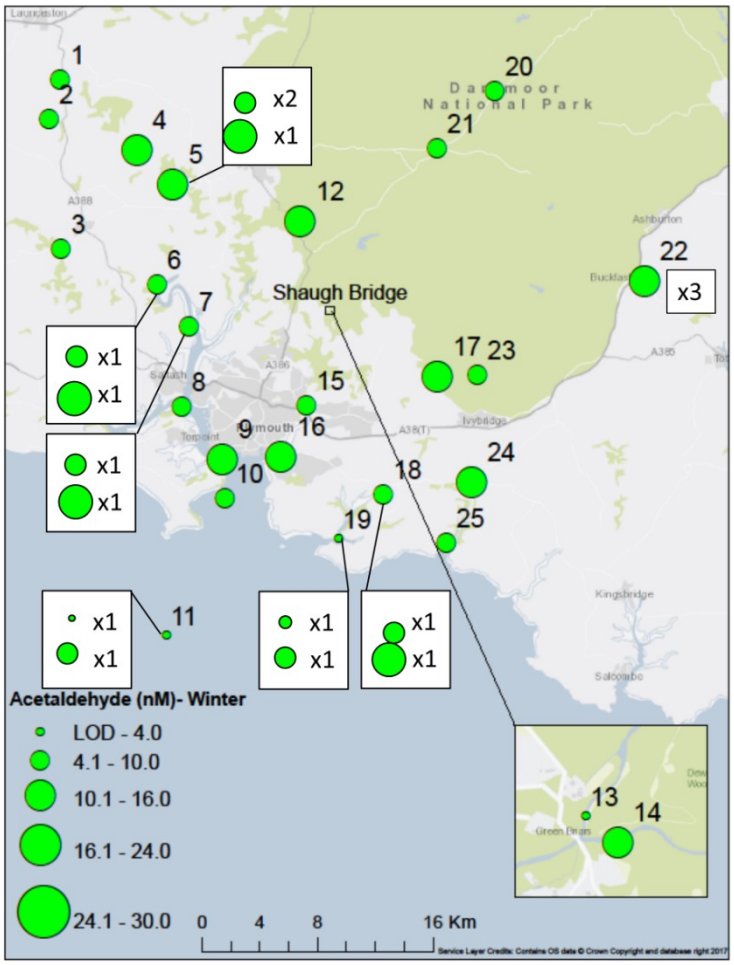
(d) Winter acetone concentrations (18.1.17-21.3.17)



(e) Summer acetaldehyde concentrations (22.6.16-26.7.16)



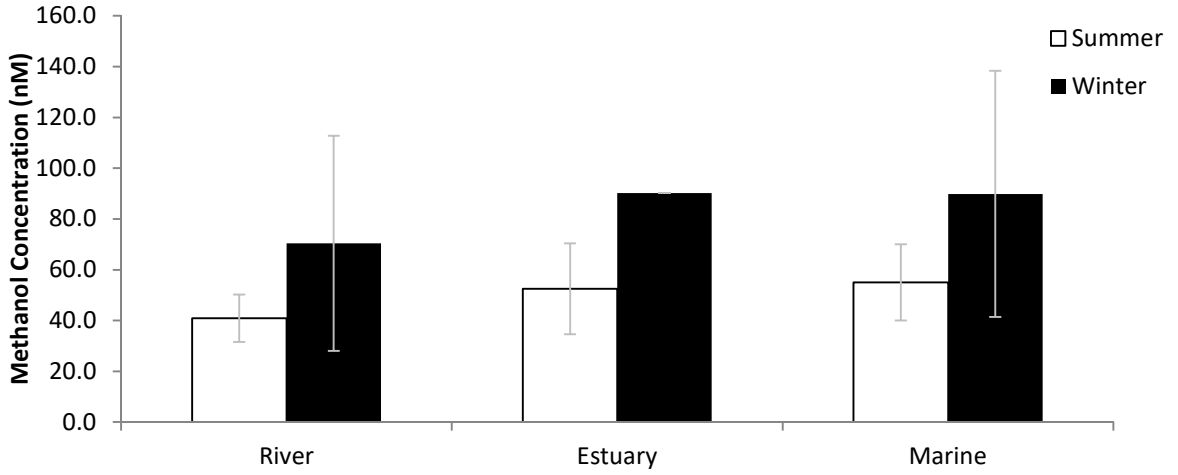
(f) Winter acetaldehyde concentrations (18.1.17-21.3.17)



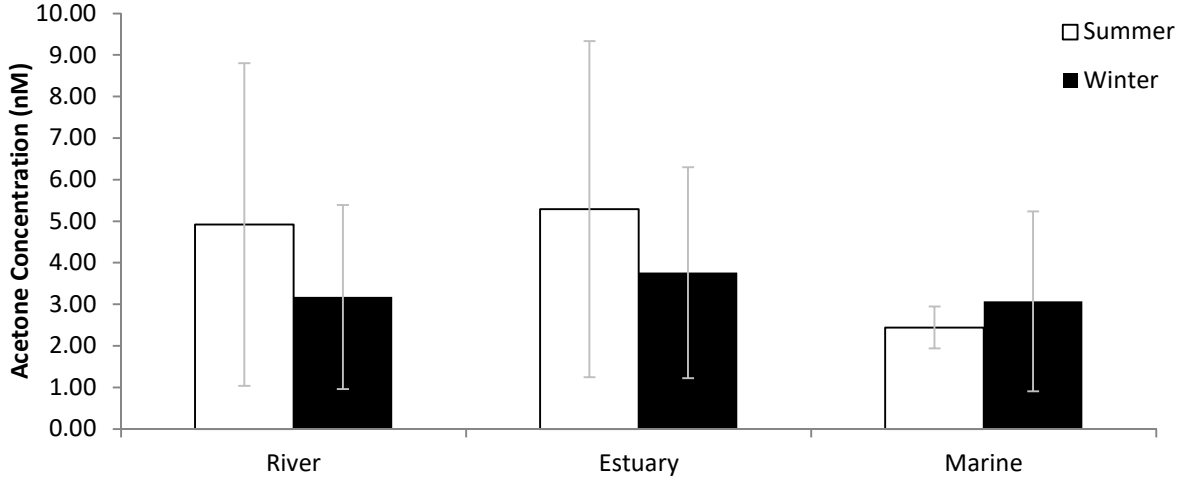
Acetone concentrations in summer ranged between 0.3-14 nM, whilst winter concentrations were 0.5-8.7 nM. The average concentration of acetone during the summer was 4.8 ± 3.7 nM (n=19) which was not significantly higher than the winter mean of 3.3 ± 2.2nM (n=29) when a student's t-test was applied at the 95% confidence level (n=48, t=2 $p>0.05$). Generally, for summer, the average concentration of acetone was higher in rivers and estuaries compared to marine environments (Figure. 3.3) and this is shown in the summer river and estuary mean of 5.3±4.0 and 4.9± 3.9nM respectively, in comparison to the marine mean at 2.4±0.5nM. Some of the highest average acetone concentrations (8.7 ± 4.0 nM, n=4) were found during the summer in the upper reaches of the River Tamar (sites 1-4 on Figure 3.2c). All sites over the non-tidal upper section of the Tamar River and its associated tributaries had higher than average measured levels of acetone (average of 4.76±3.7 nM in summer, and 6.6±2.3 nM in winter), an area primarily identified as draining agricultural land. Lower concentrations were found on Dartmoor (3.9 ±1.9 n=6) and further down the Tamar Estuary (3.4 ± 0.47 n=3, sites 7-9). In comparison, winter concentrations showed the highest concentrations in the Tamar Estuary (6.0±2.3nM, n=5 for sites 6, 7, 9 and 10, Figure 3.2d) and across Dartmoor (6.6±1. 9nM, n=3 for stations 12, 20 and 21 on Figure 3.2d).

Acetaldehyde concentrations in summer ranged between 4.7-28 nM and were generally lower during winter ranging below the LOD (0.7nM) to 16 nM. The average acetaldehyde concentrations were significantly higher during summer (12.5 ± 6.34nM) compared to winter (8.5 ± 3.8nM, where n=53, t=2.5 $p<0.05$, Figure. 3.2e+f). In summer the highest concentrations were determined in the run-off river water from Dartmoor (20±5.4 nM, n=6 for stations 13-15, 17, 23 and 24). During the winter some Tamar river water stations (9.0±3.6nM, n=3, stations 4-5) showed some of the higher concentrations compared to the average during this season. Acetaldehyde concentrations in rivers (10.4 ± 5.3nM, n=32) and estuaries (11.3 ± 4.7nM, n=14)) sampled were statistically higher than those samples from the coastal station (4.8 ± 2.2nM, n=7, where n=35,21, t=2.8, 3.4, $p<0.01$ for rivers and estuaries respectively).

a) Methanol*



b) Acetone



c) Acetaldehyde

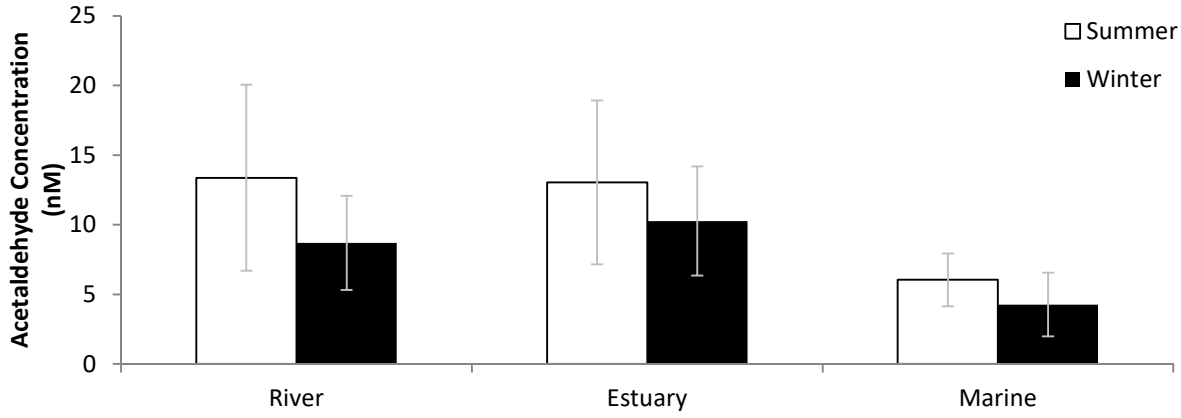


Figure 3.3. Seasonal averages for (a) methanol, (b) acetone and (c) acetaldehyde. Error bars represent the standard deviation calculated for each season, compound and site combination. n=56, error bars represent one standard deviation.

3.4 Discussion

3.4.1 Methanol

Methanol concentrations found in this study were found to be broadly in line with those reported by Beale et al (2015) for near-shore marine waters (16-78nM). Overall, the concentrations of methanol found in this study were lower in riverine and estuarine systems compared to near shore regions such as L4. This relationship is found in both this work and previous studies in the same near-shore coastal environments (Beale et al. 2015) which either suggests that riverine and estuarine systems are not significant sources of methanol, or that consumption/loss processes in freshwater and brackish systems are more than production rates. In oceans, methanol has a significant loss to microbial utilisation, either oxidation or uptake for growth (Dixon et al. 2013b), although in the near-shore coastal environment, less than 1% of total methanol was assimilated into cell carbon. Highest rates of methanol dissimilation have previously been noted in February in near-shore site L4 (Sargeant et al. 2016), suggesting the very low (<LOD) concentrations at marine and estuarine sites in this work could also be due to a significant microbial sink, like those seen in Sargeant et al (2016).

Methanol was found to be significantly lower in the summer sampling period when constrained to the estuarine and riverine systems, with elevated levels shown in winter ($n=11$, $t=1.7$, $p=0.0507$), see Figure 3.3a. The suspected primary sources of terrestrial derived methanol, plant growth and biomass decay (Millet et al. 2008) could both have a strong seasonality as well, potentially causing an influence on these concentrations. Furthermore, any uptake or consumption process is likely to be seasonally linked, with marine study indicating winter months having a higher methanol dissimilation rate. This significant biological sink, or significantly decreased production may be the reasoning behind the very low concentrations, below the LOD, seen in both summer and winter in marine and terrestrial sites. Furthermore, any terrestrial source may not be as significant as any marine source, such as phytoplankton (Heikes 2002; Mincer and Aicher 2016) of types not seen in estuarine or riverine waters. The higher concentration shown in Figure 3.2a/b showed no correlation between any other factor, suggesting unknown point sources or as yet unknown pathways may be responsible for methanol hotspots. Beale et al (2015) made measurements at the coastal site L4 over an annual cycle. While the results from the current study showed a higher maxima (152nM) than the annual study presented in Beale of 16-78nM (Beale et al. 2015), the reason for this is unclear, with the site L4 subject to a wide range of localised and regional impacts such as boreal and warm temperate species fishing and riverine nutrient input (Smyth et al. 2010).

Methanol concentrations showed no statistical difference at the 95% confidence level between the marine, estuaries and rivers' data for either season for a student's T test (n=1, 3, 8 p>0.1) or the use of similarity analysis (ANOSIM) (Clarke and Warwick 1994). Methanol concentrations in coastal waters have been noted as having significant inter-annual variability (Beale et al. 2015), which has also been seen in Atlantic transects, (Beale et al. 2013; Yang et al. 2014). Considering that the riverine and estuarine results in this study are lower and more variable than the measurements from coastal stations, suggesting over a typical watercourse, rivers and estuaries have little effect on coastal waters and are unlikely to be a source of methanol to coastal waters in this region. While inter-annual variation has been noted at station L4 (Beale et al. 2015) the causes of this are yet to be evidenced, however, methanol is biologically produced by some specific groups of phytoplankton (Halsey et al. 2017). The abundance of these groups is known to be heavily controlled by seasonal variability like that experienced at this temporal site, a relationship already noted at this site for nutrients (Rees et al. 2009) and DMS (Archer et al. 2009). PCA analysis (Figures 3.4, 3.5) shows a divide on the plot of PC1 and PC2, but no statistically significant clustering using a SIMPROF test, indicating of the sites and variables available for both seasons.

3.4.2 Acetone

Acetone concentrations detected in marine systems in this study were similar to those seen in an annual study in the same marine site (L4) of 2-10nM (Beale et al. 2015) and typically in the lower range of concentrations seen in open ocean in the Atlantic 2-36nM, (Beale et al. 2013; Yang et al. 2014) or Pacific 2-28nM, (Marandino et al. 2005). However, there are scant measurements in riverine and estuarine areas, the range of 53-1400nM found in Polish rivers being the exception (Dabrowska and Nawrocki 2013).

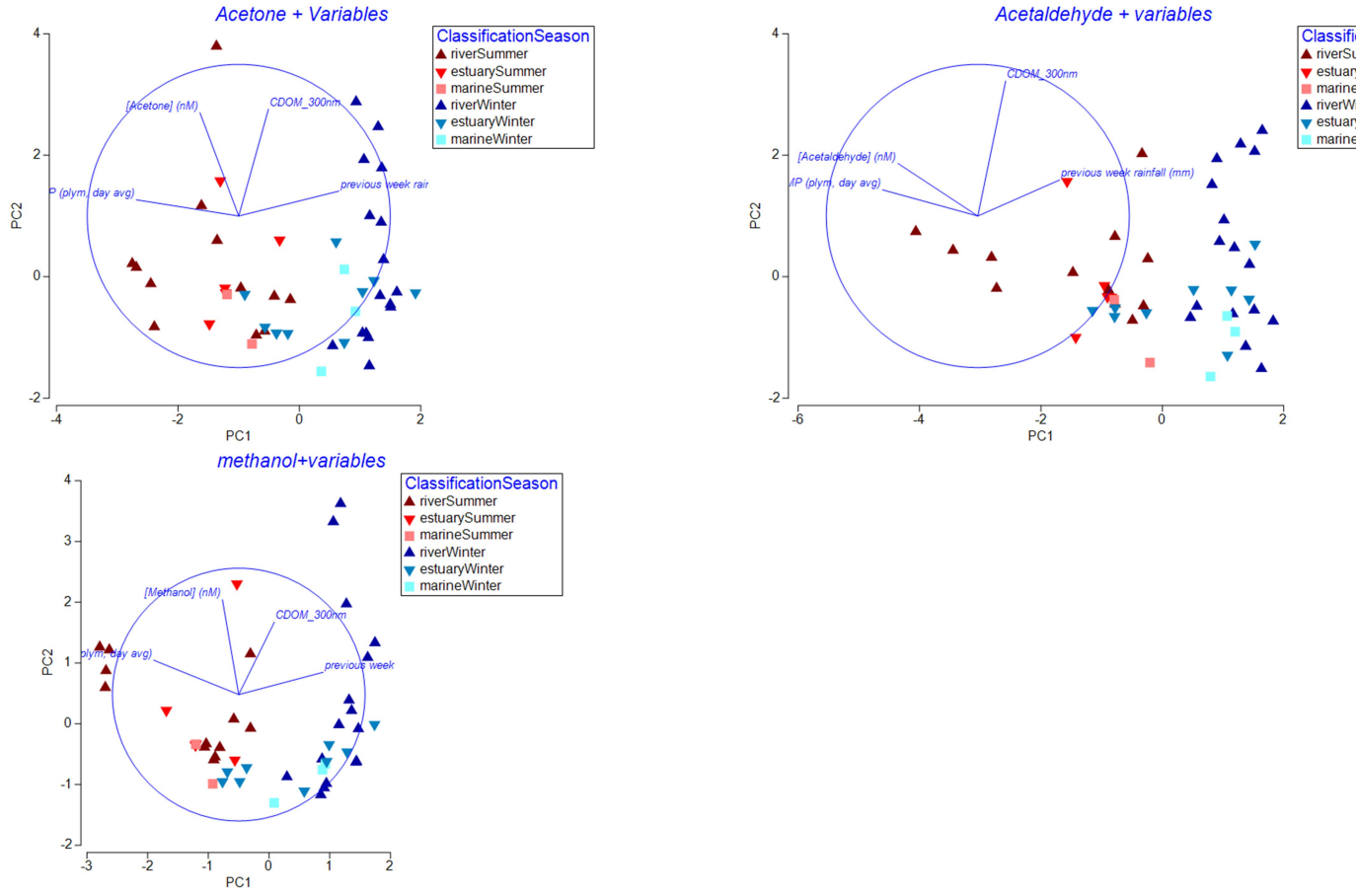


Figure 3.4. Principal component analysis with each OVOC, rainfall, air temperature and CDOM. These variables were selected as they were the only common variables in both seasons. Rainfall was a total over the 5 days prior to sampling, and air temperature was from on the day of sampling. A full breakdown of each principal component can be found in Table 3.3, below.

One of acetone's production pathways, from photochemical degradation of CDOM, (de Bruyn et al. 2011) was expected to control a high proportion of the acetone detected in riverine and estuarine water, as this had previously been observed in coastal waters (de Bruyn et al. 2011). This was indeed what was observed for acetone, as in both summer and winter, the highest concentrations of acetone were measured in those samples originating from estuaries and rivers, as shown in Figure. 3.3. This is notable, as UV would be much lower in winter than summer. However this relationship is not statistically significant in a student's t test ($n=18,28$ $p>0.05$). Furthermore, the reactions behind this are as yet uncertain, with no correlation using an ANOSIM seen between CDOM and acetone and CDOM levels not statistically elevated in riverine and estuarine waters. Estuarine and riverine measurements were also higher in summer than winter, though this was not statistically significant in either rivers ($n=28$, $t=1.5$, $p>0.05$) or estuaries ($n=14$) with a student's t test. Longer days coupled with stronger light intensity in summer could have caused increased photochemical production of acetone than in winter, particularly for sites with high levels of CDOM runoff from peat moor. While CDOM photodegradation is thought to be a

major source of acetone (Keiber et al. 1990; de Bruyn et al. 2011) and with levels of CDOM enhanced by moorland, there could be a potential sink to balance out increased acetone loss and washout in rainier areas in Dartmoor in comparison to downstream in the catchment (Meyles et al. 2003). Therefore, it is possible any seasonal increase in production could be negated via this run-off, or by an unknown increased loss process (de Bruyn et al. 2013) explaining the lack of correlation between CDOM and acetone.

