Volatile organic compounds in the marine troposphere and surface oceans: methods, measurements and biogeochemical implications.

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ABSTRACT

Volatile organic compounds (VOCs), among them non-methane hydrocarbons (NMHCs) and low molecular weight carbonyl compounds (aldehydes and ketones), affect the oxidative capacity of the atmosphere and thus pollutant lifetimes and global climate. VOCs in the surface oceans may be transported into, or derived from, the atmosphere. This thesis describes the development and optimization of chromatographic and preconcentration methods to determine volatile organic compounds (VOCs) in surface seawater and marine air, and their use to explore VOC distribution and fluxes at the sea-air interface. It includes the first measurements of many carbonyl compounds in temperate and subarctic marine waters and the first estimates of fluxes of several aldehydes from the ocean surface into the marine atmosphere.

Sea surface air, size-fractionated marine aerosols, and surface ocean water dissolved organic matter were simultaneously sampled in the Nordic seas. Nineteen C_2-C_7 NMHCs were quantified in the air samples. Site-to-site variability in NMHC concentrations was high, suggesting variable, local sources. The aerosols consisted mainly of inorganic marine material, but a culturable bacterium identified as *Micrococcus luteus* was also isolated from the 9.9 – 18 μm fraction, suggesting organic matter may be transferred from the surface oceans to the atmosphere by marine aerosols. Lastly, a number of VOCs, including acetone, were detected in the seawater samples using solid-phase microextraction (SPME), leading to the subsequent development of an SPME application for carbonyl compounds in seawater.

A mobile, economical and solventless method for the detection and quantification of carbonyl compounds in seawater, a matrix of global importance, was developed. The compounds were derivatized using O-(2,3,4,5,6-pentafluorobenzyl)-hydroxylamine (PFBHA)and then pre-concentrated by SPME for gas chromatography with mass spectrometric (GC/MS) or flame ionization (GC-FID) detection. The method was first optimized for acetone and subsequently for a suite of 23 C_1 – C_9 carbonyl compounds. The buffering capacity of seawater necessitated the use of artificial seawater for standard preparation, and acidification of seawater samples to achieve the method's optimum pH of 3.7. Sparging with UHP argon, and C-18 solid phase extraction of the dissolved PFBHA, were found to be the most effective methods for reducing the high process blanks observed for C_1-C_3 carbonyl compounds.

Using this technique, the first acetone measurements for North Atlantic and Arctic waters (5.5 –9.6 nM acetone), the first surface water measurements of carbonyl compounds from the St. Lawrence Estuary (including glyoxal, methylglyoxal and 2,4-pentanedione), and concentrations of 11 C_1 - C_9 carbonyl compounds in surface seawaters from the Labrador Sea and from the Scotian Shelf were reported. This represents the first survey of these compounds in seawaters outside of the tropics. The results suggest that the North Atlantic is a sink for glyoxal and formaldehyde. Fluxes of several C_4 - C_9 aldehydes from the ocean to the atmosphere were estimated to be -13 to +14 $\mu mol/m^2/day$.

RÉSUMÉ

Les composés organiques volatils (COV), une classe de composés qui inclut les hydrocarbures non méthaniques (HCNM) et les composés carbonylés (aldéhydes et cétones) de faibles masses moléculaires, affectent la capacité oxydante de l'atmosphère et, par consequent, le temps de résidence des polluants de même que le climat à l'échelle globale. Les COV présents dans l'eau de surface océanique peuvent être transferés de l'océan vers l'atmosphère ou vice versa. Cette thèse décrit le développement et l'optimisation de méthodes chromatographiques et de pré-concentration pour la détermination des COV dans l'eau de mer et dans l'air marin, ainsi que leur utilisation dans l'exploration de la distribution des COV et leurs flux à l'interface air-mer. Les premières déterminations de la concentration de plusieurs composés carbonylés dans l'eau de mer tempérée et subarctique, de même que les premières estimations du flux de plusieurs aldéhydes de l'océan vers l'atmosphère marin sont aussi incluses.

L'air de surface, de l'aérosol marin distribué en taille et de la matière organique dissoute présente dans l'eau de mer de surface ont été échantillonnés simultanément dans les mers nordiques. Dix-neuf hydrocarbures non méthaniques de C_2 à C_7 ont été quantifiés dans les échantillons d'air. Une grande variabilité dans les concentrations de HCNM mesurées d'un site à l'autre indique la présence de sources locales et variables. L'aérosol était composé principalement de matière inorganique d'origine marine, mais une bactérie cultivable, *Micrococcus luteus,* a été isolée à partir de la fraction des particules mesurant de 9,9 à 18 μm, ce qui suggère que le matière organique peut être transferée de l'océan à l'atmosphère par l' aérosol marin. De plus, certains COV, dont

l'acétone, ont été détectés dans les échantillons d'eau de mer grâce à la technique de *micro-extraction* sur *phase solide (SPME),* menant au développement ultérieur de cette technique pour la détection des composés carbonylés dans l'eau de mer.

Une méthode portative, économique et sans solvant a été développée pour la détermination des composés carbonylés dans l'eau de mer, une matrice environnementale d'une importance globale. Les composés sont dérivatisés au PFBHA (O-(2,3,4,5,6-pentafluorobenzyle)-hydroxylamine), pré-concentrés par SPME et analysés par chromatographie en phase gazeuse avec détection par spectrométrie de masse ou par ionisation à la flamme. La méthode a d'abord été optimisée pour la détection de l'acétone, puis adaptée pour la détection simultanée de 23 composés carbonylés de C_1 à C_9. La capacité tampon de l'eau de mer rend nécessaire l'utilisation d'eau de mer artificielle dans la préparation des solutions étalons. Il est aussi nécessaire d'acidifier les échantillons d'eau de mer afin d'atteindre un pH optimal de 3,7. Le barbotage d'argon ainsi que l'extraction sur phase solide (C-18) ont été jugées les méthodes les plus efficaces pour réduire les concentrations de composés carbonylés de C_1 à C_3 dans les analyses des blancs.

Cette technique a permis de mesurer la concentration d'acétone dans les eaux de l'Atlantique Nord et de l'océan Arctique (5.5 – 9.6 nM d'acétone) pour la première fois, la concentration de composés carbonylés dans les eaux de surface de l'estuaire du Saint-Laurent (incluant le éthanedial, le 2-oxopropanal et l'acétylacétone), aussi pour la première fois; et les concentrations de 11 composés carbonylés de C_1 à C_9 dans les eaux de surface de la mer du Labrador et du plateau néo-écossais (constituant les premières

déterminations à l'extérieur des tropiques). Les résultats indiquent que l'Atlantique Nord est un puits pour l'éthanedial et pour le formaldéhyde. Les flux de l'océan vers l'atmosphère de quelques aldéhydes de C_4 à C_9 ont été estimés entre -13 et +14 $\mu mol/m^2/jour$.