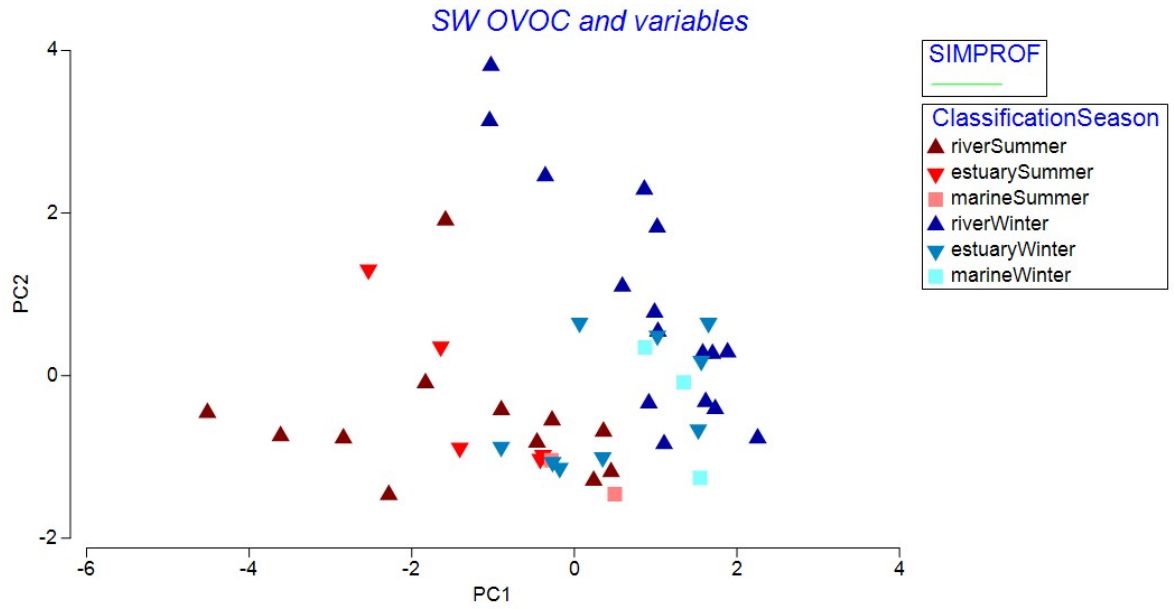


Figure 3.5. Principal component analysis of all south west UK data, showing riverine and estuarine sites to have a greater seasonality than marine.

On application of a ANOVA/ANOSIM, acetone concentrations in sites primarily comprised of peatland runoff were significantly higher than sites from a primarily agricultural runoff, suggesting a potential source or precursor available in these areas, such as CDOM other dissolved carbon. However, no statistical correlation was seen for CDOM, so there is potential for another, as yet unknown precursor, or some production mechanism unlinked with the analysed variables.

The PCA analysis (Figure 3.4) showed acetone was not closely linked with any other variable measured. One alternate potential source for acetone in terrestrial environments is biological production: while already observed in marine environments in *Vibro* species (Nemecek-Marshall et al. 1995), which were obtained from estuarine sites, suggesting this production process could impact the estuarine mixing zone, or estuaries that contain abundant Vibro populations (Nemecek-Marshall et al. 1999). A riverine influence for coastal systems for acetone production has been suggested via dissolved organic matter (Dixon et al. 2014), and this data shows that terrestrial waters not only provide additional dissolved organic matter, but also increased levels of

acetone compared to the shelf sea ecosystem. PCA analysis on acetone across both seasons showed no significant clustering using a SIMPROF (similarity profile) test, suggesting the variables measured were not sufficient to distinguish between the different sites with clear definition. As discussed above with methanol, the influence of rainfall could be interpreted from revisiting the Halton Quay site (site 6). However, again, the other revisited site, Cargreen, experienced virtually identical acetone concentrations over differing precipitation levels- 2.2nM at 56mm and 1.9nM after 5mm rain. Therefore, any precipitation effect would have to be examined separately, with further measurements.

3.4.3 Acetaldehyde

Acetaldehyde's concentrations detected in this study were broadly within the range reported in previous studies in riverine systems, with previous measurements in the River Ohta in Japan ranging between 2-12nM (Takeda et al. 2006), but up to 2160nM in the Rivers Bogdanka and Warta in Poland (Dabrowska and Nawrocki 2013). In near-shore marine waters, however, concentrations measured were similar in this work and previous study at the same site of 4-37nM (Beale et al. 2015).

Like acetone, despite the suspected link with CDOM concentration and carbonyl species (de Bruyn et al. 2011), no correlation was seen between CDOM and acetaldehyde using a student's t test across all sites. Despite previous research suggesting linked CDOM and acetaldehyde concentrations (de Bruyn et al. 2017), this relationship was not detected in this work. However, there exists a possibility that an unknown factor, precursor or anthropogenic source is additionally responsible for the elevated riverine and estuarine concentrations. Some previous research has suggested acetaldehyde production was not linked with biota (Nuccio et al. 1995) while other has noted a significant production from phytoplankton (Nightingale 1991; Read et al. 2012; Dixon et al. 2013a). Considering previous work is largely marine-based, potential other sources such as acetaldehyde photoproduction from the OH/O2 reaction (de Bruyn et al. 2011) could be significantly enhanced in riverine and estuarine systems, due to their potential greater water surface area to volume ratio and relative shallowness, allowing a greater amount of light to interact with dissolved matter.

pH measurements of estuarine waters also showed positive correlation with acetaldehyde concentration, with estuarine acetaldehyde levels significantly higher ($n=9$, $p<0.05$) at sites with a higher than average pH. Comparison of marine data to previous work suggests that acetaldehyde concentrations were similar to those previously reported at the same site (average acetaldehyde at L4 of 13±7 nM, Beale et al. 2015). Their work suggested that near-shore coastal acetaldehyde

production may be reliant on terrestrially sourced CDOM, therefore, it would be reasonable to estimate this increase in production to be true for riverine and estuarine systems. Figure 3.4, a PCA analysis of each compound separately, shows that of the three OVOCs studied, acetaldehyde is the only one closely linked with another variable- the air temperature, as a proxy for the localised environmental factors. This correlation could be incidental, or days with greater sunlight and therefore UV radiation would be likely to have a warmer air temperature. However, further investigation into this would be required, due to the lack of correlation between CDOM and acetaldehyde.

Table 3.3, PCA analysis and breakdown, along with cumulative variariance for Figure 3.4

	Acetone PC1	Acetone PC2
Acetone [nM]	-0.256	0.682
Rainfall, previous 5 days (mm)	0.662	0.164
Air Temperature (°C)	-0.677	0.107
CDOM 300 (m^{-1})	0.196	0.705
Total % variance	42.6	75.6
	Acetaldehyde PC1	Acetaldehyde PC2
Acetaldehyde [nM]	-0.528	0.347
Rainfall, previous 5 days (mm)	0.540	0.238
Air Temperature (°C)	-0.629	0.173
CDOM 300 (m^{-1})	0.184	0.891
Total % variance	51.4	77.3
	Methanol PC1	Methanol PC2
Methanol [nM]	-0.129	-0.752
Rainfall, previous 5 days (mm)	0.670	-0.177
Air Temperature (°C)	-0.674	0.273
CDOM 300 (m^{-1})	0.282	-0.574
Total % variance	41.9	73.4

3.4.4 CDOM and other variables

CDOM is thought to be a precursor for some OVOCs, particularly carbonyl compounds, (Mopper and Stahovec 1986), but displayed no correlation with any OVOC concentration, by measure of CDOM 300 or CDOM 350 after use of an ANOSIM test. However, as shown above in Table 3.3, when VOCs were individually analysed in a PCA, CDOM appeared to have more of an influence as a PCA reports values in % variance explained, rather than ANOSIM, which provides an R value. Helms SR, which is an indicator of CDOM molecular weight (Helms et al. 2008) with lower values more indicative of terrestrial CDOM, was also calculated for the samples. This relationship

between Helms SR and CDOM source was shown in this dataset, with the average Helms SR for marine samples at 1.55, estuarine average at 0.94, and riverine average at 0.75. A noticeable correlation in marine waters for acetone and acetaldehyde, suggesting increased Helms SR could lead to increased OVOC levels was seen, however, further study would be needed to confirm this due to the lack of marine datapoints for this work. However, no correlation was seen between CDOM and OVOCs for riverine and estuarine samples on a student's T test ($P>0.05$ in all cases).

Riverine and estuarine systems as contributors to shelf sea nutrients are widely reported (Bauer et al. 2013), with rivers typically containing elevated levels of dissolved oxygen, dissolved and undissolved solids, salts, minerals and a range of other nutrients compared to marine environments (Khatri and Tyagi 2015). Furthermore, anthropogenic impacts, such as eutrophication, increased soil erosion from agriculture and nutrients artificially added as fertiliser (Moss 2008) have a much greater impact on rivers than marine sites. Due to the higher expected CDOM values in rivers and estuaries (de Bruyn et al. 2011) and because *in situ* photochemical degradation of CDOM is a source of carbonyl species, we expected higher acetone and acetaldehyde levels than those reported in marine waters. Beale et al. (2015) suggest that a terrestrial influence could be causing increased CDOM or OVOC observations in an annual study at a coastal site. The results presented here, showing typically increased carbonyl OVOCs in riverine and estuarine areas, are in line with these earlier studies in the local areas for both marine systems and hypotheses for estuarine and riverine. Since CDOM is primarily involved in photodegradation reactions, shallow rivers will have a much higher proportion of water available for these reactions compared to any coastal region, with significant attenuation of light found in the first 10cm of highly humic waters (De Haan 1993). Therefore, in a river the majority of the depth is available for photochemistry, in deeper waters such as larger estuaries and marine sites, this becomes proportionately less. This could be the cause of the increased concentration of the carbonyl compounds seen in rivers and estuaries, compared to marine waters, as shown in Figure 3.2 a-f. Other variables measured such as total dissolved solids and oxidative reductive potential showed no statistical correlation with OVOCs on a student's T test ($n=13$, $R^2=0.08$) or a Pearsons rank correlation ($P>0.1$ for all other matchups) in riverine, estuarine or marine waters.

Riverine and estuarine concentrations of CDOM were on average higher than marine, however, this was not statistically significant in either summer ($n=19$, $t=0.93$, $p>0.05$) or winter ($n=28$, $t=0.17$, $p>0.05$) on a students' t test. This suggests that based on these results, terrestrial inputs could have an influence on coastal waters in this environment, however, it would not be explained through CDOM alone, either direct input of VOCs or some other precursor could have an effect.

Increased levels of acetone found in summer are potentially the result of photochemical production from CDOM, which is also thought to be a major source of acetaldehyde (de Bruyn et al. 2011; Halsey et al. 2017). CDOM is a major component of DOC (dissolved organic carbon), which has previously been shown to have a strong seasonal cycle, with highest levels around peatland released in summer (Clark et al. 2005). This seasonal CDOM increase could provide a photochemical source of acetaldehyde in summer months, in areas with strong peatland run off- supported here by the observation of elevated levels at Shaugh Bridge and in upstream waters of the Rivers Yealm and Erme (sites 13, 14, 17 and 23). In comparison, there was no significant difference between peatland and agricultural land types, in either exclusively river ($n=23$, $t=-1.07$, $p>0.1$) or riverine and estuarine stations ($n=42$, $t=1.04$, $p>0.1$) on a student's t test. This suggests any dissolved carbon increase from moorland may not be necessarily CDOM, or that agricultural land has an equivalent riverine carbon source for the days this data was collected.

The studied area, in southwest England, has a wide range of land usage, allowing comparative work to take place. The urban centre of the City of Plymouth has industry lining both the Tamar and Plym, with upstream Tamar primarily draining farmland and upstream Plym mainly peatland, specifically Dartmoor. Between the three land uses there was no overall significant difference, however, as shown in Figure 2a-f, for all three of the compounds, high points existed with each of these systems, suggesting a point source could be responsible for any of these sites. In comparison to previous studies of these compounds in marine systems, the relatively pristine mid-Atlantic (Beale et al. 2013), or the predominantly marine-influenced station L4 (Beale et al. 2015) the opportunity for anthropogenic influence, or run-off from any kind of arable or even natural environment run-off is as of yet unknown.

One further note is the influence of rainfall higher in the catchment. Previous study has noted an elevated concentration of VOCs found in rainfall (Dabrowska and Nawrocki 2013) and increased rainfall would lead to increased runoff, potentially washing dissolved carbon out of land, or causing a concentration effect of what dissolved carbon does run off (Balla et al. 2014). Concentrations determined at station 6 (Halton Quay) were not consistent between sampling dates, potentially due to differing rainfall- the higher methanol and acetone were seen when the preceding week saw 70mm rainfall, which could indicate a washing out effect. In comparison higher acetaldehyde was seen in the other analysis date, after a week of only 5mm precipitation seen in Plymouth, suggesting potentially a set amount of acetaldehyde may be released, with higher flow due to runoff having a dilution effect. The two visits to Halton Quay were also at opposing tidal states- with the salinity ≈1 on the first, wetter visit, and >10 on the second, drier visit. Therefore, it is unclear if the increased methanol and acetone were a result of the increased riverine influence. Like Halton Quay, the Cargreen site was visited at a low and high tide state. In

Cargreen the high tide visit had similar methanol and acetone concentrations, but higher acetaldehyde (12nM compared to 4nM). Neither of these effects was visible in other sites revisited in the same season, with no other revisited site above the LOD for methanol.

No correlation was found between nitrate (NO_3-) or ammonia (NH_4+) and OVOC concentrations in riverine samples, the only locations these nutrients were analysed. Dissolved oxygen had a significant positive correlation with acetone in riverine waters, ($n=14$, $p<0.05$) between sites with higher than average dissolved oxygen compared to sites with lower than average using a student's T test, however for the overall data without this grouping, no correlation was seen on a pearson's rank correlation ($p>0.1$). This again fits with the hypothesis that an oxygen-dependant reaction is involved in acetone production, previously suggested to be linked with leucine catabolisim (Nemecek-Marshall et al. 1999) or photochemical production pathways (de Bruyn et al. 2011). Further research, both mechanistic and lab-based would be required to identify if this relationship stays firm throughout all environs, as previous study has suggested dissolved oxygen is not linked to rates of either photoproduction or photobleaching of CDOM (Keiber et al. 1990). In comparison, a major sink for acetaldehyde is emission to the atmosphere (Mopper and Stahovec 1986) leading to the main atmospheric sink, reaction with OH ions (Millet et al. 2010). This could suggest oxygen may be correlated equally with acetaldehyde photoproduction and photodegradation, meaning any effect is net neutral. Considering no statistical correlation was found between CDOM and volatile compounds, it is possible this effect may be more impactful in environments with higher variation of dissolved carbon.

3.4.5 Combined analysis

ANOSIM (analysis of similarities), of the data exclusively for VOCs identified a significant difference seasonally ($R=0.111$, 2.8%), with methanol higher in winter but the carbonyl compounds higher in summer. Furthermore, it was possible to distinguish land usage in winter ($R= 0.606$, 0.1% significance) indicating, at least in this season, OVOC release from, or production in riverine and estuarine systems is linked with some by-product, runoff or other factor, as yet unknown. BEST (Bio-Env Stepwise method) analysis was used to identify the most indicative cause of the relationship and of the variables measured, CDOM was the closest, however, this was not a strong correlation at 0.128.

As shown in Figure 3.5, the PCA plot comparing season and water type indicates the most significant difference between seasons was observed at the riverine level, with greater seasonal variation seen between riverine sites than estuarine, and again between estuarine and marine. This suggests volatile compound concentration and reactions have a much greater variation

between seasons in riverine and estuarine systems, compared to the marine systems previously studied in greater detail. However, as shown by Figure 3.5, there is no distinct grouping or clumping of the sites, suggesting while different factors influence PC1 and PC2, these also vary between sites and illustrating there is no sudden change to VOC reactions in saline waters- rather, it is a gradual change moving down the watercourse. Further analysis would be needed to identify any other factors driving this correlation.

For the full range of auxiliary data, see Table 3.1.

3.4.6 Study limitations

While this study's novelty hinged upon the simultaneous measurement of multiple OVOCs with a seasonal comparison, there is still room for improvement upon methodology, sampling strategy and breadth. If this study was to be repeated or added to, it would be recommended to consider the following. Firstly, sampling strategy was focussed on sites decided in advance of this study, and primarily comprised locations upstream and a single estuarine site for a number of the rivers, such as the Yealm (site 19) and the Erme (site 25). To focus more on the estuarine processes, a similar methodology to that used in the Tamar, where samples were taken approx. every 5 points in the salinity gradient. This would create some interesting data and provide further evidence to determine if VOCs in estuarine systems have a conservative or non-conservative relationship. Furthermore, the samples were taken over the course of multiple months, as instrumental availability was a limitation. With this aside, higher intensity sampling could have allowed further analysis, such as individual rainfall events. Finally, if the sites described in this study had been sampled throughout the year, rather than summer and winter snapshots, it could have allowed a much closer tracking and unpicking of seasonal influence.

3.5 Conclusions/summary

This seasonal study represents the first assessment of OVOCs in both riverine and estuarine waters and their seasonal variability, presenting data from 25 marine, estuarine and riverine sites in the southwest UK.

Methanol concentrations were found in highest concentrations in marine sites, with riverine and estuarine typically lower. This is likely linked to decreased methanol sources, such as the lack of phytoplankton, a biological source of methanol, in terrestrial waters, with potentially similar magnitude of loss processes in both systems. Methanol was significantly higher in winter than summer, however a large proportion of measurements made in both seasons were below the

limit of detection, primarily terrestrial sites. This implies that fresh water inputs are unlikely to be a source of methanol to Station L4 and the surrounding coastal region at the times of sampling.

In comparison, the carbonyl compounds acetone and acetaldehyde were detected at higher concentrations in fresh and estuarine waters. Both were higher in summer than winter, as predicted, which was likely due to increased photodegradation of CDOM, a production pathway for carbonyl compounds. Acetone had a correlation with dissolved oxygen in fresh water, fitting in with the production pathway requirement of oxygen for biological, or in the form of OH ions for photochemical sources. There was no correlation between land types and acetone concentrations, in either rivers or estuaries.

Acetaldehyde concentration was not found to correlate with dissolved oxygen although both riverine and estuarine water had significantly more acetaldehyde than marine stations, However, no correlation was seen with CDOM, a known acetaldehyde precursor, although the CDOM photoproduction pathway could be a likely source of acetaldehyde and explain the increase in summer months, due to increased daylight hours. Again, no correlation was seen between land use in either rivers or estuaries, indicating peat moor and agricultural lands likely emit similar levels of OVOCs, CDOM, or other precursors.

It is clear from this work that rivers and estuaries have a strong influence on carbonyl OVOC concentrations in coastal waters. However, the influence on coastal methanol was less, with concentrations lower than marine stations. The influence of highly humic areas, such as the moors, was noted, and further work in areas such as these may provide greater insight into the importance and impact of run-off from these areas.

Chapter 4 VOC measurements in the Halladale Catchment

4.1 Introduction and aims

As discussed in chapter 3 the observed difference between land type and runoff source was most notable when differentiating between moorland and grassland runoff. However, in all cases, as the rivers sampled neared the shore, they inevitable become more urban, or more agricultural, not allowing for investigation into exclusively peatland run-off, particularly in estuarine waters. Furthermore, while Dartmoor has a high volume of stored carbon (Fyfe et al. 2014), a system with less confounding factors, ideally in a more remote location, could provide a more pristine environment, to increase understanding of VOC concentration and cycling. One such pristine site is the Halladale catchment, which has previously been used as an example system for research in carbon cycling (Hope et al. 1997; Worrall et al. 2003; Rathgeb et al. 2017) and therefore, was ideal for this study, to compare to the data collected for chapter 3.

LOCATE (Land Ocean CArbon TransfEr) is a project that aims, among other objectives, to "quantify the fate of terrigeneous organic matter from soils to the ocean, with particular focus on estuaries and coastal waters" (National Oceanography Centre 2020). Part of this project involved an intensive fieldwork campaign in a number of locations in the UK, in particular, locations selected for their relevance to carbon cycling- for example peatland. This chapter examines some of the work carried out in and around the River Halladale, in northern Scotland (see Figure. 4.1), a small river catchment of approximately 205 km^2 characterised by a high proportion of peatlands, mixed with forested and agricultural land.

The LOCATE program's overarching objectives to quantify and model organic matter, while out of the scope of this work, opened the opportunity to work alongside a number of other researchers, with common goals in mind. This intensive approach allowed increased auxiliary sampling data (see Table 4.2) and opportunity for collaboration in sampling and analysis.

The Halladale itself is well known for providing the run-off for an area of peat and highly organic soils, with the Halladale reported as the highest recorded carbon export in the UK at 103.4 kgC $ha^{-1}yr^{-1}$ (Worrall et al. 2003). Examining the catchment in greater detail, Figure 4.2 shows the land types around the catchment, as ascertained by the Land Cover map (Rowland C.S.;Morton 2017). Broadly, both heather grassland (Pink in Figure 4.2) and Bog (Brown) are considered high peat areas, and come under the same land type (class 6) identifier in CEH aggregate classes

(Jackson 2000). These high peat areas, which make up the majority of the land around the catchment, are known to cause a highly humic run-off, leading to the Halladale catchment often being used as an example site for a peat-based study (Hope et al. 1997; Worrall et al. 2003; Rathgeb et al. 2017).

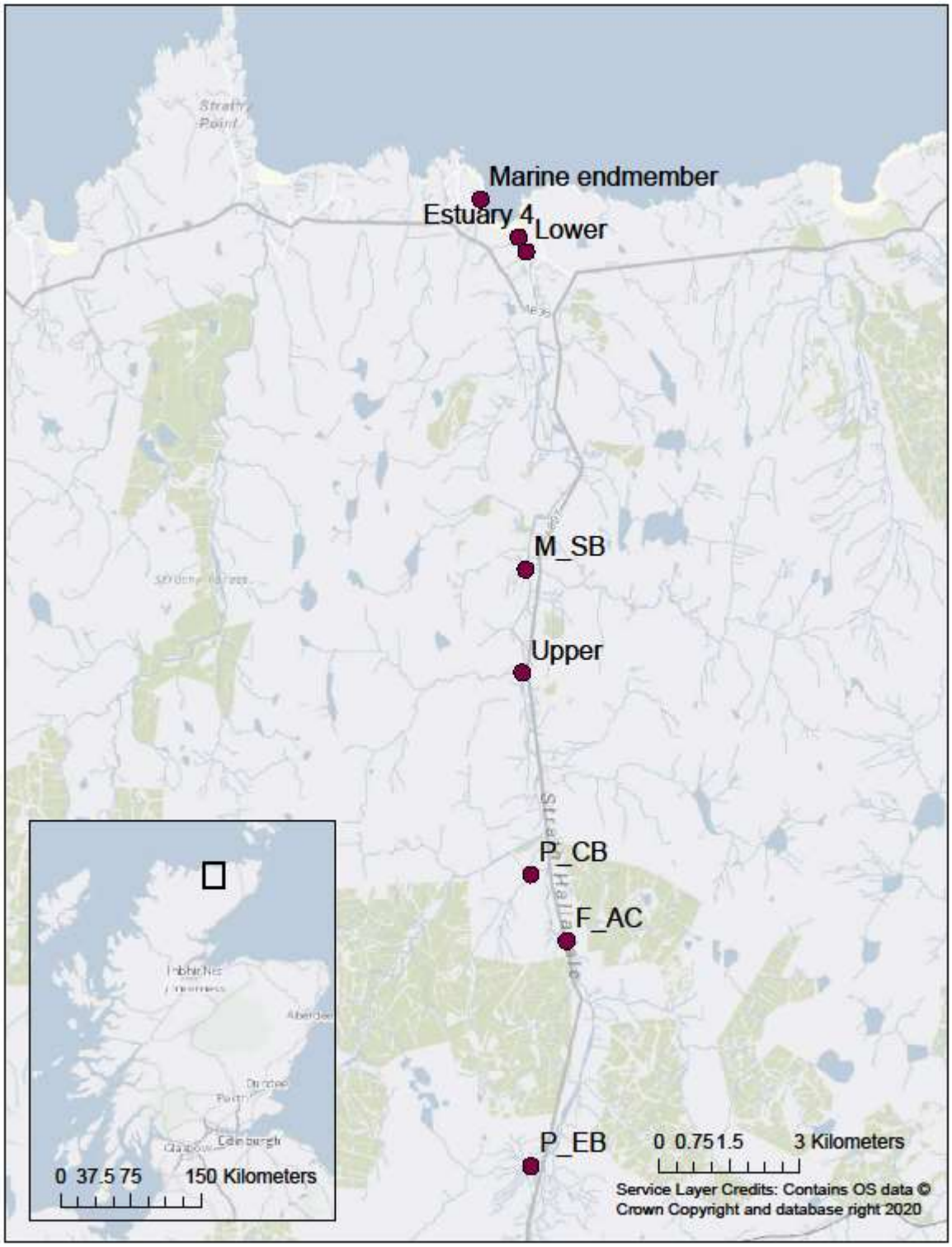


Figure 4.1, Map of Halladale catchment, including sampling sites examined in this report. Inset: location of Halladale catchment in regards to Scotland

As discussed in chapters 2 and 3, the PTR-MS OVOC study methodology (Beale et al. 2011) has been used for open ocean and a seasonal coastal study, however generally, there is a paucity of VOC data in marine systems. Furthermore, there are even fewer studies in rivers and estuaries of OVOCs, despite previous work indicating a potential linkage between terrestrial input via riverine and estuarine systems (Beale et al. 2015). A conclusion from Chapter 3, above, was that to investigate humic areas for VOC content was a natural next step to fill in this gap in the carbon cycle.

In rivers and estuaries, what little OVOC data is available is limited in scope and typically analyses only one or two compounds. Previous studies have suggested terrestrial sources of either the compounds themselves or chromophoric dissolved organic matter (CDOM), a known precursor (Keiber et al. 1990; de Bruyn et al. 2011; Dabrowska and Nawrocki 2013; Takeda et al. 2014; Beale et al. 2015) for a range of these compounds. One major source of this CDOM has been noted as highly humic run-off, including that found in peatlands (Yates et al. 2016), the subject of this work. One further advantage of analysing CDOM is that the source of the CDOM can be calculated using Helms S_r (Helms et al. 2008), a calculation which suggests a difference between the absorption curves of sea and freshwater CDOM, as discussed above in 2.5.1 and 3.4.4.

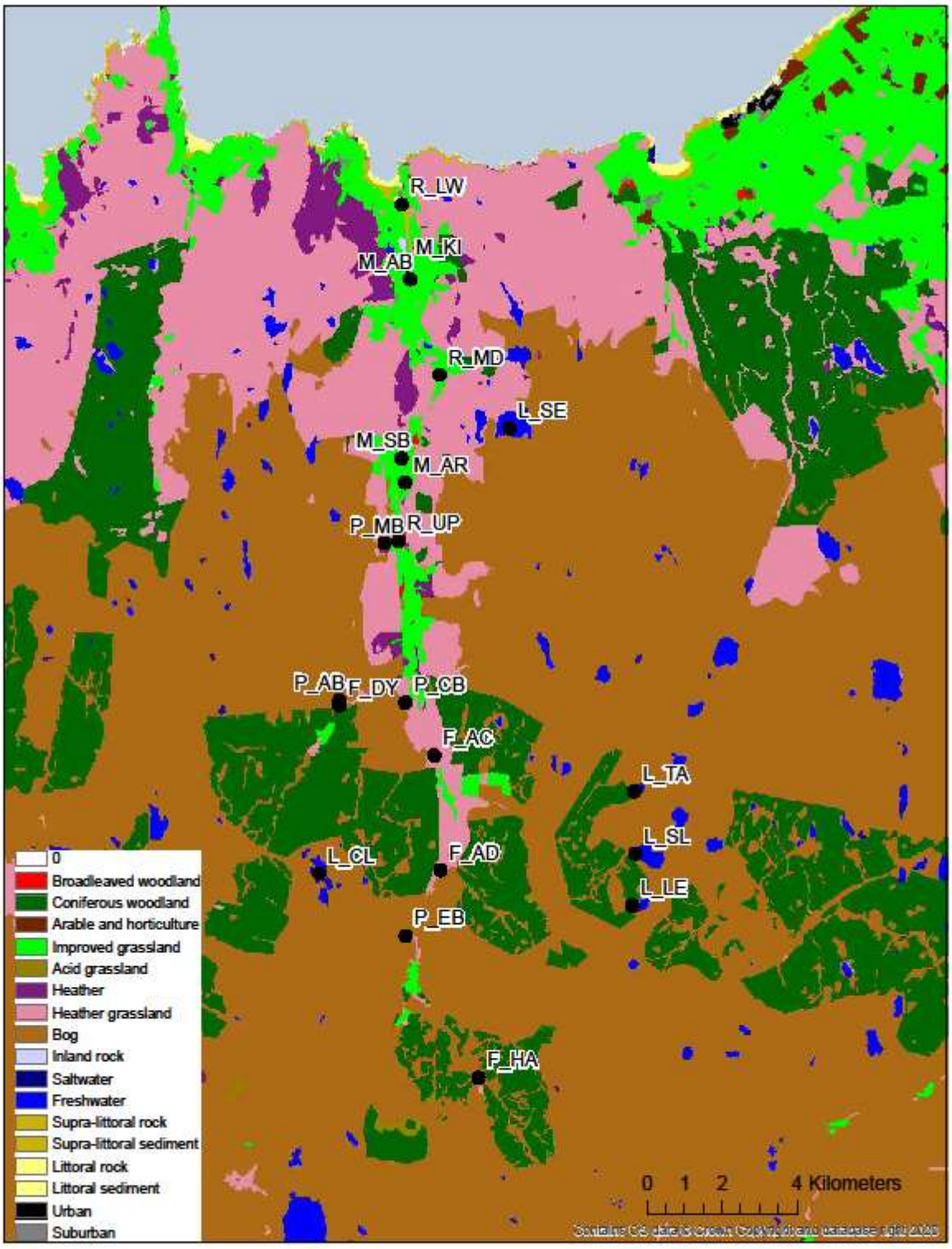


Figure 4.2, Halladale catchment and all LOCATE sample sites for the area. Land use determined by the land cover map, 2017 edition (Rowland C.S.;Morton 2017).

In comparison to chapter 3, the scope was increased to cover isoprene, as the most abundant non-methane hydrocarbon in the atmosphere (Guenther et al. 2006; Exton et al. 2012). Isoprene is known to be predominantly produced from terrestrial plant growth, with some production in marine systems from phytoplankton and macroalgae (Alvarez et al. 2009; Exton et al. 2012; Dani et al. 2017). However, again, a paucity of study in the riverine and estuarine environments means it is unknown how terrestrial influence affects marine concentrations, with suggestions for further study on coastal systems and estuarine environments largely unheeded (Exton et al. 2012). Therefore, this work aims to identify concentrations of four volatile organic compounds, methanol, acetone, acetaldehyde and isoprene, as well as investigate some of the driving factors for these concentrations in a highly peat-based ecosystem, the Halladale system in northern Scotland. A system such as the Halladale is likely to have a runoff with high levels of humic substances, which have previously been pointed toward as a source for VOCs, via UV induced photodegradation (Keiber et al. 1990), although questions remain if this would be significant in riverine and estuarine systems, which this work aims to find out.

4.1.1 Hypotheses

The Halladale LOCATE fieldwork provided an excellent opportunity to both examine the MIMS isoprene method in the field, and also to make some of the first measurements of VOCs in a highly humic environment. These objectives can be split into the following hypotheses

- The MIMS with gastight inlet is a suitable method for determination of isoprene in natural waters at environmentally relevant levels. This is examined in detail in chapter 2
- Due to highly humic runoff, samples from the Halladale catchment will contain higher concentrations of VOCs than those from coastal waters
- Isoprene will have a similar distribution to one or more VOCs, as production mechanisms and precursors are thought to be similar.

4.2 Methods

4.2.1 Study site

The study site selected for this was the Halladale catchment, as discussed above. Sites were selected within the catchment using the following logic: firstly, sites ‘upper’, ‘lower’ ‘estuary 4’ and ‘Marine’ were selected to provide a viable cross-section, from higher in the catchment, to a marine endmember. This was to determine marine influence of the Halladale upon the shelf sea offshore of Melvich, a small village around 23km west of Thurso, in the Highlands, encompassing

a full catchment survey, to assess gradients in VOC concentration. Other sites were selected for unique qualities in their surrounding land mass- as discussed in Table 4.1, a site was selected for each of the following: Peat bog, Restored bog, Forest and Mixed farmland. This allowed a clear comparison between site types, and allowed some sites to be revisited on multiple occasions (see Table 4.1). Some images from the sampling process can be seen in Appendix D.

4.2.2 Sampling

Samples were taken from the Halladale river catchment in July 2018, including marine, estuarine and freshwater sites (Figure 4.1). At the time of sampling, the region experienced an extended period of low rainfall, with some of the hottest months on record for this area of Scotland. This drought condition allowed study of the influence of run-off and deep groundwater on volatile organic compounds, as well as a comparison to the Tamar system, from data collected in winter 2015 and summer 2016. Simultaneously, as part of the LOCATE sampling programme, a suite of biochemical parameters were measured in the Halladale and associated catchment.

Two separate samples were taken at each site. One was used for analysis of OVOCs by membrane inlet proton transfer reaction mass spectrometry (MI-PTR-MS) using the method by Beale (2011). This was collected in an airtight, lighttight black 330ml bottle, from a stainless steel acid washed bucket. A second sample was collected for Isoprene analysis via membrane inlet mass spectrometry (MIMS) in a 500ml gastight bottle from the same bucket and kept in the dark. Both samples were kept at ambient temperatures until analysis, which was typically completed within 4 hours of sampling. This analysis was completed by Dr Rachael Beale alongside myself.

The MI-PTR-MS method used is described in Beale (2011), as described in section 2.3. Isoprene was analysed in parallel with both PTR-MS and MIMS, to ascertain the suitability of either method for quantification at environmentally relevant concentrations. The method via PTR-MS was physically unchanged for the method used for OVOCs, with the only addition of analysis of molar masses 41 and 69, for the carbenium ion, a common fragment of isoprene, and the protonated Isoprene molecule, respectively.

The method used for isoprene via MIMS is a modification of a method by Tortell et al (Tortell 2005), with the modifications discussed in section 2.4, above.

Auxiliary data including salinity, conductivity, pH, CDOM and nutrients was collected alongside the VOC samples on both sample days and carried out using the methods as discussed in Appendix C, and was accessible thanks to the LOCATE analysis team, as listed in the acknowledgments. Chromophoric Dissolved Organic Matter (CDOM) was detected by a Cary 60 UV/Visible

spectrophometer, using method from Kitidis (2006), as discussed in section 2.5, and this was analysed by Dr Vas Kitidis (PML). The spectrophotometer was set to scan from 800nm to 200nm, and the data analysed with a single exponential model (Kitidis et al. 2006) and slope ratio was calculated using the method of Helms (2008), as well as the ratio, which allows an approximation of the relative molecular mass of the corresponding CDOM. The full raw data obtained is shown in appendix E

Table 4.1, Halladale catchment Site data, codes and days sampled, including runoff influence where samples were not considered riverine.

Site code	Site name	Sample replicates	Day(s) visited	Principal runoff
MEM	Marine Endmember	3	10/7/18, 17/7/18	N/A
E-4	Estuary	3	10/7/18, 17/7/18	-
R_LW (Lower)	Lower Halladale	3	10/7/18, 17/7/18	-
R_UP (Upper)	Upper Halladale	3/2	10/7/18, 17/7/18	-
M_SB	Smigel Burn	1	17/7/18	Mixed farmland
P_CB	Craggie Burn	1	17/7/18	Restored peat bog
F_AC	Allt na Criche	1	17/7/18	Forest
P_EB	Ewe Burn	1	17/7/18	Peat bog

4.3 Results

4.3.1 Environmental factors

At the time of the surveys in July 2018 the Halladale catchment was under very dry conditions, with no recorded rain for the month of July. River levels were much lower than typical for the

season, with an average flow rate for July 2018 as 0.25 m^3s^{-1}, compared to a July average from 2008-2017 of 1.8 m^3s^{-1}. Furthermore, within the preceding decade this was the lowest recorded July average river level (Centre for Ecology and Hydrology (CEH) 2019). Previously, rainfall has been shown to be high in volatile compounds (Felix et al. 2014; Kieber et al. 2014), however it is unknown how much of this would enter the watercourse, and, as a result, be detected. In comparison, it is possible that a lower than expected rainfall could lead to increased concentrations of VOCs, if no change of VOC volume is released, due to their highly soluble nature, high flow is not required to wash out these compounds- if a set amount is produced via predictable mechanisms like photoproduction or plant release, low flow would only concentrate the release.

Two catchment studies were carried out, as shown in Table 4.1, with a week separating them. In the first study, all sites were visited, while on the second, only the marine, estuary, 'lower' and 'upper' sites were visited. Full data from both these catchment studies can be found in appendix E.

4.3.2 VOC distribution

The range of concentrations observed for Methanol found in the Halladale catchment was between the limit of detection (<2nM) of the method to 50nM, with a mean of 20.8nM across both days sampled (see Table 4.2). The highest methanol concentration was measured at site 'upper', at 50.39nM, however, upon revisit, this site was below the limit of detection. The lowest detected point was in the marine endmember, at 6.75nM. Again, upon revisit one week later, this was below the limit of detection. While no gradient was noticed within the overall catchment study, it is perhaps of note that Ewe Burn (P_EB) had a higher than average concentration of methanol at 34.8 nM. This is a site with runoff from unrestored bog- in comparison, the restored bog site, (P_CB) had a much lower concentration of methanol- 19.5nM. Typically, any site with a marine influence exhibited a low methanol concentration, potential seawater influence, measured on the first sampling visit at 6.75nM, could have a diluting affect upon the higher concentrations observed upstream.

Acetone was measured at between 3.5 and 76nM. The vast majority of these measurements was in the range 3-6nM, with the exception of site 'upper'. On first visit, 76nM acetone was measured, however, upon revisiting the site a week later, this was not seen again. The mean across all sites was 10±20nM including this measurement, however, if it the 'upper' datapoint is removed as anomalous, this drops to a mean of 4.6±0.72nM. This can be seen in Figure 4.4. No further correlation was seen with this data and environmental factors measured, with pearson's rank

correlation showing no values close to 0.95. The closest for acetone was a 0.91 correlation with Isoprene concentration, as discussed below in 4.4.2.Aside from that correlation, the remarkable consistency of the acetone concentration across the catchment is unlike any dataset seen, with very little influence from runoff catchment, between agricultural, moor or forest.

Acetaldehyde was also detected in the Halladale catchment at every site, with concentrations between 21 and 47 nM and a mean of 31±8.9nM. The lowest concentration was detected at site F_AC, the forest run-off, while the site' lower', just above the estuary, had above average concentrations for both visits. No strong correlation (over 0.9) was seen with a pearsons rank test with any other variable analysed. However, it is perhaps of note the concentrations seen on the second visit to sites were typically higher than the first visit (40 ± 5.9nM compared to 27 ± 6.9nM). This was one week further into the long dry spell, as described above in 4.3.1, or could be related to another variable.

Isoprene, detected via the MIMS, was below the 0.07nM LOD for 5 survey sites, including both visits to the marine site. For the remaining 7 sites, 0.18±0.1nM isoprene was detected. The highest isoprene measurement was at site 'upper', at 0.40nM, however, on a revisit, this site too was below the LOD. This matches with the acetone high point also observed at this site, and could point toward some kind of contamination at this site, or some other process linking isoprene and acetone, as discussed below in 4.4.2. The highest concentrations were seen further upstream, with any marine influence decreasing the concentration substantially, as the only marine influenced site above the LOD was the estuarine site on the first visit at 0.097nM (97pM).

The range, deviation and interquartile range can be seen in Figure 4.4, a box plot of all VOCs analysed in the Halladale catchment over the two days of the survey; methanol, acetone and acetaldehyde determined via PTR-MS and Isoprene via MIMS. Variability in the riverine samples was highest for the acetaldehyde, while acetone showed very little variability between samples, with the exception of one site (Halladale upper on 10/7) with an elevated acetone concentration, of 76nM. Otherwise, acetone was detected exclusively between 3.5 and 5.8nM, with a mean of 4.6nM. Due to the length of the Halladale estuary, there is relatively limited distinction in terms of salinity gradient- the estuary is only a few hundred metres long (see appendix D for images of the estuary in its entirety). Higher resolution sampling, for example every 5 psu in salinity, could cause difficulties, due again to the length of the estuary, putting these artificial breaks very close to one another, and potentially increasing sampling error.