Dedication

To my parents, Dr. James Hudson (1940-2002) and Johanna Hudson, who were the first scientists and teachers to inspire me, and to my siblings Helen and Dave, in whom I see them reflected.

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And lastly, my fellow bike mechanics, for reminding me that anything can be fixed with a little creativity, duct tape or a hammer, and my fellow rock climbers, for reminding me that it’s OK to attempt a climb, fall 15 feet while doing so, and go back and try it again. Analogies with research “will be left as an exercise for the reader”.

Table of Contents

List of Figures

List of Tables

List of Abbreviations

ANOVA	analysis of variance
BSW	buffered salt water (artificial seawater)
CCGS	Canadian Coast Guard Ship
CTD	conductivity-temperature-depth sensor
DMS	dimethylsulfide
DNPH	2,4-dinitrophenylhydrazine
DOC	dissolved organic carbon
DOM	dissolved organic matter
DVB	divinylbenzene
ECD	electron capture detector
EDX	energy-dispersive X-ray spectroscopy
EI	electron (impact) ionization
F/S	*Forschungsschiff* (research ship)
FSOT	fused silica open tubular
GC	gas chromatography
GC-FID	gas chromatography-flame ionization detection
GC-MS	gas chromatography-mass spectrometry
H	Henry's Law constant
HPLC	high performance liquid chromatography
K*	apparent (air-water) partition coefficient
LoD	limit of detection
MBL	marine boundary layer
MOUDI	multi-orifice uniform deposit impactor
MSD	mass selective detector
NMHC	non-methane hydrocarbons

PBL	planetary boundary layer
PDMS	polydimethylsiloxane
PFB	pentafluorobenzyl
PFBHA	O-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine
PLOT	porous layer open tubular
ppb(v)	parts per billion (volume)
ppm(v)	parts per million (volume)
ppt(v)	parts per trillion (volume)
PTR-MS	proton transfer reaction-mass spectrometry
RV	research vessel
SD	standard deviation
SE	standard error
SEM	scanning electron microscopy
SPE	solid phase extraction
SPME	solid phase microextraction
SOA	secondary organic aerosol(s)
SSML	sea surface microlayer
τ	photochemical lifetime
TOC	total organic carbon
VOC	volatile organic compounds

Contributions of Authors

Since each substantive chapter (besides the introduction and conclusions) constitutes a published or submitted manuscript or a manuscript in preparation, the contributions of individual authors to these manuscripts are delineated here**.**

Chapter 2

E.D. Hudson took the air, seawater and aerosol samples, designed and conducted the experiments/analyses on NMHCs in air, surface water DOC, and SEM/EDX of marine aerosols, and wrote the manuscript. P.A. Ariya edited/provided critical comments on the manuscript and on the experimental design and execution. *Microccocus luteus* was cultured by Dr. Roya Mortazavi, with the assistance of E.D. Hudson, and the PCR performed and the RNA sequenced at McGill's Sheldon Biotechnology Center. The entirety of the work was performed with the guidance of P.A. Ariya.

Chapter 3

The experimental work was designed and performed by E.D. Hudson and summer research assistant K. Okuda, some of which was later repeated by E. D. Hudson. E.D. Hudson wrote much of the manuscript; K. Okuda contributed the first draft of the introduction and of some material in the sections (all in 'Results and Discussion') 'Comparison of SPME fibres (adsorbents)', 'Sample and headspace volume', and 'derivatization time', as well as the data for Figure 3-6. The entire work was performed under the guidance of P.A. Ariya, who also provided critical and editorial comments on the manuscript.

Chapter 4

E.D. Hudson, under the guidance of P.A. Ariya, designed and conducted all experiments related to the development and optimization of the SPME method, performed the analysis of samples from the St. Lawrence Estuary, and wrote the manuscript. P.A. Ariya edited and provided critical comments on the manuscript and on the experimental design and execution. Y. Gélinas provided the samples from the St. Lawrence Estuary, analyzed these for dissolved organic carbon concentration, and provided ancillary oceanographic data (temperature, salinity, pH, estimated algal concentrations) and critical comments on the manuscript.

Chapter 5

E.D. Hudson took the seawater samples in the Labrador Sea and on the Scotian Shelf, and, under the guidance of P.A. Ariya, designed and conducted the sample analyses and wrote the manuscript. P.A. Ariya edited and provided critical comments on the manuscript and on the experimental design and execution.

Chapter 1. Introduction

Numerous volatile organic compounds (VOCs) occur in marine air and in surface seawaters at low parts-per-trillion (volume) (pptv) to parts-per-billion (volume) (ppbv) abundances (1 ppbv = 2.45×10^{10} molecule cm^{-3} = 44.6 pmol L^{-1} at standard temperature and pressure). The atmosphere interfaces directly with the oceans over 71% of the earth's surface, and the exchange of material between them is a critical determinant of global climate, for example by the formation of aerosols (including those with cloud nucleating ability) from substances originating in surface ocean waters. Whereas VOC budgets constitute only a small fraction, by mass, of the global carbon cycle, they play critical roles in atmospheric chemistry through oxidant formation and destruction. Figure 1-1 shows some of the processes involving VOCs which link the atmosphere and the ocean surface.

The definition of VOCs is somewhat subjective and contextual; Seinfeld and Pandis [1] refer to any "vapour phase atmospheric organics" (p. 80) as VOCs. Other authors define VOCs as organic compounds which can be readily vapourized without decomposition at room temperature, which have vapour pressures greater than that of water, or which evaporate from water under environmental conditions [2]. Methane is sometimes excluded from the definition [3], due to its higher concentration (parts per million) and considerably longer lifetime (9 years) [4] than most VOCs (the term nonmethane volatile organic compounds- NMVOCs- is sometimes used [5]). Atmospheric VOCs include hydrocarbons, alcohols, aldehydes and ketones, halocarbons, esters, alkyl nitrates and organosulfur compounds (such as dimethylsulfide, or DMS).

This thesis focuses on measurement methodologies and measurements of two interrelated classes of VOCs, non-methane hydrocarbons (NMHCs) and low molecular weight aldehydes and ketones, at the interface between the atmosphere and the oceans, and their potential links to other parts of the marine carbon cycle. The sections that follow describe in more detail their sources, roles in seawater and in the lowest hundreds of meters to 1 km of the atmosphere which is in direct, turbulent contact with the ocean surface (the marine boundary layer, MBL), and their typical occurrence and concentrations in surface seawaters and marine air, to the extent that these have been reported, as well as current techniques for their determination and the challenges typically associated with these.