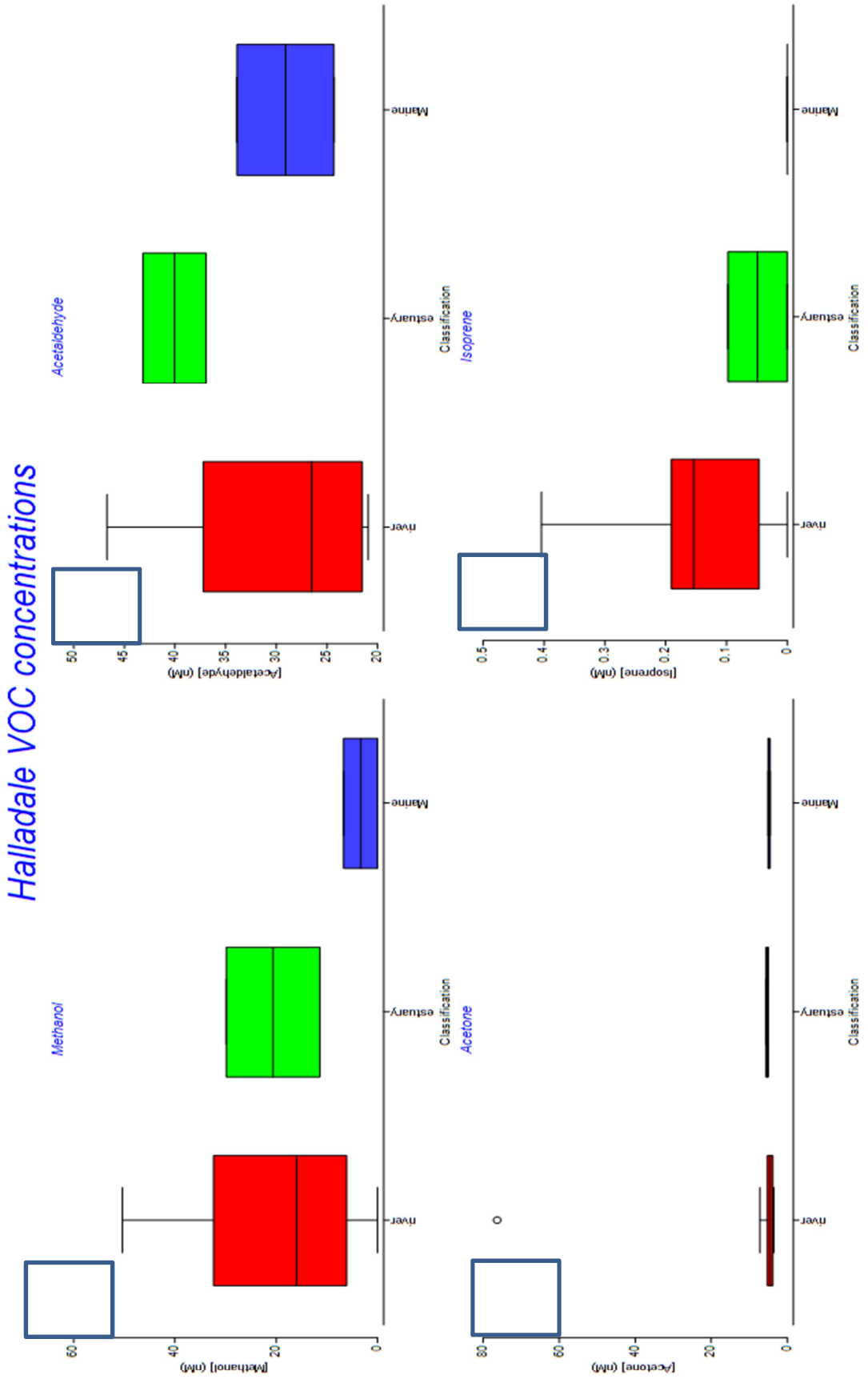
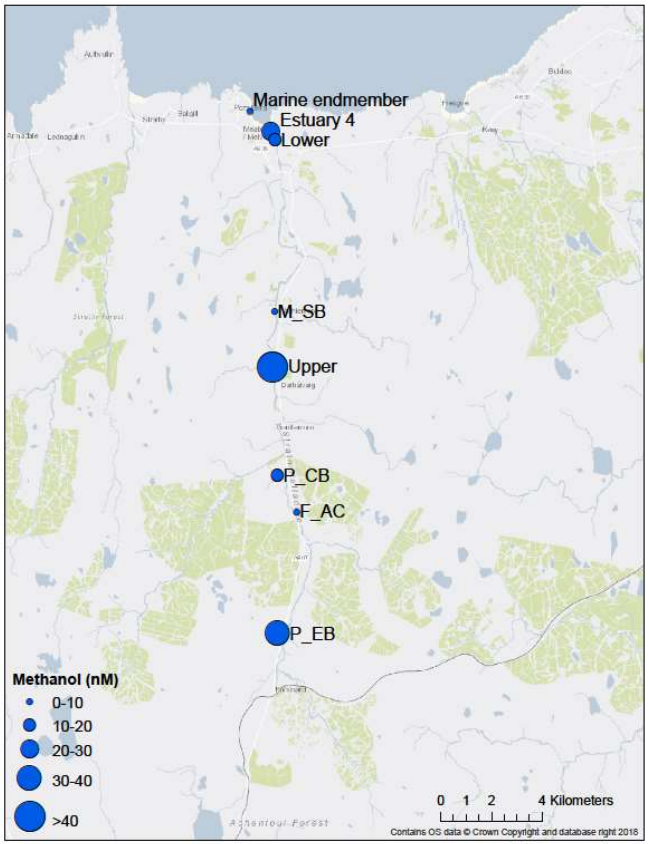


Figure 4.3, Halladale catchment VOC concentration boxplots for a) methanol, b) acetaldehyde, c) acetone, and d) isoprene, as detected by PTR-MS (a-c) and MIMS (d). n=12, where error bars represent one standard deviation.

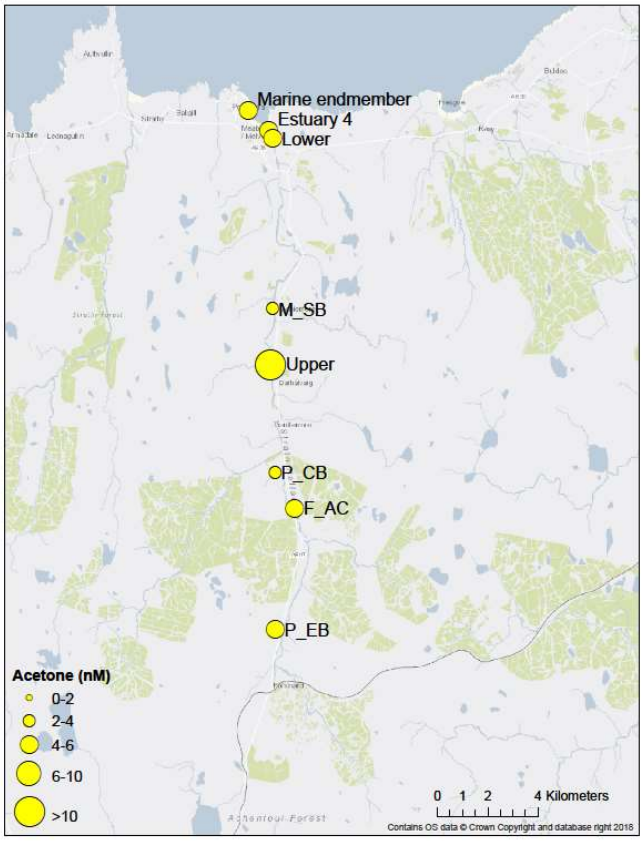
Table 4.2, VOC concentration maps for July 2018, on both dates sampled (n=12). Isoprene measurements were only completed on the first date (n=8).

Methanol- 10.7.18

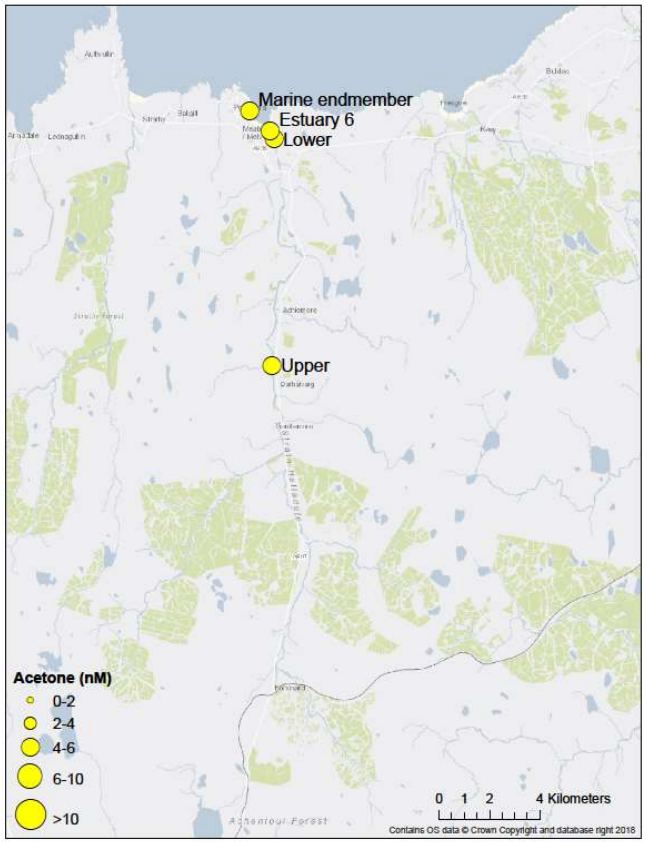


Methanol- 17.7.18

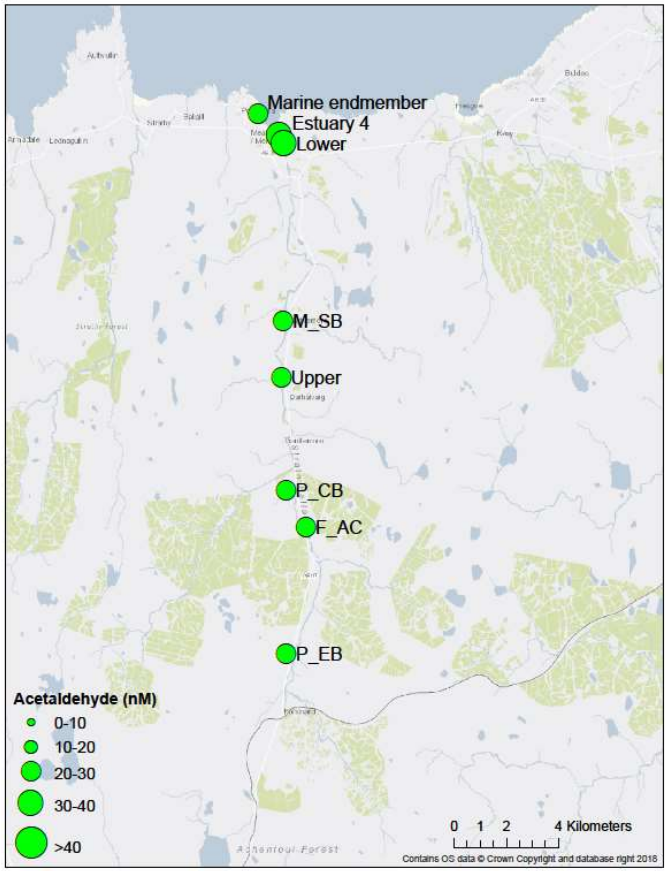
Acetone- 10.7.18



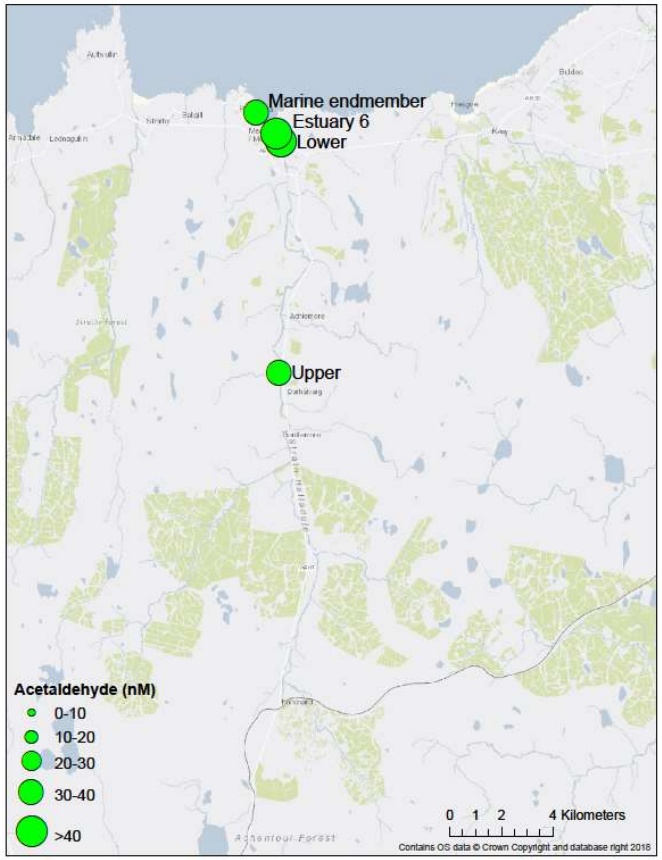
Acetone- 17.7.18



Acetaldehyde- 10.7.18



Acetaldehyde- 17.7.18



Isoprene- 10.7.18

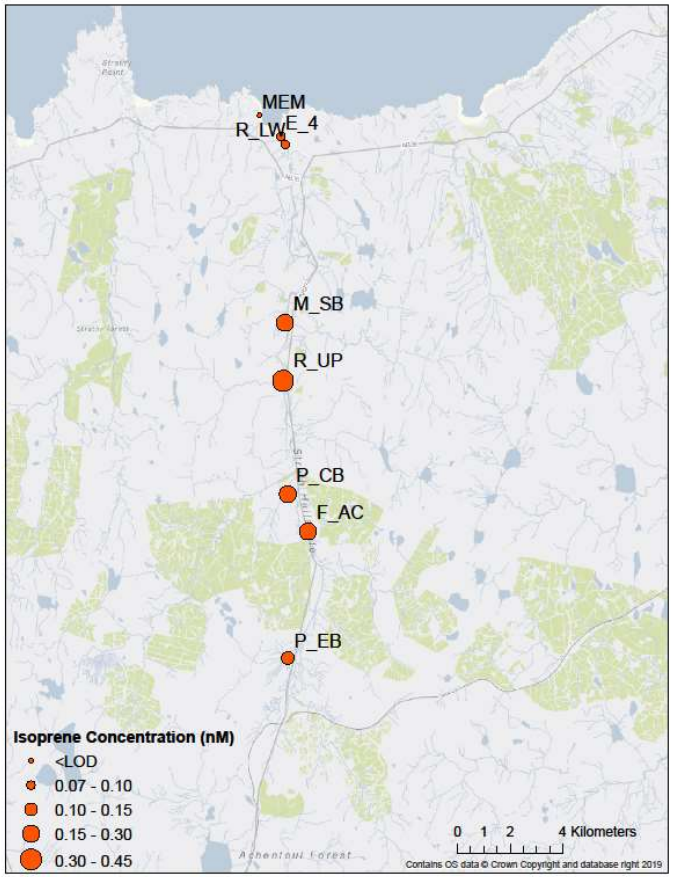


Table 4.3: Site data including sampling and VOC concentrations. Limit of detection was 2nM for methanol, 0.5nM for acetone and acetaldehyde, and 0.07nM for isoprene.

Sitename	runoff type	Date	code	Methanol (nM)	Acetone (nM)	Acetaldehyde (nM)	Isoprene (nM)	Salinity (ppt)	Conductivity (µS/cm)	pH	WATER TEMP °C
Marine endmember	Marine	10/07/2018	MEM	6.8	5.1	24.3	<LOD	33.6	39100	8	12.5
Estuary 4	Halladale	10/07/2018	E4	29.9	5.0	36.9	0.10	10.4	13810	7.8	15.2
Lower	Halladale	10/07/2018	R_ LW	12.6	4.5	38.1	0.09	0.69	1170	7.2	17.1
Upper	Halladale	10/07/2018	R_UP	50.4	76.3	28.2	0.40	0.09	155.1	7.6	17.6
P_EB	Bog	10/07/2018	P_EB	34.8	4.6	24.8	0.14	0.08	149.6	8.1	17.1
M_SB	Mixed with farming	10/07/2018	M_SB	2.9	3.5	21.5	0.16	0.1	174.7	8.2	16.1
F_AC	Forest	10/07/2018	F_AC	9.4	4.0	20.9	0.18	0.07	128.1	7.7	16
P_CB	Bog (restored)	10/07/2018	P_CB	19.5	3.6	21.6	0.20	0.08	134.4	7.6	16.6
Lower	Halladale	17/07/2018	R_LW	29.9	5.7	46.7	<LOD	12.89	18100	7.5	16.7
Upper	Halladale	17/07/2018	R_UP	<LOD	4.4	36.3	<LOD	0.08	147.9	7.7	18
Marine endmember	Marine	17/07/2018	MEM	<LOD	4.5	33.9	<LOD	34.3	41000	8	13.8
Estuary 6	Halladale	17/07/2018	E6	11.4	5.6	43.2	<LOD	27.4	35400	Na	16.3

4.4 Discussion

The summer of 2018 was one of the driest ever recorded in the Halladale catchment, with rainfall and river flows at record low levels (Centre for Ecology and Hydrology (CEH) 2019). This reduced run-off and lower flow rate could potentially cause a different makeup of runoff between groundwater influence: the Helms S_R, indicative of terrestrial influence, remained low throughout, indicating a high level of terrestrial run-off, including in the estuarine section- compared to similar data from the south west of England (see Chapter 3). However, while Helms S_R was typical of a riverine catchment (between 0.7 and 0.9, indicating terrestrially derived carbon), it was not significantly lower than the results seen in the south west in Chapter 3 (P=0.2, t= 0.81 on a students T test), indeed in some cases it was higher than the south west average. This could suggest the precise makeup of the CDOM did not change significantly, even if the volume of runoff did. Due to the low rainfall, it cannot be ascertained if this causes significantly greater CDOM levels or a different composition of the CDOM makeup, or if this in turn affects VOC levels. This decreased flow could have increased the level of groundwater and decreased run-off respectively, which may have affected VOC levels seen.

Furthermore, the Halladale catchment in particular and the northernmost area of Scotland in general, has some of the highest depositaries of dissolved organic carbon, with dissolved carbon flux in the area the highest in the UK (Hope et al. 1997). Riverine organic carbon flux has previously been reported nationally at 0.9Mt annually, with the Halladale catchment at 103.4kgC ha^{-1} yr^{-1} (Worrall et al. 2003). This dissolved carbon is ubiquitously understood as a major source of volatile organic compounds (Mopper and Stahovec 1986; Keiber et al. 1990; Zhou and Mopper 1997) and previous work in coastal waters in the South West UK (Beale et al. 2015) has suggested this may be a cause for elevated levels compared to levels seen in more oceanic environments.

The peatland common in the Halladale catchment had VOC concentrations broadly similar to previous riverine measurements made with the same methodology in the south west of the UK, which addresses the hypothesis above. Peat is one of the largest terrestrial stores of organic carbon (Parry and Charman 2013) with estimates of over 500 kg C/m^2 total carbon found in some areas of blanket peat (Fyfe et al. 2014). It could therefore be theorised this high carbon store could lead to increased carbon, and therefore carbon derived organic compounds, in run-off.

4.4.1 Methanol

Methanol's observed concentrations were broadly lower than previous marine measurements such as those from mid-Atlantic and lower than previous measurements in a near-shore site (16-

78nM, (Beale et al. 2015)). However, when compared to the work carried out in Chapter 3, these concentrations are close to what was detected in the south west UK- This will be discussed further in Chapter 5.

Across the Halladale catchment and to the marine sites, there was no significant difference between river, estuary and marine sites using an ANOSIM test (R= 0, 0.345, 0.052, Significance 66, 84 and 77% for marine/estuary, marine/river and estuary/river respectively). Running a BEST analysis on methanol data alone suggested the closest other variable was acetone, however, this only came to a correlation of 0.359, which suggests a poor correlation if any, though potentially alluding to a similar precursor or production process. However, considering a VOC was a greater correlation than any environmental factor analysed, this could also suggest if there is any other process at work, it was not from the analytes gathered.

While methanol's production mechanisms in seawater have previously been surmised as comprising primarily biological processes (Heikes 2002; Mincer and Aicher 2016), there is less research around terrestrial run-off sources, with rainfall (Felix et al. 2014) and plant growth (Heikes 2002) both proposed as notable sources. Considering the drought conditions seen in the sampling period and the likelihood that plant growth would be curtailed by this lack of water, it is unclear which of these, or if another process is responsible for these concentrations seen.

One other factor to consider is if low concentrations are seen by increased consumption, via biological or other sink processes. A biological process is already known to be the primary loss process of methanol from near-shore and oceanic waters (Dixon et al. 2011b; Sargeant et al. 2016) and if some of these processes are increased in rivers and estuaries, it is likely methanol would be lost at the same rate as produced, if not faster.

4.4.2 Acetone

While most acetone concentrations in this study were broadly similar to both those found in the South West UK (Chapter 3) and similarly, the marine measurements in both near-shore and open ocean sites (Marandino et al. 2005; Beale et al. 2013, 2015; Yang et al. 2014). However, of particular note was the single measurement made in the 'upper' site on the first sampling day. This was, not only the highest concentration in this study, but also the highest concentration seen in any marine, estuarine or riverine environment in published data (see Table 1.1 including (Williams et al. 2004b; Kameyama et al. 2010; Beale et al. 2013)). It is unknown what exactly caused this high concentration, however, as discussed below, the same site featured the highest concentrations for two other VOCs in this study and the highest ammonium recorded in this fieldwork, too, suggesting some manner of biological production or industrial contamination is

likely to blame for this site. As the ammonium was sampled and analysed separately, it is suspected any contamination is likely to be *in-situ* and therefore relevant to the marine system as this contamination would eventually end up in the sea.

Aside from this single visit to the 'upper' site, there is remarkable little variance between other sites acetone concentrations, with a very low deviation from the mean with the 'upper' site removed (4.60±0.72nM). Unsurprisingly, this was not statistically significant between river, estuarine and marine sites on an ANOSIM test. Of note is that the use of a BEST test suggested the closest correlation between acetone concentrations and isoprene concentrations detected, at a 0.602 correlation. Acetone's primary marine source is considered photochemical at 48-100% of production, however, with a noted source from marine *Vibro* species, (Nemecek-Marshall et al. 1995; Dixon et al. 2014; Halsey et al. 2017) is possible Isoprene and acetone share a source process, as isoprene has also been noted as being biologically sourced (Arnold et al. 2009; Exton et al. 2010; McGenity et al. 2018). While no simultaneous measurements have been completed between these two compounds, this could be an area for further research to determine any similarity of production between these compounds.

4.4.3 Acetaldehyde

In the Halladale catchment, acetaldehyde concentrations were consistently at or above the highest recorded concentrations seen in previous literature. In marine systems, the highest concentrations seen were at the coastal site L4, at 37nM (Beale et al. 2015), while the highest site measurement was 46nM, at the 'lower' river site.

As discussed above, it is thought in marine systems, a biotic source of acetaldehyde exists from phytoplankton (Halsey et al. 2017) however it is thought in marine systems the primary source is photochemical, from CDOM (Mopper and Stahovec 1986; Keiber et al. 1990; de Bruyn et al. 2013). While no positive correlation was specifically noted between CDOM and acetaldehyde in this study, it is well known the Halladale catchment and the peatlands of northern Scotland in general have a very high concentration of dissolved carbon (Worrall et al. 2003; Rathgeb et al. 2017) and the highest $CDOM_{300}$ across every site surveyed in both Chapter 3 and 4 was found here, in the restored bog site. Therefore, it follows to reason that if there is any bottleneck, or limiting factor for acetaldehyde production, it is not likely to be dissolved carbon.

While the lowest concentration of acetaldehyde in this field campaign was seen in the forested site F_AC, at 20.9nM, this is still greater than a number of open ocean studies (Mopper and Stahovec 1986; Takeda et al. 2006; Kameyama et al. 2010; Beale et al. 2013). Again, this suggests a significant proportion of acetaldehyde precursor production, or even acetaldehyde itself, stems

from run-off. Another question is if the drought conditions caused these consistently high levels seen, if a potentially set amount of acetaldehyde is released from the environment, but concentrated due to the significantly lower run-off seen as a result of low precipitation. A potential reason for this as the highest point could be microbial uptake, which has already been observed as a significant sink in marine systems (de Bruyn et al. 2017) and oxidation to CO_2 via microbial processes accounts for the controlling sink of acetaldehyde in oceanic systems (Dixon et al. 2013a). However, while in ocean water a < 1 day turnover rate has been observed (Dixon et al. 2013a), no work has been completed on determining a turnover rate in riverine waters, so this would require further work.

4.4.4 Isoprene

The development and use of the MIMS to determine environmentally relevant concentrations is mostly discussed in section 2.4 above. In summary, the method was found to be suitable for detecting isoprene at concentrations typical of those seen in previous studies upstream in estuaries- typically 0.15-0.20nM (Exton et al. 2012). It was therefore expected the MIMS would be able to determine concentrations in further upstream areas in the catchment.

Isoprene detection via MIMS was at an order of magnitude lower than the rest of the VOCs, and a number of the samples- 5 of a total 12- were below the limit of detection of 0.07nM. The remainder were all lower than 1 nM, the highest point, 'upper', at 0.4nM, which is broadly within the range of published data in estuarine and marine systems (Alvarez et al. 2009; Kameyama et al. 2014). Again, no significant difference was seen via an ANOSIM test between river and estuary, the two types of site with concentrations above the limit of detection of the MIMS.

Seeing as the sources of isoprene include biological, from plant growth (Müller et al. 2008) to cyanobacteria (Shaw et al. 2003), it is difficult to disentangle potentially conflicting production and loss mechanisms. Previous study suggested isoprene concentrations reducing through the watercourse, with highest concentrations found at the top of an estuary (Alvarez et al. 2009), however, this study goes further upstream, albeit on a smaller estuary and shows the highest concentrations in riverine waters. This would suggest while an amount of isoprene is produced in estuarine sediments, the primary source to estuarine waters is via the input of fresh water at the top of the estuary.

Isoprene, unlike methanol, acetone and acetaldehyde, lacks the oxygen atom, however, with the volatile nature of the compound, the single largest source of non-methane hydrocarbon in the atmosphere (Sharkey and Monson 2017). Isoprene's major marine source, terrestrial plants, (Exton et al. 2012) is thought to be a major influence on marine system concentrations,

particularly terrestrial marine systems. These new datapoints, in both concentration and relationship with riverine and marine waters, is very similar to Exton (Exton et al. 2012), where concentrations in estuarine environments was notably higher at low tide and higher up the estuary, with isoprene concentrations up to 0.25nM at lowest tide upstream, similar to this data's maxima of 0.4nM and decreasing levels seen to below the detectable limit at the marine end of the transect. This finding could suggest that the majority of estuarine isoprene was terrestrially sourced and there was no noticeable production in the estuary itself, although this may be specific to the Halladale, with its very short estuary. In both field and lab based experiments, a biological source for Isoprene in marine environments has been inferred, (Hackenberg et al. 2017) however, as the concentrations seen here are significantly higher than typical marine concentrations (Shaw et al. 2010), which could indicate the previously understood sources as understood for marine waters are not relevant in this case, with potential sources from biological material decomposition or growth (Peñuelas and Llusià 2003).

In terms of the other analytes, a BEST test was performed to identify the closest correlating other data, to determine if any other links could be seen. The closest correlation for isoprene was a correlation between methanol and acetone concentrations, however, this is a relatively low correlation of 0.219, suggesting isoprene has a somewhat different set of sources and sinks to any other VOC analysed.

4.4.5 CDOM and other variable combinations

Chromophoric dissolved organic matter (CDOM), as a precursor for photochemical production of some OVOCs (de Bruyn et al. 2011), was analysed to ascertain if there was any correlation using the Primer draftsman plot fuction, however, no significant correlation (above 0.5) was seen in the dataset. Curiously, a negative correlation of -0.59 was seen with acetaldehyde and CDOM, which is thought to be a precursor.

Of the two peat bog sites, P_CB and P_EB (Craggie Burn and Ewe Burn), one (P_CB) was restored peatland which had previously been drained for farming, while the other (P_EB) had remained a peat bog during this period. The highest concentration of CDOM $_{300}$ was seen at the restored bog site, which may be as a result of improved water retention upon the bog, or the water table levels lower than typical for the season causing a different makeup of springwater that makes up the majority of the river flow. Alternately, it could show that the bog restoration was still incomplete, and the bog was bleeding carbon out, at a rate and concentration (88) somewhat higher than the next highest CDOM value (48, from site 'upper').

A previous study in marine systems suggested photochemical processes produce a high proportion of both acetone and acetaldehyde- potentially up to 100% of acetone and 68% acetaldehyde (Dixon et al. 2013a). However, it seems in riverine waters, there may be other factors at play- the acetone concentrations seen here are mostly on the lower end of marine measurements, but the acetaldehyde are somewhat greater. This suggests that either a significant acetone sink, or comparatively reduced source, or an acetaldehyde source or reduced sink, can be found in riverine waters. The weak or lack of correlation between CDOM and OVOCs seen, despite previous work suggesting production of OVOCs in these highly humic waters, suggests if these VOCs are not photochemically produced, biota may preferentialise other compounds, or VOCs may not be directly linked to CDOM levels.

Neither site type nor runoff type was statistically significant (above 0.5 correlation) with an Analysis of Similarity (ANOSIM) test across all VOCs, or individually. However, it was possible to distinguish the sites by CDOM, when compared with a non metric multidimentional scaling (nMDS) analysis (primer-7, see Chapter 3 for methodology), there is a statistical difference between riverine and estuarine sites, which is unsurprising considering the differing makeup of CDOM in marine and riverine environments (de Bruyn et al. 2011) and this was illustrated by the Helms S_R as a low ratio (between 0.7 and 0.9) which indicates terrestrial rather than marine waters (Helms et al. 2008).

The site 'upper', has highest concentrations seen of isoprene, methanol, and most notably, the highest ever concentration observed of acetone on the visit on the 10th. On revisit a week later, the concentrations were broadly typical, although of note is the acetone concentration was 5.7nM, significantly reduced from the 76nM seen from the first visit. Considering other sites both up and downstream did not have particularly increased volatile content, this suggests a point source, very close to the 'upper' site, potentially agricultural pollution or other solvent spill. One other hypothesis could be some manner of biological production, such as a small algal bloom- this site had the highest ammonium concentration seen in the sampling campaign, however, at 0.33mg l^{-1}, it was lower than some sites in the south west, as featured in Chapter 3.

Isoprene's concentrations were an order of magnitude lower than the OVOCs, with highest points further upstream and the lowest concentrations in the marine site, which was below the limit of detection of 0.07nM. This follows previous measurements of both isoprene (Exton et al. 2012) and OVOCs (see Chapter 3) in estuarine systems, illustrating while isoprene is found ubiquitously in the atmosphere, it is sparingly soluble and therefore not found in as high concentrations as the highly soluble oxygenated compounds. It is likely there is a biological production of both Isoprene

and OVOCs in river water and further research could help to identify the significance of this to coastal waters as a whole.

4.4.6 Study Limitations

While this study produced some novel results, and a valuable new dataset, if it were to be repeated, a few adjustments would be recommended. Firstly, while a valuable exercise to coordinate with the remainder of the LOCATE sampling, this coordination did have the limitation of requiring another person to be visitng the sample sites, for the purposes of sample gathering. On the methodology side, as discussed in chapter 2, the comparison between the PTR-MS and MIMS for isoprene analysis could have been completed at a lower concentration if the isoprene methodology did not require ethanol as a solvent, as this caused issues with the PTR-MS, but was required to use a master standard, due to isoprene's low miscibility.

A further limitation was the sample site selection itself, as a number of sites were inaccessible by any method other than trekking through peat moor and bushland, causing difficulty to access and preventing higher intensity sampling or repeated trips. Again, while this was an artefact of sampling with the LOCATE program. However, with a little timing and planning ahead, there could be some opportunities to add to this, for example by taking an increased number of samples in the estuarine area for a smaller, higher resolution transect of fresh and saltwater mixing. Finally, the LOCATE intensive sampling campaign could only be a snapshot, and to return to the site in other seasons, or even in the same season under non-drought conditions could provide some more interesting comparative data.

4.5 Conclusions/summary

As previously discussed in Chapter 2, the MIMS is a suitable methodology for investigation for isoprene at environmentally relevant concentrations. Further work may allow it to be used to examine the rest of the VOCs studied in this chapter, however, this is likely to require further refinement and potentially a larger membrane, again, as discussed in Chapter 2.

The results presented in this study, as some of the first riverine and estuarine measurements of VOCs in an organic-rich system. Insights into the sources and outflow suggest estuarine mixing processes have little influence in OVOC or isoprene concentrations and a new method to identify isoprene at environmentally relevant levels was tested. Correlations between chromophoric dissolved organic matter and VOCs were presented and the influence of record low flow levels identified as a potential confounding factor. The modification of a previously used method to

analyse for isoprene provided useful data and provides a baseline for further research in this direction.

To address the hypotheses that this fieldwork examined:

The different volatiles had differing influence from the high dissolved carbon. Broadly, methanol and acetone were found in similar or lower concentrations than marine systems, with the exception of one very high concentration of acetone, while isoprene was found at a higher concentration than marine systems, yet similar to previous work in estuaries. Acetaldehyde was found in significantly higher concentrations than previous marine or terrestrial measurements and this could be put down to the differing composition or concentration of CDOM, although no correlation was seen with gathered CDOM data.

Isoprene's distribution was similar to other VOCs, albeit an order of magnitude lower. The highest concentrations were found upstream and marine systems were below the limit of detection for the method. A disadvantage of using this opportunity for method development was it is not possible to confirm if this relationship would hold true in different environments, including the more common agricultural land or forests found in the south west, as discussed in Chapter 3.

Finally, some VOCs were found upstream in higher concentration than in estuarine or marine samples, suggesting a VOC dilution effect by the seawater influence upon these sites. This in turn could suggest there is little additional VOC input or production in estuarine waters, certainly in this case, for methanol and isoprene, while acetaldehyde and acetone ('upper' site nonwithstanding) were found in similar concentrations to the marine site. This seems to run counter to the previous work- see Chapter 3- indicating acetone and acetaldehyde were found in higher concentration in terrestrial waters. Further analysis of this can be found in Chapter 5, conclusions.

Chapter 5 Conclusions

5.1 Achievements and aims

5.1.1 Method development

The analysis of isoprene had previously required specialised analytical equipment, pressurised gases, a purge and trap system, a highly hands on operating procedure, or a combination of the above. This thesis presents the first recorded usage of a membrane inlet mass spectrometer for analysis of the volatile organic compound isoprene in natural waters. Isoprene has been analysed via MIMS previously in air and volatile compounds have been analysed in water via the method (Ketola et al. 2002), this still remains the first usage of this combination of equipment and environment. This method was developed, validated and used for environmental samples in the Halladale catchment and proved to produce reliable results at environmentally relevant concentrations.

The use of gastight syringes for sample insertion, as featured in the MIMS method, was also used as a new modification for the PTR-MS membrane inlet system. This meant the method retained the high sensitivity and low LOD, while decreasing the points for contamination, reducing the size of equipment and requiring the use of one fewer pressurised gas canister.

5.1.2 Hypothesis

In Chapter 3, the VOC measurements in rivers and estuaries of the South West UK, the hypothesis stated these environments were an influence on near-shore marine concentrations of volatile organic compounds, and determine if any effect has a seasonal variance, by comparing summer and winter measurements.

For the question of shelf sea influence, it was shown that for the carbonyl compounds acetone and acetaldehyde, elevated levels were observed in riverine and estuarine sites. This suggests riverine and estuarine sites are a source of these compounds. In comparison, methanol was not found in elevated levels and thus assessed to not have a direct influence on near shore coastal zone concentrations. Further detail on this is shown in section 3.4.

Acetone and acetaldehyde concentrations were higher in summer than winter, while again, this relationship was not seen for methanol. More detail to this comparison is in section 3.4.

For Chapter 4, the work aimed to determine if in a highly humic environment an elevated level of VOCs would be detected and how these concentrations compared to the measurements made in Chapter 3. Furthermore, the suitability of the use of a membrane inlet mass spectrometer for analysis of isoprene was examined, and compared to a pre-existing method, that of a PTR-MS.

The overarching aim of this project was to determine the influence of land type, season and salinity upon the concentration of VOCs in terrestrial water to near-shore systems, as discussed in section 1.4. Addressing those aims:

1. The development of a new isoprene analysis methodology using the MIMS is validated in Chapter 2 and used in research in Chapter 4, showing consistent results at environmentally relevant concentrations.
2. The summer/winter variation in the Tamar catchment has been determined and is discussed in Chapter 3, showing a seasonal variation with higher concentrations of acetone and acetaldehyde in the summer season, with methanol higher in the winter.
3. The influence of highly humic soils is analysed in Chapter 4, showing typically elevated levels of acetaldehyde, but no correlation with CDOM. .

5.2 Fieldwork Comparison

5.2.1 Sites studied

As discussed in Chapters 3 and 4, this work presents the first simultaneous measurements of riverine and estuarine VOC concentrations, from a range of sites in both the South West UK and Northern Scotland. The sites studied across these catchments included run-off from a range of typical UK land uses including forested, grassland, agricultural, urban, and moor. In particular, the south west region was sampled with the aim of capturing as much of this variation as possible, while the Scottish sample sites were selected more as a best case scenario for high levels of dissolved organic carbon.

5.2.2 OVOC distribution

5.2.2.1 Methanol

Methanol's average concentration in the Tamar and surrounding catchments, 66.6±36.7nM, was significantly higher than Halladale catchment average of 20.8±15.1 nM using an ANOSIM test ($R=0.135$, $p=0.001$) when constrained to the peatland/moor influenced samples, however, this difference was not significant (ANOSIM $R=0.262$, $p=0.095$). This suggests, moorland has a broadly

similar influence on methanol in the Dartmoor and Halladale catchments, and, as discussed in Chapter 3, this does not have a significant influence on marine systems. A BEST analysis, also done in Primer, suggested the factors best correlating with methanol concentrations to be a combination of Isoprene concentrations, and total organic carbon (TOC). However, this was not a strong correlation, at 0.259, and close to TOC alone, at 0.258. Furthermore, TOC data was only available in the Halladale catchment, and therefore, it is of note that the best correlation did not have an influence from the Tamar catchment. When the BEST analysis was repeated using only the Scottish data, as discussed in chapter 4, the closest correlation was in fact isoprene concentration, at 0.492. This correlation could be driven by similar sources, as both isoprene and methanol are known to be produced by phytoplankton (Shaw 2001; Shaw et al. 2003; Mincer and Aicher 2016), however, further investigation would be required to check if this correlation could be repeated in different environments, or if this is coincidental.

Considering as the primary sources of methanol to the environment is biological, both for the atmosphere (Jacob et al. 2005) and ocean (Mincer and Aicher 2016), this suggests farmland, forests and agricultural land are more important to methanol input than the peat moor found in Dartmoor in the south west catchment and the peatland found across the entirety of the Halladale catchment.

5.2.2.2 Acetone

Acetone in the Tamar and local area (3.9±2.9nM) and in the Halladale (10.6±20.7nM) was significantly different with a student's T test ($t=2.2$, $P<0.05$). However, an ANOSIM test was also used, which is more able to cope with a high variance, considering the single high concentration point found in the Halladale, as discussed in Chapter 4. Using the ANOSIM test, with the inclusion of the 'upper' datapoint, the difference was just significant (R 0.151, P= 0.049). When the 'upper' point is removed, both the ANOSIM (R= 0.103, P-0.15) and T test ($t=0.77$, $p=0.22$) were not significant, showing that the only variance between the south west and Scotland in terms of acetone concentration, is the one particularly high point observed in the Halladale.

Production of acetone in marine systems, as discussed above, is predominantly photochemical, from dissolved organic matter (Dixon et al. 2013a). Therefore, it is perhaps unsurprising the use of a BEST analysis showed the closest variable across both systems was CDOM analysed at 300nm. While not a strong correlation (0.221) it did illustrate the link between CDOM and acetone. However, while this was the strongest relationship observed within the data, it is not statistically significant, indicating there are likely more confounding factors, as yet unknown, between the amount of CDOM and acetone in riverine and estuarine water, such as alternative sources or precursors, and air-water exchange happening in the riverine system.

5.2.2.3 Acetaldehyde

Acetaldehyde's concentration measured in the Tamar area (9.9±5.2nM) is significantly lower than the concentrations from the Halladale catchment (31.4±9.0nM) using either a student's T test (t=11.13, p=8.1) or an ANOSIM (R= 0.801, p=0.001). Of particular note is how much higher the concentrations of acetaldehyde were in the Halladale catchment, which could be related to the peatland, or the drought conditions seen in the Halladale. Acetaldehyde in marine systems is thought to be primarily photochemically produced, like acetone (de Bruyn et al. 2011), but unlike acetone, does not have a significant photochemical sink, as the primary loss process is biological (Dixon et al. 2013a; de Bruyn et al. 2017). This could suggest between the extended sunlight hours in Scotland and the seasonal effect already observed with a summer peak (see Chapter 3), the northern end of Scotland could be the area of the UK with highest acetaldehyde export.

A BEST analysis on the acetaldehyde distribution across all catchments suggested the best correlation is found with a combination of acetone and isoprene concentrations, total organic carbon and *in situ* temperature, which formed a 0.406 correlation. Considering the production processes for acetone and acetaldehyde are considered to be similar, including a production mechanism from organic carbon, this relatively close correlation is perhaps unsurprising, although there is clearly room for additional factors in the production or loss of acetaldehyde. Again, TOC data was only available for the Halladale catchment, which also shows this low correlation would be yet lower, if this was excluded.

5.2.3 Distribution in regard to salinity

To determine the nature of the VOC distribution in estuarine systems, estuarine datapoints above the LOD were plotted against the salinity, as shown below in figure 5.1. As shown, insufficient data exists for isoprene to determine any relationship in regards to a conservative or non conservative behaviour. For both acetaldehyde and acetone, no relationship is clear, while the three datapoints available suggest methanol may diverge from the law of constant proportions. This has previously been observed in estuarine waters with dissolved organic matter (DOM) (Asmala et al. 2016) but in any case, further data would be required to confirm or refute this assertation for methanol, as discussed in section 3.4.6.

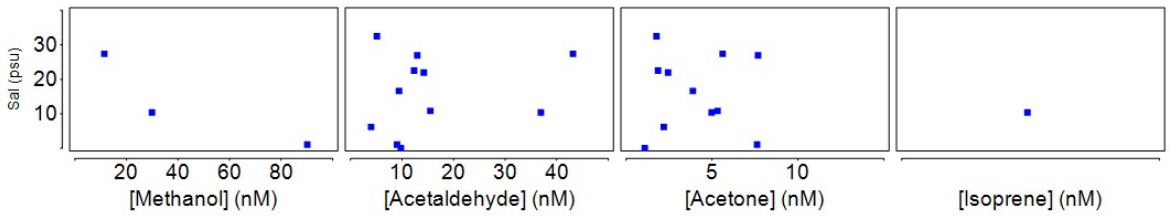


Figure 5.1, Plot of VOC concentration against salinity across all datasets, removing concentrations below the LOD.

5.2.4 Multivariate analysis

A comparative NMDS plot (Primer 7, as discussed in Chapter 3 (Clarke and Gorley 2015b)), was created to compare the sites and seasons. As shown in Figure 5.2, the Halladale sites, tended toward the bottom of this plot, but kept the same general trend between marine (to the left) and riverine (toward the right).