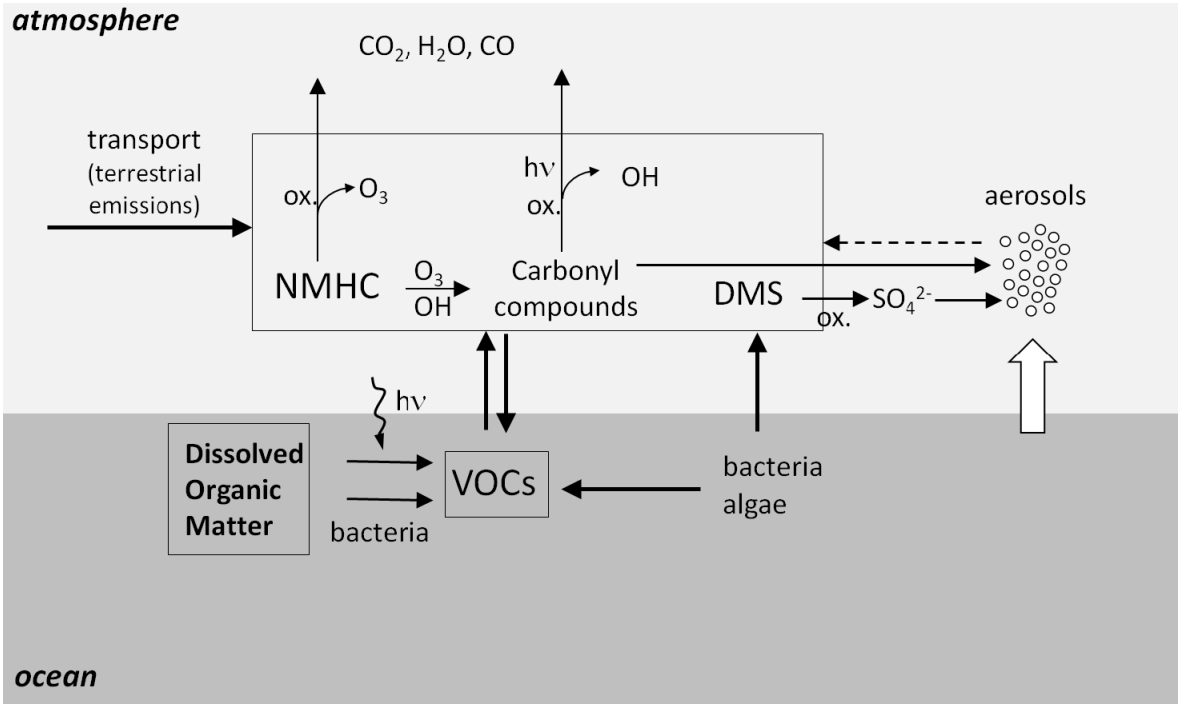


Figure 1-1. Interrelationships between and among VOCs in the surface oceans and the marine troposphere, including their sources and sinks. ox. = unspecified oxidation processes

1.1 Volatile organic compounds in the surface oceans

The surface oceans, generally defined as the top ~ 100 m of the water column [6-7], are those waters which are in contact with the atmosphere on timescales of hours to weeks (as opposed to deep waters, which are considered to be isolated from the atmosphere for up to 1500 years). They are therefore the waters which have an immediate impact on the composition and chemistry of the local or global atmosphere, and which are conversely affected by constituents of the atmosphere. Surface seawaters also receive sufficient light penetration to support photosynthesis.

VOCs which have been measured in surface seawaters include many halocarbons, methyl nitrate, sulfur compounds, hydrocarbons and carbonyl compounds. Methyl chloride, bromide and iodide [8-12] have significant marine sources, including production by algae and abiotic photochemistry. Methyl nitrate produced in the oceans [13] may be an important source of reactive nitrogen (NO) in the remote marine troposphere [14]. Picomolar concentrations of non-methane hydrocarbons typically occur in surface waters. Sulfur compounds including carbon disulfide (CS_2) [15-16] and DMS [17] are emitted from the oceans; DMS and its precursor dimethyl sulfopropionate (DMSP) are produced by marine bacteria and are thought to influence climate through their conversion to sulfate aerosols which act as cloud condensation nuclei, increasing cloud albedo (reflectivity) over the oceans [17-18]. Lastly, low molecular weight carbonyl compounds including aldehydes and ketones have been measured in seawater at high picomolar to low nanomolar concentrations [19-20].

1.2 Sources, distribution and chemistry of volatile organic compounds in the marine atmosphere

The concentration of any chemical species in the atmosphere is influenced by emission, by chemistry (production or loss), by advective (bulk fluid) transport and by deposition (wet or dry) [21]; these same processes influence the distribution of a chemical species in the oceans, although gravitational deposition would only occur for compounds associated with sedimenting particles. The sections below discuss the physical behavior and properties of the atmosphere and oceans which must be taken into account in determining the distribution and chemistry of VOCs in the environment.

1.2.1 Physical influences on the occurrence and distribution of VOCs

1.2.1.1 Atmospheric dynamics and the transport of VOCs

Atmospheric dynamics (the motion and thermodynamic state of the atmosphere [22]) influences the distribution and concentration of VOCs. Both diffusion and gravitational sedimentation contribute negligibly to the movement of chemical species in the troposphere [21-23] (the lowest layer of the atmosphere, in direct contact with the Earth's surface, which extends up to 7-17 km altitude and in which temperature generally decreases with height). The distribution of chemical species in the atmosphere will thus depend on larger-scale dynamical processes as well as on (photo)chemical reactivity, and is often an indication of how the timescales for transport and chemistry compare. Vertical mixing occurs readily in the troposphere, in particular in the planetary boundary layer (PBL), the layer of the troposphere immediately adjacent to the surface in which

surface friction and topography lead to turbulent mixing on timescales of hours or less [22]. Convection typically mixes the entire height of the troposphere in 1-2 days [22], although strong convection in the intertropical convergence zone (ITCZ)- within 10° latitude of the equator- may cause transport of VOCs from the sea surface to the tropopause (top of the troposphere) within hours [23]. Thus VOCs are typically homogeneously distributed in the troposphere.

Due to the larger distances involved in horizontal transport, and the lack of consistent convective instability, horizontal mixing times for chemical species are considerably greater than vertical mixing times, leading to potentially much greater variability in concentrations [21-22], especially for short-lived species such as isoprene [24-25]. Zonal (longitudinal) intercontinental transport of air masses typically requires *ca.* 1 week [22]. Thus, for a species to be uniformly distributed longitudinally requires 1-2 months [4] and an atmospheric lifetime of several weeks or greater [22]. Meridional (latitudinal) transport occurs on longer timescales, typically months [21-23]. Interhemispheric transport (across the equator) typically requires 1-2 years [21], which may lead to substantial differences in the concentration of VOCs between hemispheres, especially since the amount of human and industrial activity, and the distribution of natural sources of VOCs including terrestrial plants and the oceans, differ substantially between hemispheres.

The time scales of chemistry and physical transport in the troposphere are comparable and both may influence a compound's distribution. These complexities require "frequent, accessible measurement" (Kley, p. 1044 [23]) of compounds of interest to properly establish their distribution and behavior.

1.2.1.2 Gas exchange across the sea surface

As noted previously, numerous VOCs have been measured in surface seawaters. For bulk gas and liquid (solution) phases in contact, the concentration of a gaseous or volatile compound in each phase, at equilibrium, will be determined by Henry's Law (equation 1-1).

$$C_X = H_X P_X \qquad (1\text{-}1)$$

The concentration of the gas X in solution (C_X) is proportional to its partial pressure P_X (or strictly, its fugacity) in the gas phase and to the Henry`s Law constant H (sometimes denoted $K_{H,X}$) , in M atm^{-1} or mol kg^{-1} atm^{-1} , which is temperature- and salinity-dependent.

When seawater concentrations and atmospheric partial pressure for a particular gas are out of equilibrium, a flux *F* of the gas out of or into the ocean will result. The flux is dependent on the gas concentration in the air (C_a) and liquid (C_l) [26] according to

$$F = K_l (C_a/H - C_l) \qquad (1\text{-}2)$$

which may also be depicted as [7]

$$F = G \cdot ([C_l]-[C_{sat}]) \qquad (1\text{-}3)$$

where G represents a mass transfer coefficient normalized to surface area [7] in m day^{-1}, and C_{sat} is the saturation concentration. As depicted here, the constant K_l represents

resistance to mass transfer in the liquid phase, which may be modelled in various ways. Two of the most common are the thin film (or stagnant boundary layer) model and the surface renewal model (Fig. 1-2). While a diffusive, interfacial layer can be considered

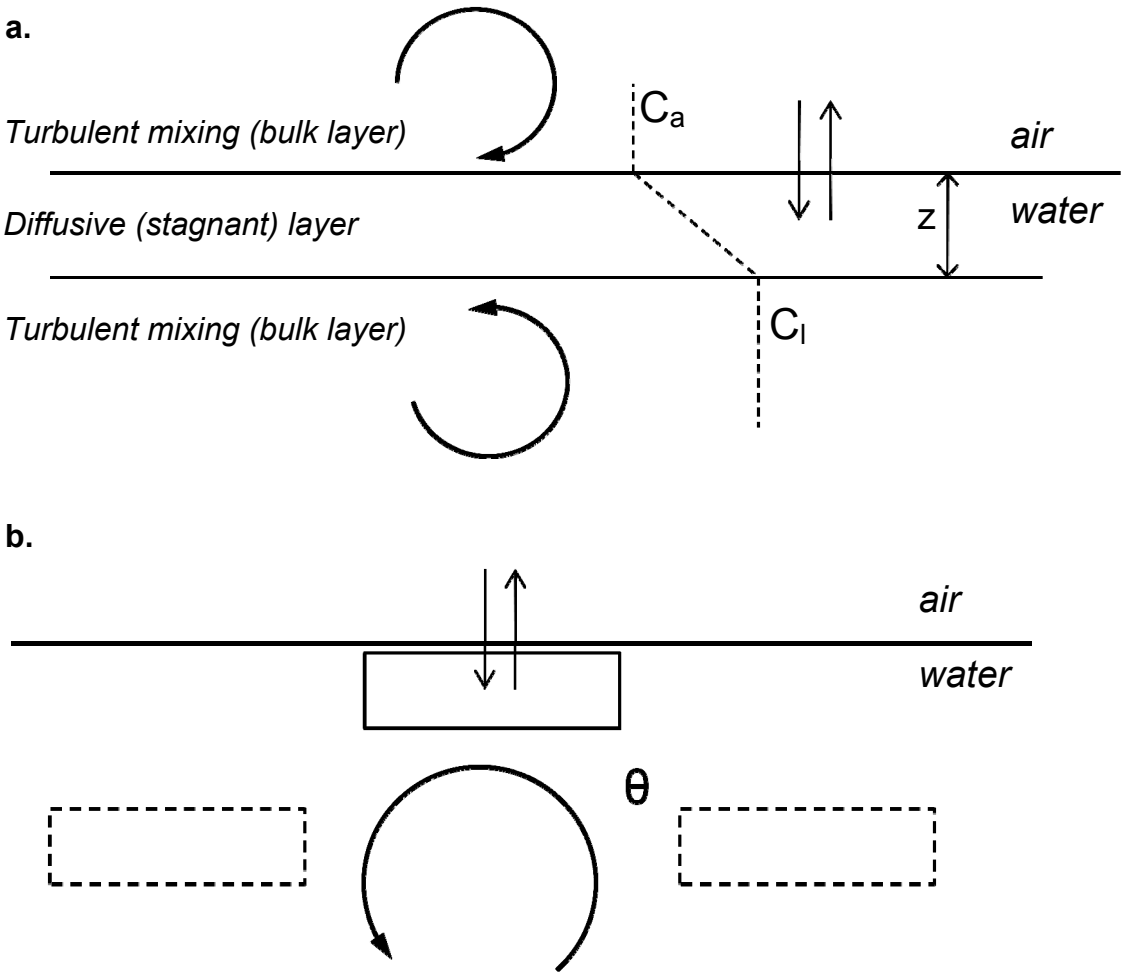


Figure 1-2. Models for the transfer of gases/volatile compounds at the sea-air interface. a. Thin film model. b. Surface renewal model, showing renewal of surface parcel with frequency θ. After Emerson & Hedges [7], Libes [27] and Liss & Slater [26].

to exist on both sides of the air-water interface [26], diffusion in the gas phase is much faster than in the liquid phase and thus both models regard the effect of any gas diffusive layer as negligible and treat the air as being entirely turbulent (well mixed). In the thin film model, the flux is controlled by diffusion according to a diffusion coefficient *D* across a static, diffusive liquid layer of thickness *z*:

$$F = \frac{D}{z}(C_l - C_a) \qquad (1\text{-}4)$$

The film thickness *z* is 10 to 60 μm [27] (typically 20- 40 μm [7]), depends on a number of factors including wind speed, and may be determined by, among others, radiochemical and dual tracer methods [7, 28]. The ratio D/z, known as the piston velocity, is a mass transfer coefficient similar to that in equation 1-3. While conceptually straightforward, the thin film model performs poorly in predicting the effect of wind speed on gas transfer [7].

The surface renewal model [27, 29] views the sea surface as consisting of parcels or slabs of water which turbulent mixing transports to the surface. While at the surface, the gas concentration at the top of the slab, $C_{l\,(top)}$, equilibrates with the atmosphere, while the concentration at the bottom of the slab remains that of bulk seawater, C_l [27]. The overall flux is then determined by θ, the frequency of slab replacement (renewal) at the surface, according to

$$F = \sqrt{\frac{D}{\theta}}(C_{l(top)} - C_l) \qquad (1\text{-}5)$$

These descriptions of gas transfer across the sea surface are further complicated by other factors including bubble processes, thermal mixing, and the effect of the sea surface microlayer.