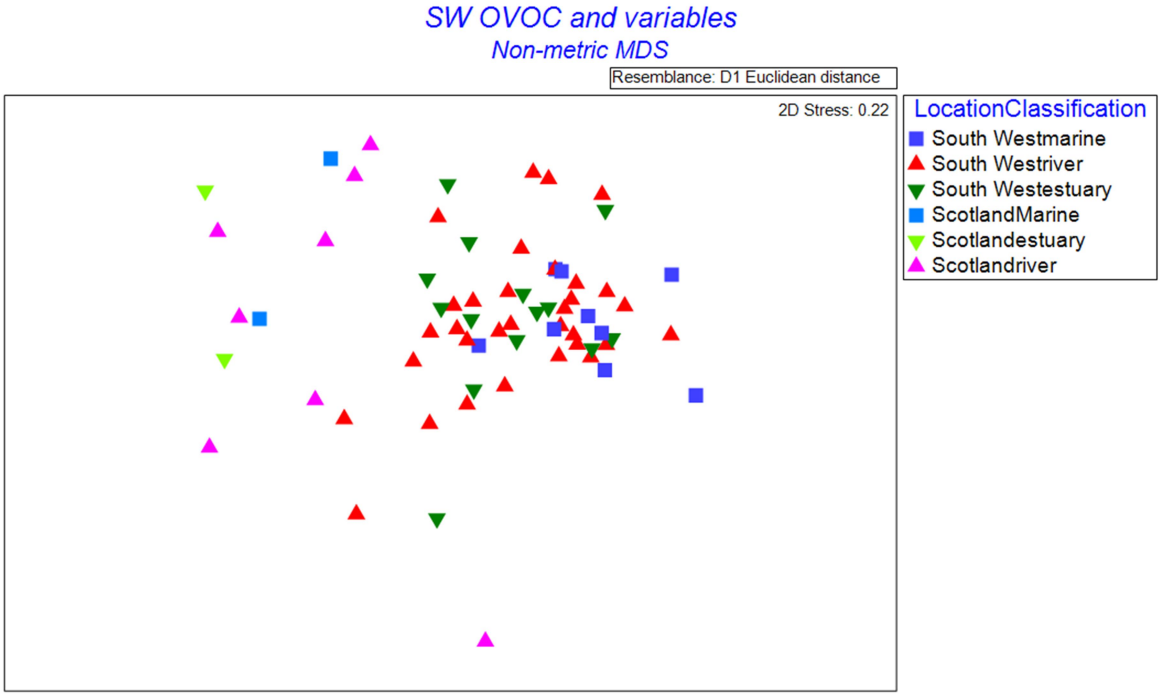


Figure 5.2, NMDS plot comparing all sites VOC concentration in South west UK and Scotland

This was further analysed with a comparison of all riverine moor influenced-sites. This comprised all the riverine sites in the Halladale catchment and the sites comprising high amounts of Dartmoor run-off from the south-west. Specifically, the River Plym at Shaugh bridge, the River Erme at Hartford bridge, the River Walkham, the River Yealm at Cornwood, and all sites (Postbridge, Two bridges and the combined Dart) on the River Dart. This analysis showed on an ANOSIM test, the two catchments were still distinguishable, from all data (R=0.399, p=0.001) and from VOCs alone (R=0.666, p=0.001). This difference is perhaps easiest explained by the

acetaldehyde concentration, as shown in Figure 5.2, which is significantly higher in the Scottish sites compared to methanol and acetone. As discussed above, while acetone and acetaldehyde tend to have similar production mechanisms, the loss processes are different, acetone tending toward a smaller biological oxidation rate with acetaldehyde more biological in nature (Dixon et al. 2013a; de Bruyn et al. 2017), so this insinuates loss processes are more impactful on acetone than acetaldehyde in the Scottish dataset.

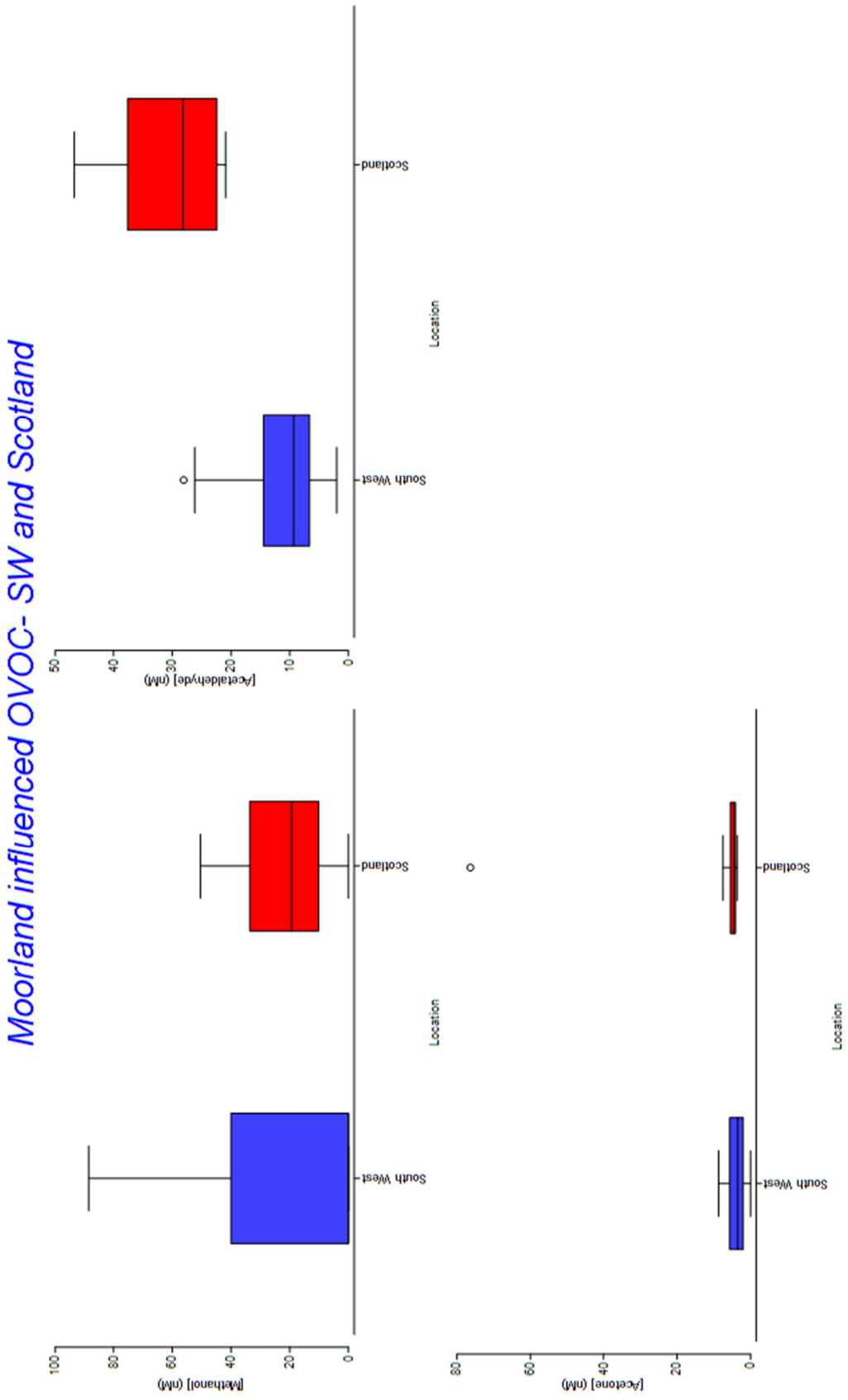


Figure 5.3, Boxplot of moorland influenced OVOC concentrations between the south west UK and River Halladale, with error bars representing standard deviation

A BEST analysis was also completed on the resemblance generated from the moorland sites as discussed above. Of all the auxiliary data, the best correlation was found with a combination of air temperature, TDS, NO_3, TOC and CDOM, at 0.356. Of interest is that a number of these variables were only available in one of the two datasets- air temperature, NO_3 and TDS were only recorded in the south west, while TOC was only available in the Halladale. This suggests if any of these variables are linked to the responsiblity for the variation seen, in particular the acetaldehyde concentration variation noted in Figure 5.3, then this likely would not have been observable with the data collected. Alternately, if another factor was more important for the variation, as suggested by the reasonably low correlation, then it would require disentanglement from the dataset at large and perhaps further analysis.

5.2.5 The bigger picture

To extrapolate from the two short-term datasets presented here and the total average water flow (9615 $m^3 s^{-1}$ in summer, and 1797 $m^3 s^{-1}$ in winter respectively for 2013 (National Hydrological Monitoring Programme: NERC Centre for Ecology & Hydrology 2014)), provides the data shown in Table 5.1. Error is propagated from both the variance in river flow over the preceding 10 years and the standard deviation of all summer or winter riverine concentrations measured.

Table 5.1, An approximate extrapolation and propagated error for annual riverine VOC export in the British mainland, calculated from the results presented above.

Methanol-Summer	Methanol-Winter	Acetone Summer	Acetone Winter	Acetaldehyde Summer	Acetaldehyde Winter	Isoprene-Summer
60.99	314.07	16.49	23.41	29.76	44.92	0.61
53.77	175.08	34.71	16.69	24.75	23.01	0.42

This, naturally, comes with a number of assumptions and extrapolations. Firstly, seeing as this work only contains summer and winter data, if there is a previously unknown short term peak or trough, this would not be seen. Secondarily, river flow is calculated from averages and variation from the last decade of data available (2003-2013), so any recent changes in flow or whole UK trend up or down would not be reflected. Thirdly, extrapolation from the variation of riverine concentrations observed, in both the south west and northern Scotland may not encompass the entire UK and therefore, the error across this data may be greater. Nonetheless, it represents the first approximations of VOC export across the UK.

5.3 Chapter summary

In regards to this chapter, for acetaldehyde, the concentrations detected were significantly higher than those detected before in the environments of the south west UK. In comparison, no difference was detected for acetone, or methanol, with the exception of one acetone 'hot spot' with an exceedingly high concentration. For MIMS method validation, isoprene concentrations were reliably measured on both instruments, however the MIMS was able to successfully measure samples faster and with a lower limit of detection (0.07nM on the MIMS, compared to lowest PTR-MS calibration at 0.5nM), suggesting it is a suitable method for analysis.

5.4 This work vs published data

5.4.1 Suitability of method

The MI-PTR-MS method discussed in Chapter 2 is a reliable pre-existing method which has been determined as highly suitable for VOC analysis in marine systems, and with this work, has been shown to reliably measure concentrations in less saline waters with the same level of consistency. In comparison, the MIMS method, as discussed in Chapters 2 and 4, is a new method, albeit inspired by a number of previous works (Ketola et al. 2002; Tortell 2005). As discussed above, with some modifications to improve sensitivity and reliability, measurements at an environmentally relevant level of Isoprene in riverine, estuarine and marine systems.

5.4.2 VOC distribution

While a small number of measurements have been made in riverine and estuarine systems, the majority of these are either individual compounds or single site studies. In comparison, a number of measurements have been made of OVOCs in marine systems, and, as shown in Table 1.1 and Table 3.2, measurements made in this study are broadly similar to previous studies. More importantly, where the same site has been visited in previous work, measurements made in this study were broadly in line within these (Beale et al. 2015).

5.5 Further research

In recent years, during the data collection and compilation of this thesis, a number of new publications have examined VOCs from a range of environments, from polar concentrations (Wohl et al. 2019) to bacterial production and cycling (Halsey et al. 2017). One area that still has relatively little work is the importance of VOC input from rivers and estuaries, as discussed in this

work. However, a significant constraint is the breath of environments studied and further work outside temperate climates, would be important to fully understand the worldwide importance, and to determine an overall flux from river and estuary to marine systems. Similarly, in the last few years, a number of works have been published discussing isoprene, particularly work on isoprene atmospheric flux (Hackenberg et al. 2017). Again, being able to consider riverine and estuarine influence could increase understanding of this compound, particularly with the availability of a faster analysis method such as the one developed using the MIMS.

The question of a VOC diurnal cycle has been briefly discussed in the past in the context of seawater, with data from open ocean (Mopper and Stahovec 1986, Beale (pers.comm)) and nearer shore (Takeda et al. 2014). However the relative larger surface area of riverine and estuarine waters has not been addressed, and this could be hiding an array of photochemical reactions and production mechanisims as yet uncertain. Further study in this area, ideally an hourly or bi-hourly sampling for a full 24 hour period, would allow comparison between flow, photochemical processes and, if in an estuary, tidal cycling.

While the diurnal cycle has at least a couple of published datasets, a cycle that does not appear to have had any published research is that of OVOC tidal cycling. While previous study has indicated methane has a tidal cycle (Bahlmann et al. 2015), to be able to repeat this and distinguish any cycling for the compounds this thesis examines would be fascinating. A potential weakness with a tidal study, however, would be the ability to disentangle tidal state from time of day- as discussed in chapter 3, while tidal comparative measurements were taken in some sites, two samples on different days at different tidal states could have any number of confounding factors.

As briefly discussed in chapter 2, the comparison of summer and winter could be further improved by more reglar sampling and analysis, to turn this work into a true seasonal cycle, in a similar manner to the annual study completed at L4 (Beale et al. 2015). Picking a smaller number of study sites, for example the sites down the salinity gradient on the Tamar, and visiting them at a higher resolution- ideally weekly, or potentially monthly, would create a fascinating dataset to reveal the variation in much higher resolution.

While the sample sites in both chapter 3 and 4 were selected for convenience of access, which inevitably has to be an area for consideration, VOC production from anthropogenic sources, be that farming, industrial or marine traffic. More targeted sampling, be that upstream in farmland, near sewage outflows or any other site,

The use of radiochemical tracers to produce production and consumption rates of VOCs has been studied in a number of situations, but most relevantly, site L4 as discussed in chapter 3 has had

studies for both methanol (Sargeant et al. 2016) and acetone (Dixon et al. 2014). The techniques used for the radiochemical determination of production and consumption, via radiochemical tracer carbon-14, could also be used for rate calculation for all 4 compounds of interest in riverine and estuarine systems, provided a suitable tracer was available. To name some specific tracer studies, calculating how microbial turnover of VOCs varied by salinity, and determining assimilation if possible, seems to be a natural first step.

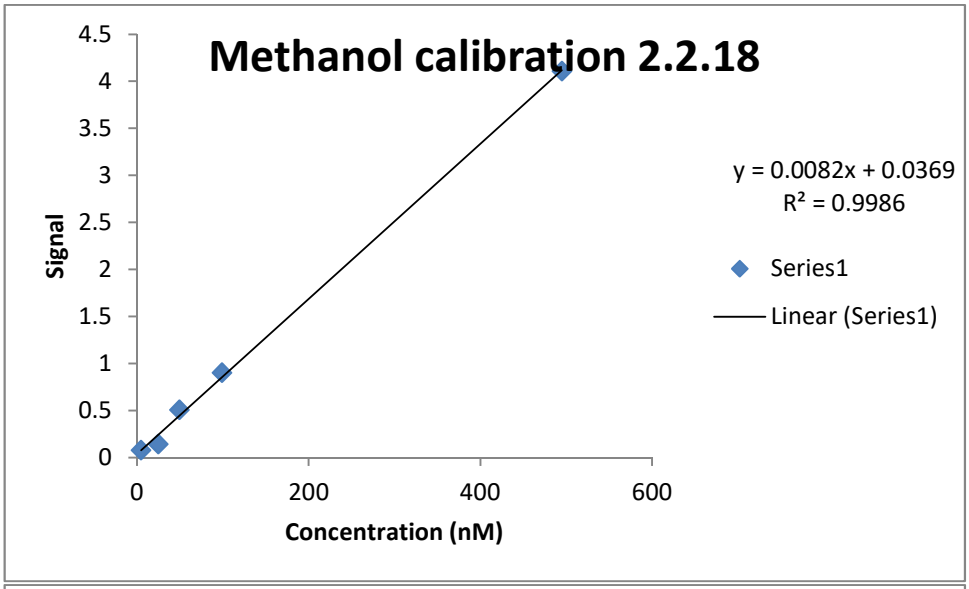
While biota is a known source for VOCs in both marine and atmospheric situations (many sources, a broad marine study is (Halsey et al. 2017) but many examples exist), the capability of quantifying rates of emission, uptake or any other process is increased in complexity by the plethora of factors present in the environment. One method of removing some of these factors is to complete a mesocosm experiment, such as the one used by Sinha et al (2007) to investigate VOCs after a phytoplankton bloom (Sinha et al. 2006), which could effectively provide comparisons between larger scale biota, in a similar manner to the radiochemical work could on smaller organisims

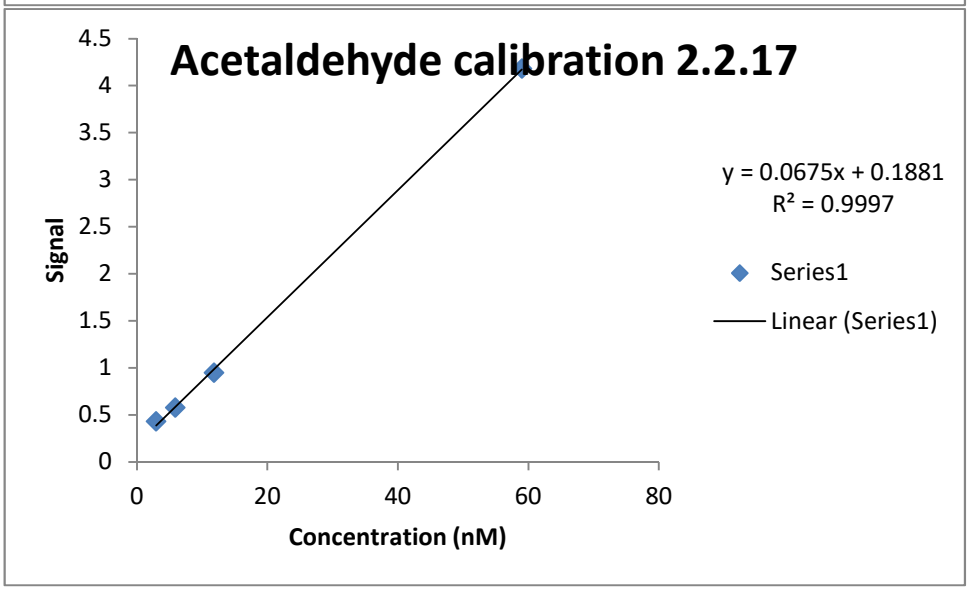
Even new emerging science that may not intrinsically be associated to VOCs have potential to be applied in the context of volatiles. For example, new study suggest microplastics may emit VOCs in degradation in the environment (Castelvetro et al. 2021), and in a similar way to the question of biota, studies in controlled laboratory environments may reveal new sources for these compounds,

On the methodological side, as briefly discussed in chapter 2, the MIMS method for detection of isoprene could be expanded, either with the detection of further analytes, or by an increase in sensitivity via the use of a larger surface area membrane, such as a hollow fibre type sealed capsule. This type of membrane has previously been used in marine dissolved gas detection (Sims et al. 2017) and potentially could increase the available membrane surface area, and therefore recede detection limits by theoretical orders of magnitude, leading to hugely increased high quality data compared with methods requiring purge and trap.

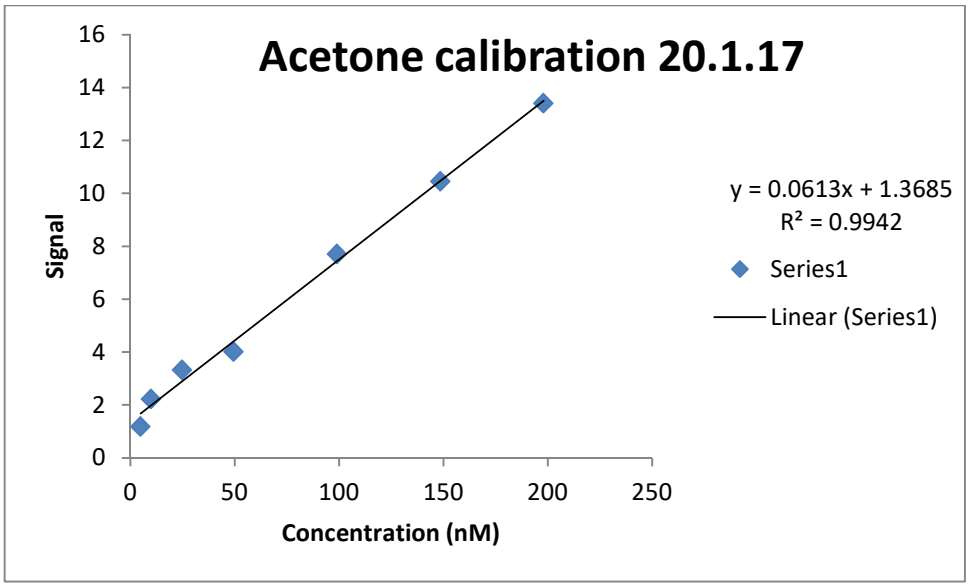
While a great deal of these proposals would require extensive method development, planning and analysis, each one would provide further pieces in the puzzle of VOC compound cycling . should that work be completed, it would be hoped to inform a much greater understanding of these important compounds.