The action of breaking waves entrains air bubbles into surface waters, and injection of, or gas exchange with, these bubbles leads to supersaturation of gases in surface waters, even though there may in fact be no net flux of gases from the ocean to the atmosphere in the region. Emerson and Hedges [7] summarize this steady state as

$$F_{AWI} = (-)F_B = G_C([C]-[C_{sat}]) \qquad (1\text{-}6)$$

The (outward) sea-air flux F_{AWI} is balanced by the injection or transfer from bubbles F_B, and is equal to $G_C([C]-[C_{sat}])$ (see equation 1-3), giving a supersaturated concentration C. Injection (complete dissolution) of bubbles or influx of gases from bubbles results from the hydrostatic overpressure at the depth to which bubbles are entrained; at 1 m depth this is already 0.1 atm greater than at the sea surface [7].

Mixing of two water masses of different temperatures, each saturated in a trace gas with respect to the atmosphere, will produce a supersaturated water mass, due to the non-linear dependence of gas solubility on temperature [7, 30]. Similarly, seasonal cooling of ocean waters may lead to supersaturated waters if it occurs faster than outgassing and re-equilibration with the atmosphere can occur [30]. In these cases, the

net result will still eventually be transfer of gases from the ocean to the atmosphere. However, Moore [30] (reporting on dichloromethane in the surface Atlantic Ocean) cautions that supersaturation of trace gases in surface waters do not necessarily imply *in situ* marine chemical or biological sources and could instead have resulted from the physical processes described above, with the gas being earlier derived from the atmosphere itself.

The final complicating influence discussed here is that of the sea surface microlayer (SSML) which occurs at the ocean surface, is typically tens of micrometers thick and is enriched in organic and biological material. For inert gases or for the major constituents of the atmosphere, the main influence of an organic microlayer on the ocean surface is in attenuating wave action (and thus also bubble entrainment) at a given wind speed. These gases typically diffuse through organic (hydrophobic) solutions faster than through water and thus the organic microlayer imposes no additional diffusive barrier [7]. However, the SSML may be enriched in VOCs relative to the underlying bulk seawater [20] and may thus facilitate their transfer between the oceans and the atmosphere.

1.2.2 Sources and chemistry of VOCs in marine air

1.2.2.1 Oxidation of VOCs

Oxidation by the hydroxyl radical, OH·, is the principal chemical loss mechanism of VOCs in the troposphere [31-32], although VOC oxidation by halogen radicals (Cl· and Br·) may also be important in polar and marine environments [33] and NO_3· can contribute significantly to nighttime oxidation [32, 34]. For alkenes, the reaction with O_3 may also be an important loss process, comparable to the reaction with OH [5]. Lifetimes

of VOCs against oxidation are the major factors (along with transport) influencing their distribution, although certain VOCs may themselves lead to the formation of oxidants. The major tropospheric source of OH· is

$$O_3 \xrightarrow{h\nu} O_2 + O(^1D) \qquad (1\text{-}7)$$

$$H_2O + O(^1D) \rightarrow 2OH\cdot \qquad (1\text{-}8)$$

Thus, assuming a steady state concentration of OH·, VOC oxidation kinetics can be treated as first order, and the oxidation lifetime of a VOC in the troposphere, τ, can be defined as

$$\tau_{OH} = \frac{1}{k_{OH}[OH\cdot]} \qquad (1\text{-}9)$$

with respect to OH· oxidation. Lifetimes with respect to other, or several, oxidants can be similarly expressed. For example, when tropospheric ozone (O_3) and OH· both oxidize the VOC directly, equation 1-10 applies.

$$\tau_{OH,\,O_3} = \frac{1}{k_{OH}[OH\cdot] + k_{O_3}[O_3]} \qquad (1\text{-}10)$$

Table 1-1 shows the expected lifetime of selected VOCs, focusing on NMHCs and carbonyl compounds, the principal foci of this work, although several other compounds are included for comparison. For certain carbonyl compounds, direct photolysis is also an important loss pathway [31]. Furthermore, in the MBL, these

Table 1-1. Tropospheric chemical lifetimes for selected VOCs at 25 °C. Data are from Warneck [5] and include OH· and O_3 oxidation, based on rate constants from Atkinson [35], except [a] calculated from data of Atkinson [31] (including loss by photolysis).

Substance	τ (days)
Aliphatic hydrocarbons	
ethane	56
ethene (ethylene)	1.4
ethyne (acetylene)	18
propane	12
propene	0.4
n-butane	5.7
i-butane	6.2
n-pentane	3.7
isoprene	0.1
Aromatic hydrocarbons	
benzene	12
toluene	2.4
Carbonyl compounds	
formaldehyde[a]	0.14
acetaldehyde[a]	0.35
benzaldehyde	1.1
acetone[a]	28
glyoxal[a]	0.18
methylglyoxal[a]	0.07
Other oxygenates	
methanol	15
ethanol	4.4
formic acid	30

lifetime values must be considered upper limits, since they do not include oxidation by Cl·.

Since dilution of an air parcel will affect the concentrations of all VOCs equally, but the relative rates of VOCs' reactions with oxidants will affect them differently, changes in concentrations of VOCs relative to each other can be used to distinguish the roles and relative (or even absolute) concentrations of different oxidizing species in the troposphere. These oxidants determine the atmospheric lifetime and fates of many other substances of atmospheric interest, including mercury, persistent organic pollutants, and methane. Spatial and temporal patterns of in the mixing ratios of reactive NMHC in the troposphere may provide information about oxidative efficiency [36]. A variety of approaches to comparing the importance of different
oxidizing radicals, or to calculating radical concentrations, are possible [37-41]; the approach below is described by Rudolph *et al.* [39] and Arsene *et al.* [38]

For simultaneous oxidation of NMHCs A, B and C, in an air parcel undergoing only dilution with 'clean' background air, the logarithms of their concentrations should be linearly related by

$$\ln\left(\frac{[A]}{[C]}\right) = a \ln\left(\frac{[B]}{[C]}\right) + b \qquad (1\text{-}11)$$

If oxidation is by both OH· and Cl· radicals, the slope $\alpha_{Cl,\ OH}$ will depend on the rate constants for the reactions of the NMHCs with OH· and Cl·, by

$$a_{Cl,\ OH} = \left(\frac{(k_{OH})_C + r(k_{Cl})_C - (k_{OH})_A - r(k_{Cl})_A}{(k_{OH})_C + r(k_{Cl})_C - (k_{OH})_B - r(k_{Cl})_B}\right) \qquad (1\text{-}12)$$

in which *r* is the ratio [Cl·]/[OH·]. Rearranging gives

$$\frac{[Cl\cdot]}{[OH\cdot]} = \frac{a_{Cl,OH}((k_{OH})_C-(k_{OH})_B)+(k_{OH})_A-(k_{OH})_C}{a_{Cl,OH}((k_{Cl})_B-(k_{Cl})_C)+(k_{Cl})_C-(k_{Cl})_A} \qquad (1\text{-}13)$$

which allows the ratio of [Cl·]/[OH·] to be determined by plotting logarithms of the ratios of suitable hydrocarbon pairs. To determine an absolute [Cl·], [OH·] can first be estimated from the decay with time (*t*) of a suitable hydrocarbon ('D') assuming only OH· oxidation [38], as per equation 1-14.

$$\ln\left(\frac{[D]_0}{[D]}\right) = k_{OH}[OH\cdot]t \qquad (1\text{-}14)$$

Using these methods, the relative variation of several NMHCs at a Cretan coastal site was used to calculate a [OH·] of (1.3-4.0) × 10^6 cm^{-3} and [Cl·] of (0.6-4.7) × 10^4 cm^{-3} over the Eastern Mediterranean [38]. These methods assume steady state oxidant concentrations in the air mass under study, and yield results which represent an average concentration over the time period 0 to *t*.

1.2.2.2. Non-methane hydrocarbons

NMHCs are principal players in tropospheric ozone formation and have played a role in the general increase in tropospheric ozone concentration over the past century [34]. Their atmospheric lifetimes vary from many days to mere hours, with carbon number, degree of unsaturation, and aromaticity being among the factors which influence

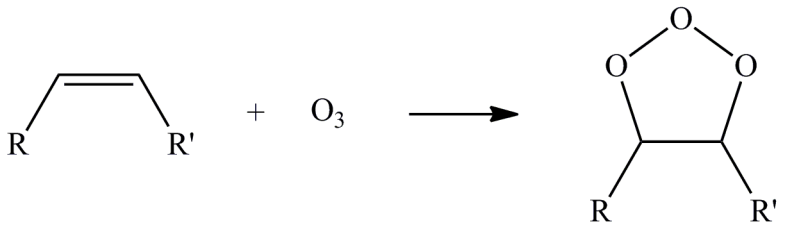
their rate constants with respect to oxidation by OH· and other oxidants (Table 1-1) [36]. NMHCs in the marine boundary layer may come from anthropogenic or natural continental sources, in the case of longer-lived hydrocarbons such as ethane [42]; these include biomass burning and natural gas exploitation. Alkenes in the MBL are more likely to be emitted from the oceans themselves. Low molecular weight alkenes are produced upon the irradiation of dissolved organic matter in seawater [43-45]; ethene and ethane may result from the breakdown of lipids from plankton [46]. Isoprene and monoterpenes produced by algae are also emitted to the marine troposphere [47-49].

In the MBL, alkanes are most likely to undergo OH· oxidation, via

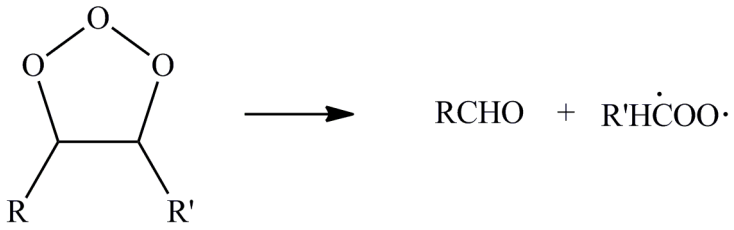
$$RH + OH\cdot \rightarrow R\cdot + H_2O \qquad (1\text{-}15)$$

$$R\cdot + O_2 + M \rightarrow RO_2\cdot + M \qquad (1\text{-}16)$$

where M is an inert molecule (such as N_2) which stabilizes the products by removing energy [4]. This process leads eventually to the formation of aldehydes and ketones (see equations 1-19 to 1-22). Alkenes, in addition to oxidation by OH·, may also react with ozone via [5]



(1-17)



(1-18)

The diradical produced in equation 1-18 (the so-called Criegee intermediate) may decompose by routes leading to CO_2, CO, hydroperoxide radicals (R'COOH) or odd hydrogen ($HO\cdot + HO_2\cdot$).

Model results by Donahue and Prinn [50], and subsequent measurements of NMHCs in the marine troposphere, suggest that short-lived NMHCs from the oceans may govern the chemistry of the remote MBL. Unlike over the continents, in the remote MBL, NMHCs may actually lead to overall tropospheric ozone destruction rather than production [50-51] (see equations 1-17 to 1-18), with resultant influences on the OH· budget (equations 1-7 and 1-8).

1.2.2.3 Aldehydes and ketones

Aldehydes and ketones may be emitted directly to the atmosphere from natural or anthropogenic sources, or result from the gas-phase oxidation of other VOCs, especially hydrocarbons (Fig 1-3). Conversely, in seawater, photochemistry of carbonyl compounds may lead to alkene formation [45]. Gas phase oxidation of methane by OH·, for example, leads to formaldehyde via [21]

$$CH_4 + OH\cdot \rightarrow CH_3\cdot + H_2O \qquad (1\text{-}19)$$

$$CH_3\cdot + O_2 + M \rightarrow CH_3O_2\cdot + M \qquad (1\text{-}20)$$

$$CH_3O_2\cdot + HO_2\cdot \rightarrow CH_3OOH + O_2 \qquad (1\text{-}21)$$

$$CH_3OOH + OH\cdot \rightarrow CH_2O + OH\cdot + H_2O \qquad (1\text{-}22)$$

Similarly, 80 % of the propane emitted into the troposphere is oxidized to acetone [52] (Fig 1-3) . The oxidation of isoprene and terpenes produces carbonyl compounds including glyoxal [53] and methylglyoxal [53-54], and is the source of 47% and 79 % of the atmospheric burden of glyoxal and methylglyoxal, respectively [53]. Some of these links between tropospheric hydrocarbons and carbonyl compounds are shown in Figure 1-3. Carbonyl compounds may be further oxidized to other carbonyl compounds, as in the formation of methylglyoxal from acetone [53].

Carbonyl compounds play many critical roles in the oxidant chemistry of the marine troposphere. They are among the principal sources of free radicals (including $OH\cdot$, $HO_2\cdot$, $\cdot RO\cdot$, $RO_2\cdot$) [55] in the troposphere. Formaldehyde, particularly, photolyzes readily at wavelengths below 330 nm via [34]

$$HCHO \xrightarrow{h\nu} H + HCO\cdot \qquad (1\text{-}23)$$

which leads to odd-hydrogen formation via

$$H\cdot + O_2 + M \rightarrow HO_2\cdot + M \qquad (1\text{-}24)$$

Acetone is likely an important contributor to the odd hydrogen budget of the upper troposphere [56-57]. Its relatively long photochemical lifetime (20-30 days) allows it to

reach the drier upper troposphere, where the formation of OH· from O_3 photolysis and reaction with water vapour (reactions 1-7 and 1-8) is less important due to the low relative humidity. In the upper troposphere, 30 % of OH· [57] may thus originate from acetone photochemistry (Fig 1-3). Carbonyls including acetone, propanal and acetaldehyde may also form peroxyacyl nitrates (PAN) via

$$R(CO)R' \rightarrow R(CO)\cdot + R'\cdot \qquad (1\text{-}25)$$

$$R(CO)\cdot + O_2 \rightarrow R(CO)OO\cdot \qquad (1\text{-}26)$$

$$R(CO)OO\cdot + NO_2 \rightarrow R(CO)OONO_2\cdot \qquad (1\text{-}27)$$

PAN then acts as a reservoir for the transport of reactive nitrogen (NO_x) [34], which is important to tropospheric ozone formation and nighttime VOC oxidation. Lastly, reaction with aldehydes is terminal for bromine radicals [58-59] (equation 1-28). This influences the capacity of Br· (which is thought to originate from sea surface waters) to catalytically destroy ozone, or to oxidize elemental gaseous mercury [58-59].

$$RCHO + Br\cdot \rightarrow HBr + RCO\cdot \qquad (1\text{-}28)$$

The role of carbonyl compounds in tropospheric chemistry has been highlighted in a review by Larry and Shallcross [60].