Appendix A Example Calibration curves for MI-PTR-MS

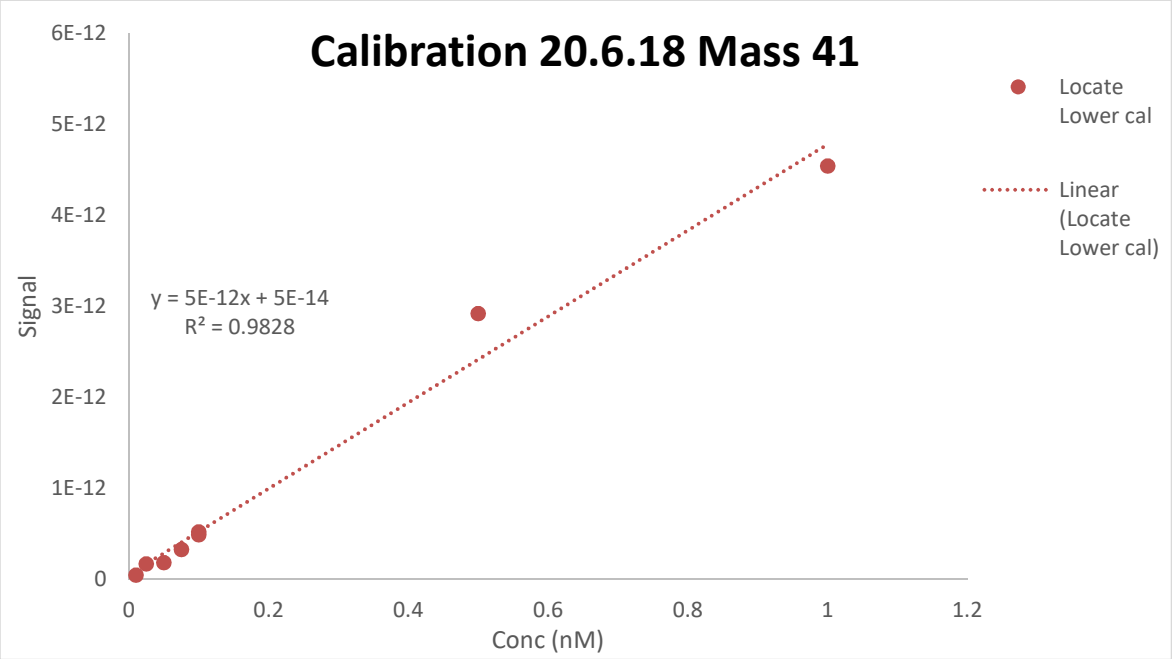




Appendix A


Acetone calibration 20.1.17
Signal
Concentration (nM)
0
2
4
6
8
10
12
14
16
0
50
100
150
200
250
y = 0.0613x + 1.3685
R² = 0.9942
Series1
Linear (Series1)

Appendix B Example Calibration curve for MIMS



Appendix C Methodology used for auxiliary data on LOCATE

Methodology carried out either *in situ*, or sent back to labs at NOC Southampton, CEH Lancaster and BGS Wallingford.

Analyte	Instrument	Method
NH4-N	Seal_AQ2	http://onto.nerc.ac.uk/CAST/167
NO3-N	DIONEX_ICS2000	http://onto.nerc.ac.uk/CAST/181
NPOC	FORMACS	http://onto.nerc.ac.uk/CAST/164.html
PO4-P	SEAL_AQ2	http://onto.nerc.ac.uk/CAST/167
TDC	FORMACS	http://onto.nerc.ac.uk/CAST/164.html
POC	Flash EA 1112 Series Elemental Analyser connected via a Conflo III to a DeltaPlus XP isotope ratio mass spectrometer	Method followed UKAS ISO 17025

Appendix D Images from sampling

Estuarine site E4

Above- River Halladale, centre of catchment. Below- Site F_AC.

Above- Site R_UP (Upper) Below- Site R_LW (Lower)

Appendix E Raw Halladale Data

Number	R_ LW	R_UP	P_EB	M_SB	F_AC	P_CB	R_LW	R_up	MEM	E6
[Methanol] (nM)	12.6	50.4	34.8	2.86	9.42	19.5	29.9			11.4
[Acetaldehyde] (nM)	38.1	28.2	24.8	21.45	20.94	21.63	46.7	36.3	33.9	43.2
[Acetone] (nM)	4.48	76.33	4.64	3.52	4.02	3.59	5.72	4.44	4.53	5.62
[Isoprene] (nM)	0.0922	0.404	0.144	0.164	0.181	0.200				
NH4 mg/l	0.319	0.330	0.202	0.133	0.218	0.317			0.0709	
Sal (psu)	0.69	0.09	0.08	0.1	0.07	0.08	12.9	0.08	34.3	27.4
pH	7.2	7.6	8.1	8.2	7.7	7.6	7.5	7.7	8	
TOC (mg/L)	6.0	7.69	6.7	7.45	9.06	13.35	5.37	7.61	1.25	3.26
Temp-Situ	17.1	17.6	17.1	16.1	16	16.6	16.7	18	13.8	16.3
CDOM_300nm	36.9	42.00	32.9	43.0	36.9	88.0	19.6	48.7		17.1
CDOM_350nm	18.7	20.67	16.23	21.58	18.69	45.54	9.47	24.7		7.63
S290-350	0.0122	0.0124	0.0124	0.0120	0.0122	0.0115	0.0131	0.0117		0.0139
S285-650	0.0128	0.0130	0.0131	0.0127	0.0128	0.0124	0.0125	0.0125		0.0142
Helms 275-295:	0.0137	0.0138	0.0138	0.0133	0.0137	0.0123	0.0147	0.0125		0.0160
Helms 350-400:	0.0167	0.0173	0.0176	0.0171	0.0167	0.0175	0.0169	0.0171		0.0181
Depth	surface	surface	surface	surface	surface	surface	surface	surface	surface	surface
Dominent runoff influence	Mixed	Mixed	Bog	Mixed with farming	Forest	Bog (restored)	Mixed	Mixed		
Sampling Date	10/07/2018	10/07/2018	10/07/2018	10/07/2018	10/07/2018	10/07/2018	17/07/2018	17/07/2018	17/07/2018	17/07/2018

List of References

Allen, T. M., T. M. Falconer, M. E. Cisper, A. J. Borgerding, and C. W. Wilkerson. 2001. Real-time analysis of methanol in air and water by membrane introduction mass spectrometry. Anal. Chem. **73**: 4830–4835. doi:10.1021/ac010315c

Alvarez, L. A., D. A. Exton, K. N. Timmis, D. J. Suggett, and T. J. McGenity. 2009. Characterization of marine isoprene-degrading communities. Environ. Microbiol. **11**: 3280–3291. doi:10.1111/j.1462-2920.2009.02069.x

Andrews, S. J., S. C. Hackenberg, and L. J. Carpenter. 2015. Technical Note: A fully automated purge and trap GC-MS system for quantification of volatile organic compound (VOC) fluxes between the ocean and atmosphere. Ocean Sci. **11**: 313–321. doi:10.5194/os-11-313-2015

Arnold, S. R., D. V. Spracklen, J. Williams, and others. 2009. Evaluation of the global oceanic isoprene source and its impacts on marine organic carbon aerosol. Atmos. Chem. Phys. **9**: 1253–1262. doi:10.5194/acpd-8-16445-2008

Asmala, E., H. Kaartokallio, J. Carstensen, and D. N. Thomas. 2016. Variation in riverine inputs affect dissolved organic matter characteristics throughout the estuarine gradient. Front. Mar. Sci. **2**: 1–15. doi:10.3389/fmars.2015.00125

Asmus, K. D., H. Mockel, and A. Henglein. 1973. Pulse radiolytic study of the site of OH · radical attack on aliphatic alcohols in aqueous solution. J. Phys. Chem. **77**: 1218–1221. doi:10.1021/j100629a007

Atkinson, R. 1986. Kinetics and Mechanisms of the Gas-Phase Reactions of the Hydroxyl Radical with Organic Compounds under Atmospheric Conditions. Chem. Rev. **86**: 69–201. doi:10.1021/cr00071a004

Atkinson, R. 2000. Atmospheric chemistry of VOCs and NO(x). Atmos. Environ. **34**: 2063–2101. doi:10.1016/S1352-2310(99)00460-4

Atkinson, R., D. L. Baulch, R. A. Cox, and others. 2006. Evaluated kinetic and

photochemical data for atmospheric chemistry: Volume II – gas phase reactions of organic species R. Atmos. Chem. Phys. **63**: 694–700. doi:10.1209/epl/i2003-00571-0

Bahlmann, E., I. Weinberg, J. V. Lavrič, T. Eckhardt, W. Michaelis, R. Santos, and R. Seifert. 2015. Tidal controls on trace gas dynamics in a seagrass meadow of the Ria Formosa lagoon (southern Portugal). Biogeosciences **12**: 1683–1696. doi:10.5194/bg-12-1683-2015

Balla, D., A. Papageorgiou, and D. Voutsa. 2014. Carbonyl compounds and dissolved organic carbon in rainwater of an urban atmosphere. Environ. Sci. Pollut. Res. **21**: 12062–12073. doi:10.1007/s11356-014-3080-8

Beale, R. 2011a. Quantification of Oxygenated Volatile Organic Compounds in Seawater. Univesity of East Anglia.

Beale, R. 2011b. Quantification of oxygenated volatile organic compounds (OVOCs) in seawater.

Beale, R., J. L. Dixon, S. R. Arnold, P. S. Liss, and P. D. Nightingale. 2013. Methanol, acetaldehyde, and acetone in the surface waters of the Atlantic Ocean. J. Geophys. Res. Ocean. **118**: 5412–5425. doi:10.1002/jgrc.20322

Beale, R., J. L. Dixon, T. J. Smyth, and P. D. Nightingale. 2015. Annual study of oxygenated volatile organic compounds in UK shelf waters. Mar. Chem. **171**: 96–106. doi:10.1016/j.marchem.2015.02.013

Beale, R., P. S. Liss, J. L. Dixon, and P. D. Nightingale. 2011. Quantification of oxygenated volatile organic compounds in seawater by membrane inlet-proton transfer reaction/mass spectrometry. Anal. Chim. Acta **706**: 128–134. doi:10.1016/j.aca.2011.08.023

Bell, R. J., R. T. Short, F. H. W. Van Amerom, and R. H. Byrne. 2007. Calibration of an in situ membrane inlet mass spectrometer for measurements of dissolved gases and volatile organics in seawater. Environ. Sci. Technol. **41**: 8123–8128. doi:10.1021/es070905d

Brewer, P. G., and J. P. Riley. 1965. The automatic determination of nitrate in sea water.

Deep. Res. Oceanogr. Abstr. **12**: 765–772. doi:10.1016/0011-7471(65)90797-7

Broadgate, W. J., P. S. Liss, A. Penkett, and M. June. 1997. Seasonal emissions of isoprene and other reactive hydrocarbon gases from the ocean. Geophys. Res. Lett. **24**: 2675–2678.

Broadgate, W. J., G. Malin, F. C. Küpper, A. Thompson, and P. S. Liss. 2004. Isoprene and other non-methane hydrocarbons from seaweeds: A source of reactive hydrocarbons to the atmosphere. Mar. Chem. **88**: 61–73. doi:10.1016/j.marchem.2004.03.002

de Bruyn, W. J., C. D. Clark, L. Pagel, and H. Singh. 2013. Loss rates of acetone in filtered and unfiltered coastal seawater. Mar. Chem. **150**: 39–44. doi:10.1016/j.marchem.2013.01.003

de Bruyn, W. J., C. D. Clark, L. Pagel, and C. Takehara. 2011. Photochemical production of formaldehyde, acetaldehyde and acetone from chromophoric dissolved organic matter in coastal waters. J. Photochem. Photobiol. A Chem. **226**: 16–22. doi:10.1016/j.jphotochem.2011.10.002

de Bruyn, W. J., C. D. Clark, M. Senstad, O. Barashy, and S. Hok. 2017. The biological degradation of acetaldehyde in coastal seawater. Mar. Chem. **In press**. doi:10.1016/j.marchem.2017.02.008

Carpenter, L. J., D. Archer, R. Beale, and S. D. Archer. 2012. Ocean-atmosphere trace gas exchange. Chem. Soc. Rev. 6473–6506. doi:10.1039/c2cs35121h

Carpenter, L. J., A. C. Lewis, J. R. Hopkins, K. A. Read, I. D. Longley, and M. W. Gallagher. 2004. Uptake of methanol to the North Atlantic Ocean surface. Global Biogeochem. Cycles **18**: 1–8. doi:10.1029/2004GB002294

Castelvetro, V., A. Corti, G. Biale, and others. 2021. New methodologies for the detection, identification, and quantification of microplastics and their environmental degradation by-products. Environ. Sci. Pollut. Res. doi:10.1007/s11356-021-12466-z

Centre for Ecology and Hydrology (CEH). 2019. National River Flow Archive. Natl. River Flow Arch.

Ciuraru, R., L. Fine, M. Van Pinxteren, B. D'Anna, H. Herrmann, and C. George. 2015. Unravelling New Processes at Interfaces: Photochemical Isoprene Production at the Sea Surface. Environ. Sci. Technol. **49**: 13199–13205. doi:10.1021/acs.est.5b02388

Clarke, K. R., and R. N. Gorley. 2015a. User manual v7a,.

Clarke, K. R., and R. N. Gorley. 2015b. Getting started with PRIMER v7. PRIMER-E: Plymouth, Plymouth Marine Laboratory.

Clarke, K. R., and R. M. Warwick. 1994. Change in marine communities. An approach to Stat. Anal. Interpret. Mar. Lab. Plymouth.

Cleveland, C. C., and J. B. Yavitt. 1997. Consumption of atmospheric isoprene in soil. Geophys. Res. Lett. **24**: 2379–2382. doi:10.1029/97GL02451

Dabrowska, A., and J. Nawrocki. 2013. Aldehyde concentrations in wet deposition and river waters. Sci. Total Environ. **452**–**453**: 1–9. doi:10.1016/j.scitotenv.2013.02.037

Dani, K. G. S., A. M. Silva, M. Michelozzi, G. Peluso, G. Torzillo, and F. Loreto. 2017. Relationship between isoprene emission and photosynthesis in diatoms , and its implications for global marine isoprene estimates. Mar. Chem. **189**: 17–24. doi:10.1016/j.marchem.2016.12.005

Dixon, J. L., R. Beale, and P. D. Nightingale. 2011a. Microbial methanol uptake in northeast Atlantic waters. ISME J. **5**: 704–716. doi:10.1038/ismej.2010.169

Dixon, J. L., R. Beale, and P. D. Nightingale. 2011b. Rapid biological oxidation of methanol in the tropical Atlantic: Significance as a microbial carbon source. Biogeosciences **8**: 2707–2716. doi:10.5194/bg-8-2707-2011

Dixon, J. L., R. Beale, and P. D. Nightingale. 2013a. Production of methanol, acetaldehyde, and acetone in the Atlantic Ocean. Geophys. Res. Lett. **40**: 4700–4705. doi:10.1002/grl.50922

Dixon, J. L., R. Beale, S. L. Sargeant, G. A. Tarran, and P. D. Nightingale. 2014. Microbial acetone oxidation in coastal seawater. Front. Microbiol. **5**: 1–9. doi:10.3389/fmicb.2014.00243

Dixon, J. L., and P. D. Nightingale. 2012. Fine-scale variability in methanol uptake and oxidation: From the microlayer to 1000 m. Biogeosciences **9**: 2961–2972. doi:10.5194/bg-9-2961-2012

Dixon, J. L., S. Sargeant, P. D. Nightingale, and J. Colin Murrell. 2013b. Gradients in microbial methanol uptake: Productive coastal upwelling waters to oligotrophic gyres in the Atlantic Ocean. ISME J. **7**: 568–580. doi:10.1038/ismej.2012.130

Exton, D. A., D. J. Smith, T. J. McGenity, M. Steinke, A. J. Hills, and D. J. Suggett. 2010. Application of a Fast Isoprene Sensor (FIS) for measuring isoprene production from marine samples. Limnol. Oceanogr. **8**: 185–195. doi:Doi 10.4319/Lom.2010.8.185

Exton, D. A., D. J. Suggett, M. Steinke, and T. J. McGenity. 2012. Spatial and temporal variability of biogenic isoprene emissions from a temperate estuary. Global Biogeochem. Cycles **26**: 1–13. doi:10.1029/2011GB004210

Fall, R., and S. D. Copley. 2000. Bacterial sources and sinks of isoprene, a reactive atmospheric hydrocarbon. Environ. Microbiol. **2**: 123–130. doi:10.1046/j.1462-2920.2000.00095.x

Felix, J. D., S. B. Jones, G. B. Avery, J. D. Willey, R. N. Mead, and R. J. Kieber. 2014. Temporal variations in rainwater methanol. Atmos. Chem. Phys. **14**: 10509–10516. doi:10.5194/acp-14-10509-2014

Firpo, G., E. Angeli, L. Repetto, and U. Valbusa. 2015. Permeability thickness dependence of polydimethylsiloxane (PDMS) membranes. J. Memb. Sci. **481**: 1–8. doi:10.1016/j.memsci.2014.12.043

Fischer, E. V., D. J. Jacob, D. B. Millet, R. M. Yantosca, and J. Mao. 2012. The role of the ocean in the global atmospheric budget of acetone. Geophys. Res. Lett. **39**: 3–7. doi:10.1029/2011GL050086

Fyfe, R. M., R. Coombe, H. Davies, and L. Parry. 2014. The importance of sub-peat carbon storage as shown by data from Dartmoor, UK. Soil Use Manag. **30**: 23–31. doi:10.1111/sum.12091

Galbally, I. E., and W. Kirstine. 2002. The production of methanol by flowering plants and

the global cycle of methanol. J. Atmos. Chem. **43**: 195–229. doi:10.1023/A:1020684815474

Greenberg, J. P., and P. R. Zimmerman. 1984. Nonmethane hydrocarbons in remote tropical, continental, and marine atmospheres. J. Geophys. Res. **89**: 4767. doi:10.1029/JD089iD03p04767

Griebel, G. E., and L. D. Owens. 1972. Nature of the transient activation of soil microorganisms by ethanol or acetaldehyde. Soil Biol. Biochem. **4**: 1–8. doi:10.1016/0038-0717(72)90036-3

Guenther, A. B., and A. J. Hills. 1998. Eddy covariance measurement of isoprene fluxes. J. Geophys. Res. Atmos. **103**: 13145–13152. doi:10.1029/97JD03283

Guenther, A., T. Karl, P. Harley, C. Wiedinmyer, P. I. Palmer, and C. Geron. 2006. Estimates of global terrestrial isoprene emissions using MEGAN (Model of Emissions of Gases and Aerosols from Nature). Atmos. Chem. Phys. Discuss. **6**: 107–173. doi:10.5194/acpd-6-107-2006

Hackenberg, S. C., S. J. Andrews, R. Airs, and others. 2017. Potential controls of isoprene in the surface ocean. Global Biogeochem. Cycles under review. doi:10.1002/2016GB005531

Halsey, K. H., S. J. Giovannoni, M. Graus, Y. Zhao, Z. Landry, J. C. Thrash, K. L. Vergin, and J. de Gouw. 2017. Biological cycling of volatile organic carbon by phytoplankton and bacterioplankton. Limnol. Oceanogr. doi:10.1002/lno.10596

Heikes, B. G. 2002. Atmospheric methanol budget and ocean implication. Global Biogeochem. Cycles **16**: 1–13. doi:10.1029/2002GB001895

Helms, J. R., A. Stubbins, J. D. Ritchie, E. C. Minor, D. J. Kieber, and K. Mopper. 2008. Absorption spectral slopes and slope ratios as indicators of molecular weight, source, and photobleaching of chromophoric dissolved organic matter. Limonology Oceanogr. **53**: 955–969. doi:10.4319/lo.2008.53.3.0955

Herrmann, A. 2010. Volatiles – An Interdisciplinary Approach, *In* The Chemistry and Biology of Volatiles.

Hills, A. J., and P. R. Zimmerman. 1990. Isoprene measurement by ozone-induced cherniluminescence. Anal. Chem. **62**: 1055–1060. doi:10.1021/ac00209a017

Holzinger, R., C. Warneke, A. Hansel, A. Jordan, W. Lindinger, D. H. Scharffe, G. Schade, and P. J. Crutzen. 1999. Biomass burning as a source of formaldehyde, acetaldehyde, methanol, acetone, acetonitrile, and hydrogen cyanide. Geophys. Res. Lett. **26**: 1161–1164. doi:10.1029/1999GL900156

Hope, D., M. F. Billett, and M. S. Cresser. 1997. Exports of organic carbon in two river systems in NE Scotland. J. Hydrol. **193**: 61–82. doi:10.1016/S0022-1694(96)03150-2

Insam, H., and M. S. A. Seewald. 2010. Volatile organic compounds (VOCs) in soils. Biol. Fertil. Soils **46**: 199–213. doi:10.1007/s00374-010-0442-3

Jackson, D. 2000. Guidance on the interpretation of the Biodiversity Broad Habitat Classification (terrestrial and freshwater types) Definitions and the relationship with other habitat.