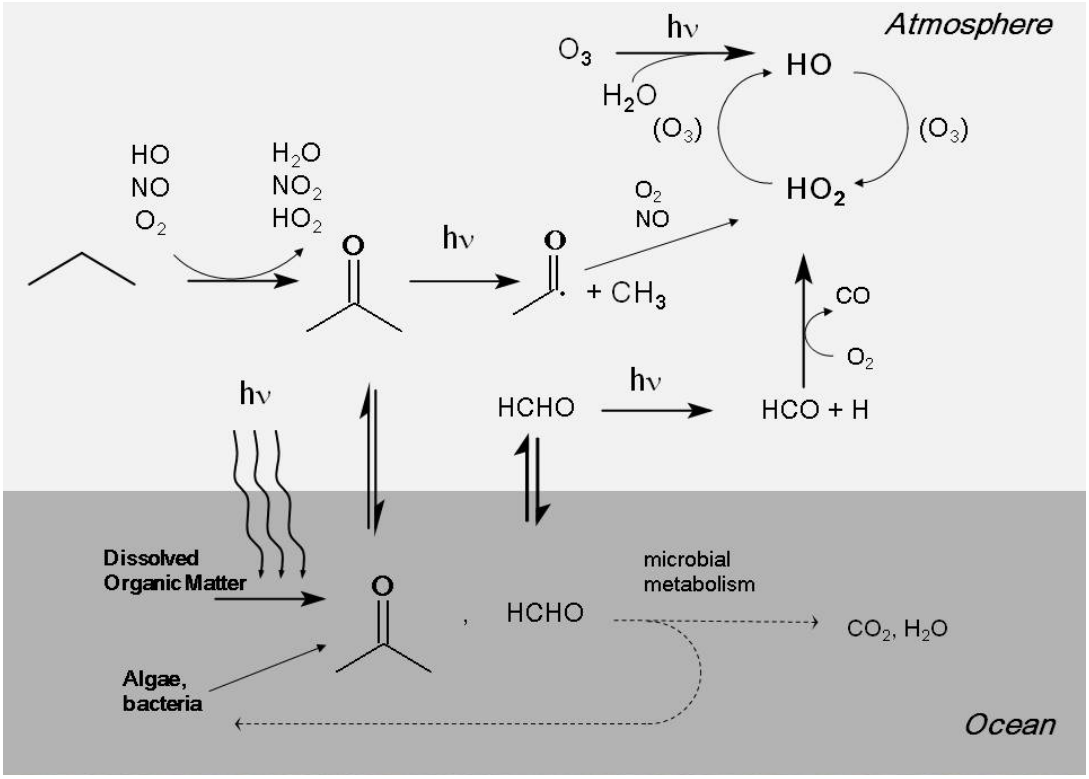


Figure 1-3. Simplified schematic of sources and sinks of carbonyl compounds, as represented by acetone and formaldehyde, in the surface oceans and marine troposphere.

1.2.3 Links between VOCs and marine aerosols

Aerosols, defined as suspensions of liquid droplets or solid/multiphase particles in the atmosphere, play important direct and indirect roles in climate [61], influence visibility, attenuate solar irradiation at the ground or sea surface, and provide surfaces for heterogeneous chemical reactions; these latter two effects have important consequences for the budgets and distributions of trace gases in the atmosphere [18]. Marine aerosols may also impact adjacent coastal land areas. In the marine troposphere, these aerosols may be derived from VOCs of marine origin, which can be converted to secondary organic aerosols (SOAs) [53] or inorganic aerosols (through oxidation of DMS to

sulfates) [18]. Carbonyl compounds including glyoxal and methylglyoxal are important sources of SOAs [53, 62-63]. These two dicarbonyl compounds are readily oxidized to low-volatility carboxylic acids, or oligomerize under the influence of OH and other radicals in cloud water droplets [62-63]. Oxidation of NMHCs, especially unsaturated species such as isoprene and terpenes [64], similarly leads to SOA formation, a process which occurs through carbonyl or carboxyl-containing intermediates including glyoxal, methylglyoxal, hydroxyacetone and C_1-C_3 carboxylic acids and oxoacids [53, 65]. SOA formation from isoprene alone may account for 30 % of sub-micron aerosol organic carbon over the tropical oceans (30 °N - 30 °S) [66]. Such processes represent the removal of VOCs from the MBL. Matsumoto *et al.* [67-69] reported that much of the organic matter in aerosols at island sites in the Northwestern Pacific was of marine origin. While the bulk of marine aerosol mass consists of sea salt [70], aerosols produced at the sea surface from the bursting of bubbles or jet drops are generally enriched in organic matter [71-74], which may include intact microbes (bacteria or viruses [72-73, 75], algae and their byproducts [76]). This is due to the formation of these aerosols at the sea surface microlayer (SSML), which is greatly enriched in organic matter relative to bulk seawater, constituting another means by which marine organic matter may enter the MBL. Recent studies using satellite remote sensing have estimated that 22 Tg yr^{-1} of organic carbon is produced directly as aerosols (Primary Organic Aerosols, POA) from the global ocean surface [66]. Studies using time-of-flight secondary ion mass spectrometry and energy-dispersive X-ray spectroscopy (EDX) have revealed fatty acids in sea-salt aerosols, enriched on their surfaces [77-78]. Nevertheless, while the formation of SOAs from marine VOCs has been relatively well characterized, the reverse process-

the contribution of organic aerosol material of direct marine origin to the formation of VOCs, if any- is poorly understood.