Jacob, D. J., B. D. Field, E. M. Jin, I. Bey, Q. Li, J. A. Logan, R. M. Yantosca, and H. B. Singh. 2002. Atmospheric budget of acetone. J. Geophys. Res. Atmos. **107**. doi:10.1029/2001JD000694

Jacob, D. J., B. D. Field, Q. Li, and others. 2005. Global budget of methanol: Constraints from atmospheric observations. J. Geophys. Res. D Atmos. **110**: 1–17. doi:10.1029/2004JD005172

Johnson, J. E. 1999. Evaluation of a seawater equilibrator for shipboard analysis of dissolved oceanic trace gases. Anal. Chim. Acta **395**: 119–132. doi:10.1016/S0003-2670(99)00361-X

Kameyama, S., H. Tanimoto, S. Inomata, and others. 2010. High-resolution measurement of multiple volatile organic compounds dissolved in seawater using equilibrator inlet-proton transfer reaction-mass spectrometry (EI-PTR-MS). Mar. Chem. **122**: 59–73. doi:10.1016/j.marchem.2010.08.003

Kameyama, S., S. Yoshida, H. Tanimoto, S. Inomata, K. Suzuki, and H. Yoshikawa-Inoue. 2014. High-resolution observations of dissolved isoprene in surface seawater in the

Southern Ocean during austral summer 2010-2011. J. Oceanogr. **70**: 225–239. doi:10.1007/s10872-014-0226-8

Keiber, J. R., X. Zhou, and K. Mopper. 1990. Formation of carbonyl compounds from UV-induced photodegradation of humic compounds in the sea. Limnol. Oceanogr. **35**: 1503–1515. doi:10.1038/353060a0

Kesselmeier, J., and M. Staudt. 1999. Biogenic Volatile Organic Compunds (VOC): An Overview on Emission, Physiology and Ecology. J.Atmos.Chem. **33**: 23–88.

Ketola, R. A., J. T. Kiuru, V. Tarkiainen, J. T. Kokkonen, J. Räsänen, and T. Kotiaho. 2006. Detection of volatile organic compounds by temperature-programmed desorption combined with mass spectrometry and Fourier transform infrared spectroscopy. Anal. Chim. Acta **562**: 245–251. doi:10.1016/j.aca.2006.01.069

Ketola, R. A., T. Kotiaho, M. E. Cisper, and T. M. Allen. 2002. Environmental applications of membrane introduction mass spectrometry. J. Mass Spectrom. **37**: 457–476. doi:10.1002/jms.327

El Khawand, M., A. T. Crombie, A. Johnston, and others. 2016. Isolation of isoprene degrading bacteria from soils, development of isoA gene probes and identification of the active isoprene-degrading soil community using DNA-stable isotope probing. Environ. Microbiol. **18**: 2743–2753. doi:10.1111/1462-2920.13345

Kieber, R. J., S. Tatum, J. D. Willey, G. B. Avery, and R. N. Mead. 2014. Variability of ethanol and acetaldehyde concentrations in rainwater. Atmos. Environ. **84**: 172–177. doi:10.1016/j.atmosenv.2013.11.038

Kirstine, W., I. Galbally, Y. Ye, and M. Hooper. 1998. Emissions of volatile organic compounds (primarily oxygenated species) from pasture. J. Geo **103**.

Kitidis, V., A. P. Stubbins, G. Uher, R. C. Upstill Goddard, C. S. Law, and E. M. S. Woodward. 2006. Variability of chromophoric organic matter in surface waters of the Atlantic Ocean. Deep. Res. Part II Top. Stud. Oceanogr. **53**: 1666–1684. doi:10.1016/j.dsr2.2006.05.009

Kolb, S. 2009. Aerobic methanol-oxidizing Bacteria in soil. FEMS Microbiol. Lett. **300**: 1–

10. doi:10.1111/j.1574-6968.2009.01681.x

Lewis, A. C., J. R. Hopkins, L. J. Carpenter, J. Stanton, K. A. Read, and M. J. Pilling. 2005. Sources and sinks of acetone, methanol, and acetaldehyde in North Atlantic marine air. Atmos. Chem. Phys. **5**: 1963–1974. doi:10.5194/acp-5-1963-2005

Lide, D. R., and G. Baysinger. 2005. CRC Handbook of Chemistry and Physics, 85th ed. CRC press.

Lindinger, W., A. Hansel, and A. Jordan. 1998a. Proton-transfer-reaction mass spectrometry (PTR–MS): on-line monitoring of volatile organic compounds at pptv levels. Chem. Soc. Rev. **27**: 347. doi:10.1039/a827347z

Lindinger, W., A. Hansel, and A. Jordan. 1998b. On-line monitoring of volatile organic compounds at pptv levels by means of proton-transfer-reaction mass spectrometry (PTR-MS) medical applications, food control and environmental research. Int. J. Mass Spectrom. Ion Process. **173**: 191–241. doi:10.1016/S0168-1176(97)00281-4

Long, G. L., and J. D. Winefordner. 1983. Limit of Detection: A Closer Look at the IUPAC Definition. Anal. Chem. **55**: 713A–724A. doi:10.1021/ac00258a724

Luo, G., and F. Yu. 2010. A numerical evaluation of global oceanic emissions of α-pinene and isoprene. Atmos. Chem. Phys. **10**: 2007–2015. doi:10.5194/acp-10-2007-2010

Mantoura, R. F. C., and E. M. S. Woodward. 1983. Optimization of the indophenol blue method for the automated determination of ammonia in estuarine waters. Estuar. Coast. Shelf Sci. **17**: 219–224. doi:10.1016/0272-7714(83)90067-7

Mao, H., R. Talbot, C. Nielsen, and B. Sive. 2006. Controls on methanol and acetone in marine and continental atmospheres. Geophys. Res. Lett. **33**: 1–4. doi:10.1029/2005GL024810

Marandino, C. A., W. J. de Bruyn, S. D. Miller, M. J. Prather, and E. S. Saltzman. 2005. Oceanic uptake and the global atmospheric acetone budget. Geophys. Res. Lett. **32**: 2–5. doi:10.1029/2005GL023285

McGenity, T. J., A. T. Crombie, and J. C. Murrell. 2018. Microbial cycling of isoprene, the

most abundantly produced biological volatile organic compound on Earth. ISME J. doi:10.1038/s41396-018-0072-6

van Meeningen, Y., G. Schurgers, R. Rinnan, and T. Holst. 2016. BVOC emissions from English oak (Quercus robur) and European beech (Fagus sylvatica) along a latitudinal gradient. Biogeosciences **13**: 6067–6080. doi:10.5194/bg-13-6067-2016

Mendes, M. A., M. N. Eberlin, T. Kotiaho, and others. 2000. Trace level analysis of VOCs and semi-VOCs in aqueous solution using a direct insertion membrane probe and trap and release membrane introduction mass spectrometry. Analyst **125**: 21–24. doi:10.1039/a908654d

Millet, D. B., A. Guenther, D. a. Siegel, and others. 2010. Global atmospheric budget of acetaldehyde: 3-D model analysis and constraints from in-situ and satellite observations. Atmos. Chem. Phys. **10**: 3405–3425. doi:10.5194/acp-10-3405-2010

Millet, D. B., D. J. Jacob, T. G. Custer, and others. 2008. New constraints on terrestrial and oceanic sources of atmospheric methanol. Atmos. Chem. Phys. Discuss. **8**: 7609–7655. doi:10.5194/acpd-8-7609-2008

Mincer, T. J., and A. C. Aicher. 2016. Methanol production by a broad phylogenetic array of marine phytoplankton. PLoS One **11**: 1–17. doi:10.1371/journal.pone.0150820

Monson, R. K. 2010. Reactions of Biogenic Volatile Organic Compounds in the Atmosphere. Chem. Biol. Volatiles 363–388. doi:10.1002/9780470669532.ch14

Mopper, K., and D. J. Kieber. 1991. Distribution and biological turnover of dissolved organic compounds in the water column of the Black Sea. Deep. Res. Part I-Oceanographic Res. Pap. **38**: S1021–S1047. doi:10.1016/S0198-0149(10)80022-6

Mopper, K., and W. L. Stahovec. 1986. Sources and sinks of low molecular weight organic carbonyl compounds in seawater. Mar. Chem. **19**: 305–321. doi:10.1016/0304-4203(86)90052-6

Müller, J.-F., T. Stavrakou, S. Wallens, and others. 2008. Global isoprene emissions estimated using MEGAN, ECMWF analyses and a detailed canopy environment model. Atmos. Chem. Phys. **8**: 1329–1341. doi:10.5194/acpd-7-15373-2007

National Hydrological Monitoring Programme: NERC Centre for Ecology & Hydrology, M. O. 2014. Average outflow and total rainfall for the United Kingdom: 1980 to 2013.

National Oceanography Centre. 2020. LOCATE Homepage.

Nemecek-Marshall, M., C. Wojciechowski, J. Kuzma, G. M. Silver, and R. Fall. 1995. Marine Vibrio species produce the volatile organic compound acetone. Appl. Environ. Microbiol. **61**: 44–47.

Nightingale, P. D. 1991. Low molecular weight halocarbons in seawater. University of East Anglia: Norwich, UK.

Orr, R. J., and H. Leverne Williams. 1951. The polymerization of isoprene and 2,3-dimethylbutadiene and copolymerization with styrene at -. Can. J. Chem. **30**: 108–122.

Palmer, P. I., and S. L. Shaw. 2005. Quantifying global marine isoprene fluxes using MODIS chlorophyll observations. Geophys. Res. Lett. **32**: 1–5. doi:10.1029/2005GL022592

Parry, L. E., and D. J. Charman. 2013. Modelling soil organic carbon distribution in blanket peatlands at a landscape scale. Geoderma **211**–**212**: 75–84. doi:10.1016/j.geoderma.2013.07.006

Peñuelas, J., and J. Llusià. 2003. BVOCs: Plant defense against climate warming? Trends Plant Sci. **8**: 105–109. doi:10.1016/S1360-1385(03)00008-6

Pfister, G. G., L. K. Emmons, P. G. Hess, and others. 2008. Contribution of isoprene to chemical budgets: A model tracer study with the NCAR CTM MOZART-4. J. Geophys. Res. Atmos. **113**. doi:10.1029/2007JD008948

Qin, T., X. Xu, V. Pacáková, K. Štulík, and L. Jech. 1997. A simple method for the trace determination of methanol, ethanol, acetone and pentane in human breath and in the ambient air by preconcentration on solid sorbents followed by gas chromatography. Talanta **44**: 1683–1690. doi:10.1016/S0039-9140(97)00073-8

Rathgeb, A., T. Causon, R. Krachler, and S. Hann. 2017. From the peat bog to the estuarine mixing zone: Common features and variances in riverine dissolved organic matter

determined by non-targeted analysis. Mar. Chem. **194**: 158–167. doi:10.1016/j.marchem.2017.06.012

Read, K. A., L. J. Carpenter, S. R. Arnold, and others. 2012. Multiannual observations of acetone, methanol, and acetaldehyde in remote tropical Atlantic air: Implications for atmospheric OVOC budgets and oxidative capacity. Environ. Sci. Technol. **46**: 11028–11039. doi:10.1021/es302082p

Rosado-Reyes, C. M., and J. S. Francisco. 2007. Atmospheric oxidation pathways of propane and its by-products: Acetone, acetaldehyde, and propionaldehyde. J. Geophys. Res. Atmos. **112**. doi:10.1029/2006JD007566

Rowland C.S.;Morton, R. D. ;Carrasc. L. ;McShan. G. ;O'Nei. A. W. ;Woo. C. M. 2017. Land Cover Map 2015 (vector, GB).doi:10.5285/6c6c9203-7333-4d96-88ab-78925e7a4e73

Sargeant, S. L., J. C. Murrell, P. D. Nightingale, and J. L. Dixon. 2018. Basin-scale variability of microbial methanol uptake in the Atlantic Ocean. 1–28.

Sargeant, S. L., J. C. Murrell, P. D. Nightingale, and J. L. DIxon. 2016. Seasonal variability in microbial methanol utilisation in coastal waters of the western English Channel. Mar. Ecol. Prog. Ser. **550**: 53–64. doi:10.3354/meps11705

Schlundt, C., C. A. Marandino, S. Tegtmeier, S. T. Lennartz, A. Bracher, W. Cheah, K. Krüger, and B. Quack. 2017. Oxygenated volatile organic carbon in the western Pacific convective centre: ocean cycling, air-sea gas exchange and atmospheric transport. Atmos. Chem. Phys. Discuss. 1–29. doi:10.5194/acp-2017-9

Schwarz, K., W. Filipiak, and A. Amann. 2009. Determining concentration patterns of volatile compounds in exhaled breath by PTR-MS. J. Breath Res. **3**. doi:10.1088/1752-7155/3/2/027002

Seco, R., J. Peñuelas, and I. Filella. 2007. Short-chain oxygenated VOCs: Emission and uptake by plants and atmospheric sources, sinks, and concentrations. Atmos. Environ. **41**: 2477–2499. doi:10.1016/j.atmosenv.2006.11.029

Sharkey, T. D., and R. K. Monson. 2017. Isoprene research - 60 years later, the biology is still enigmatic. Plant. Cell Environ. 1–8. doi:10.1111/pce.12930

Shaw, S. L. 2001. The Production of Non-Methane Hydrocarbons by Marine Plankton. Massachusetts Institute of Technology.

Shaw, S. L., S. W. Chisholm, and R. G. Prinn. 2003. Isoprene production by Prochlorococcus, a marine cyanobacterium, and other phytoplankton. Mar. Chem. **80**: 227–245. doi:10.1016/S0304-4203(02)00101-9

Shaw, S. L., B. Gantt, and N. Meskhidze. 2010. Production and Emissions of Marine Isoprene and Monoterpenes: A Review. Adv. Meteorol. **2010**: 1–24. doi:10.1155/2010/408696

Sims, R. P., U. Schuster, A. J. Watson, M. X. Yang, F. E. Hopkins, J. Stephens, and T. G. Bell. 2017. A measurement system for vertical seawater profiles close to the air/sea interface. Ocean Sci. Discuss. 1–23. doi:10.5194/os-2017-7

Singh, H. B., M. Kanakidou, P. J. Crutzen, and D. J. Jacob. 1995. High concentrations and photochemical fate of oxygenated hydrocarbons in the global troposphere. Nature **378**: 50–54. doi:10.1038/378050a0

Singh, H. B., D. O ’hara, D. Herlth, W. Sachse, D. R. Blake, J. D. Bradshaw, M. Kanakidou, and P. J. Crutzen. 1994. Acetone in the atmosphere: Distribution, sources, and sinks. J. Geophys. Res. **99**: 1805–1819. doi:10.1029/93JD00764

Singh, H. B., L. J. Salas, R. B. Chatfield, and others. 2004. Analysis of the atmospheric distribution, sources, and sinks of oxygenated volatile organic chemicals based on measurements over the Pacific during TRACE-P. J. Geophys. Res. D Atmos. **109**. doi:10.1029/2003JD003883

Singh, H., Y. Chen, A. Tabazadeh, and others. 2000. Distribution and fate of selected oxygenated organic species in the troposphere and lower stratosphere over the Atlantic. J. Geophys. Res. Atmos. **105**: 3795–3805. doi:10.1029/1999JD900779

Sinha, V., J. Williams, M. Meyerhöfer, U. Riebesell, a. I. Paulino, and a. Larsen. 2006. Air-sea fluxes of methanol, acetone, acetaldehyde, isoprene and DMS from a Norwegian fjord following a phytoplankton bloom in a mesocosm experiment. Atmos. Chem. Phys. Discuss. **6**: 9907–9935. doi:10.5194/acpd-6-9907-2006

Steinke, M., B. Hodapp, R. Subhan, T. G. Bell, and D. Martin-Creuzburg. 2018. Flux of the biogenic volatiles isoprene and dimethyl sulfide from an oligotrophic lake. Sci. Rep. **8**. doi:10.1038/s41598-017-18923-5

Takeda, K., S. Katoh, Y. Mitsui, S. Nakano, N. Nakatani, and H. Sakugawa. 2014. Spatial distributions of and diurnal variations in low molecular weight carbonyl compounds in coastal seawater, and the controlling factors. Sci. Total Environ. **493**: 454–462. doi:10.1016/j.scitotenv.2014.05.126

Takeda, K., S. Katoh, N. Nakatani, and H. Sakugawa. 2006. Rapid and highly sensitive determination of low-molecular-weight carbonyl compounds in drinking water and natural water by preconcentration HPLC with 2,4-dinitrophenylhydrazine. Anal. Sci. **22**: 1509–14. doi:JST.JSTAGE/analsci/22.1509 [pii]

Tanimoto, H., S. Kameyama, T. Iwata, S. Inomata, and Y. Omori. 2014a. Measurement of air-sea exchange of dimethyl sulfide and acetone by PTR-MS coupled with gradient flux technique. Environ. Sci. Technol. **48**: 526–533. doi:10.1021/es4032562

Tanimoto, H., S. Kameyama, Y. Omori, S. Inomata, and U. Tsunogai. 2014b. High-Resolution Measurement of Volatile Organic Compounds Dissolved in Seawater Using Equilibrator Inlet-Proton Transfer Reaction-Mass Spectrometry (EI-PTR-MS). West. Pacific Air-Sea Interact. Study 89–115. doi:10.5047/w-pass.a02.001

Taylor, D. G., P. W. Trudgill, R. E. Cripps, and P. R. Harris. 1980. The microbial metabolism of acetone. J. Gen. Microbiol. **118**: 159–170. doi:10.1099/00221287-118-1-159

Tie, X., A. Guenther, and E. Holland. 2003. Biogenic methanol and its impacts on tropospheric oxidants. Geophys. Res. Lett. **30**: 3–6. doi:10.1029/2003GL017167

Tortell, P. D. 2005. Dissolved gas measurements in oceanic waters made by membrane inlet mass spectrometry. Limnol. Oceanogr. Methods **3**: 24–37. doi:10.4319/lom.2005.3.24

Warneke, C., J. A. De Gouw, W. C. Kuster, P. D. Goldan, and R. Fall. 2003. Validation of atmospheric VOC measurements by proton-transfer-reaction mass spectrometry using a gas-chromatographic preseparation method. Environ. Sci. Technol. **37**: 2494–2501. doi:10.1021/es026266i

Warneke, C., T. Karl, H. Judmaier, A. Hansel, A. Jordan, W. Lindinger, and P. J. Crutzen. 1999. Acetone, methanol, and other partially oxidized volatile organic emissions from dead plant matter by abiological processes: Significance for atmospheric HO(X) chemistry. Global Biogeochem. Cycles **13**: 9–17. doi:10.1029/98GB02428

Williams, J., R. Holzinger, V. Gros, X. Xu, E. Atlas, and D. W. R. Wallace. 2004a. Measurements of organic species in air and seawater from the tropical Atlantic. Geophys. Res. Lett. **31**: 1–5. doi:10.1029/2004GL020012

Williams, J., R. Holzinger, V. Gros, X. Xu, E. Atlas, and D. W. R. Wallace. 2004b. Measurements of organic species in air and seawater from the tropical Atlantic. Geophys. Res. Lett. **31**: 1–5. doi:10.1029/2004GL020012

Wohl, C., D. Capelle, A. Jones, W. T. Sturges, P. D. Nightingale, B. G. T. Else, and M. Yang. 2019. Segmented flow coil equilibrator coupled to a proton-transfer-reaction mass spectrometer for measurements of a broad range of volatile organic compounds in seawater. Ocean Sci. **15**: 925–940. doi:10.5194/os-15-925-2019

Worrall, F., M. Reed, J. Warburton, and T. Burt. 2003. Carbon budget for a British upland peat catchment. Sci. Total Environ. **312**: 133–146. doi:10.1016/S0048-9697(03)00226-2

Yang, M., R. Beale, P. Liss, M. Johnson, B. Blomquist, and P. Nightingale. 2014. Air-sea fluxes of oxygenated volatile organic compounds across the Atlantic Ocean. Atmos. Chem. Phys. **14**: 7499–7517. doi:10.5194/acp-14-7499-2014

Yang, M., P. D. Nightingale, R. Beale, P. S. Liss, B. Blomquist, and C. Fairall. 2013. Atmospheric deposition of methanol over the Atlantic Ocean. Proc. Natl. Acad. Sci. U. S. A. **110**: 20034–20039. doi:10.1073/pnas.1317840110

Yates, C. A., P. J. Johnes, and R. G. M. Spencer. 2016. Assessing the drivers of dissolved organic matter export from two contrasting lowland catchments, U.K. Sci. Total Environ. **569**–**570**: 1330–1340. doi:10.1016/j.scitotenv.2016.06.211

Zhang, H.-H., J.-L. Li, G.-P. Yang, Y.-C. Song, and N. Jin. 2015. Purge- trap Gas Chromatography and Mass Spectrometric Method for Analysis of Isoprene in Natural Waters. Chinese J. Anal. Chem. **43**: 333–337. doi:10.1016/S1872-2040(15)60812-X

Zhou, X., and K. Mopper. 1997. Photochemical production of low-molecular-weight carbonyl compounds in seawater and surface microlayer and their air-sea exchange. Mar. Chem. **56**: 201–213. doi:10.1016/S0304-4203(96)00076-X