1.3 Concentrations of VOCs in the surface oceans and the marine atmosphere

1.3.1 Non-methane hydrocarbons

Concentrations of NMHCs in MBL air and in surface seawaters from a variety of studies, globally distributed, are given in Tables 1-2a and 1-2b, respectively. Only marine air data which can reasonably be assumed to be free of continental influences are included. Atmospheric concentrations range from low pptv to low ppbv, generally decreasing with carbon number (Table 1-2a). Over the Atlantic, Koopmann *et al*. [79] reported that ethane was evenly distributed with latitude (which would be consistent with its long lifetime), while ethene, acetylene and propene exhibited maxima around 40°N; the same maximum has been reported for propane [80]. For ethane, concentrations are generally higher in the northern hemisphere and show greater seasonal variation [42]. High concentrations of isoprene and monoterpenes (<100 - 200 pptv) have been observed in the South Atlantic surface atmosphere over high chlorophyll regions of the ocean [49]. Alkenes over the remote oceans are generally thought to be of oceanic origin because their short photochemical lifetimes preclude transport from continental sources [79]. For butanes both marine and continental sources may contribute to their observed concentrations in the marine atmosphere (despite their short photochemical lifetimes), since these concentrations could not be maintained by oceanic fluxes alone [5, 81]. Few benzene and toluene measurements have been reported in marine air; these compounds are presumed to be of anthropogenic origin, and low benzene/toluene ratios are generally

indicative of an aged air mass or aged hydrocarbon source [82] (see Table 1-1). Strong vertical gradients consistent with rapid oxidation have been reported for some areas [83], while in others the lack of a vertical gradient was interpreted as indicating rapid turbulent mixing [84].

Seawater concentrations for NMHCs typically range from low pM to hundreds of pM (Table 1-2b), and may show considerable variability even at specific sites [83]. They are generally supersaturated with respect to the atmosphere, often by 2-3 orders of magnitude [47, 85-87], suggesting that the oceans are net sources of these compounds to the atmosphere. Alkene concentrations are generally higher than those of alkanes. In the South Pacific, NMHC concentrations in seawater were observed to decrease with increasing latitude [87]. In the mid-Atlantic, ethane, propane, ethene and propene concentrations increased from North to South [88], with a pronounced maximum at 30°N occurring in some years but not others [86, 88]. In contrast, other data sets show no latitudinal trends [89], consistent with substantial local variability associated with algal and photochemical production and with temperature and salinity variations [89]. Subsurface concentration maxima in the euphotic zone have also been observed for C_2-C_4 alkenes and ethane [88]. A seasonal concentration cycle observed for isoprene, many other C_2-C_5 alkenes, and several alkanes is consistent with biological or photochemical production in the oceans [47, 90]. Bonsang *et al.* [51] measured NMHCs at Kerguelen Island in the Southern Ocean (Table 1-2a), where air masses were free of any recent continental influence. A pronounced diurnal cycle for alkene mixing ratios indicated a marine photochemical source for alkenes, while the lack of such a cycle, but increased

Table 1-2a. Non-methane hydrocarbon mixing ratios (pptv) reported in marine surface air. - = not reported. BDL = below detection limit. [1]mean (± SD); [2]range; [3]median. *Pooled value for all butene, pentene or hexane isomers.

	Location									
	Atlantic and Arctic Oceans			Pacific Ocean			Indian Ocean		Southern Ocean	
	A1[1]	A2[1]	B[2]	C1[3]	C2[2]	D[2]	E[2]	F[1]	G[1]	H[1]
ethane	429 ± 24	416 ± 8	150 – 1050	814	310 – 1500	360 – 1459	430 – 2180	183 ± 46	-	142 ± 12
propane	39 ± 9	29 ± 3	~10 – 700	87	30 – 200	102 – 1353	100 – 760	35 ±13	41±32	8.8 ± 1.7
n-butane	4.7 ± 1.9	3.1 ± 0.7	15 -250	18	7 - 35	51 – 447	30 – 700	20 ± 11	23±22	9.9 ± 1.9
i-butane	3.1 ± 1.0	2.1 ± 0.5	15 – 80	12	9 – 12	10 – 86	<10 - 290	-	11±20	5.6 ± 0.9
n-pentane	9.5 ± 3.5	7.9 ± 0.8	-	-	18 – 33	65 – 753	60 – 1800	12 ± 9	-	3.2 ± 0.6
i-pentane	4.3 ± 1.9	2.8 ± 0.4	-	-	2 – 10	10 – 116	<10 – 1010	14 ± 8	-	2.3 ± 0.5
n-hexane	3.4 ± 1.5	3.4 ± 0.9	-	-	-	26 – 773	50 – 860	-	-	1.7 ± 0.4
ethene	22 ± 9	17 ± 4	8 – 110	426	39 – 99	151 – 4833	680 – 21,220	223 ± 123	162 ± 60	9.3
propene	6.5 ± 2.0	6.0 ± 0.8	-	159	22 – 75	286 – 3573	330 – 11,190	95 ± 45	46 ± 21	5.2
1-butene	2.7 ± 1.2	3.1 ± 0.9	-	-	2 – 7	90 – 736	70- 3020*	-	-	-
i-butene	10.5 ± 4.3	11 ± 2	-	-	-	170 – 785	-	-	40±21	-
c-2-butene	-	-	-	-	0.4 – 1.8	10 – 116	-	-	-	-
t-2-butene	2.2 ± 0.4	2.2 ± 0.4	-	-	2 – 6	11 – 164	-	-	-	-
1-pentene	-	-	-	-	0.4 – 4	90 – 1236	140 - 1400*	-	-	-
1-hexene	-	-	-	-	-	20 – 161	<10 - 1340*	-	-	-
isoprene	1.9 ± 0.8	0.9 ± 0.4	-	-	-	-	-	-	BDL	5.7
acetylene	31 ± 6	25 ± 4	30 – 240	-	-	22 – 227	BDL	22 ± 9	-	6-20
benzene	57 ± 28	45 ± 10	-	-	-	-	-	-	-	-
toluene	43 ± 33	29 ± 5	-	-	-	-	-	9 ± 7	-	-

Table 1-2b. Non-methane hydrocarbon concentrations (pmol L^{-1}) in surface seawaters. - = not reported. BDL = below detection limit. [1]mean (± SD); [2]range; [3]median. [a]sum of 1- and *i*-pentenes; [b]sum of *n*- and *i*-butanes; [c]butene-pentene isomer not specified

	Location(s)									
	Atlantic and Arctic Oceans					Pacific Ocean			Indian Ocean	Southern Ocean
	I[2]	J[2]	K[1]	L[1]	M[2]	N[1]	O[2]	P[1]	Q[2]	R[2]
ethane	5.6 – 57.9	-	96 ± 129	14 ± 5.5	19 - 80	7.0 ± 0.3	-	12 ± 2	6.3 - 135.7	-
propane	2.7 – 28.2	-	29 ± 38	6.4 ± 3.6	1 – 41	3.7 ± 0.7	0.9 – 11	12 ± 2	23.7 - 261.2	4.5 – 21.9
n-butane	-	-	15 ± 31	3.5 ± 2.4	0.4 – 11[b]	0.8 ± 0.2	2 – 26	8 ± 2[b]	10.3 - 126.8	25.8 – 110.1
i-butane	0.7 – 9.7	-	2.7 ± 3.1	1.4 ± 1.1	-	0.2 ± 0.1	0.6 – 16	-	5.4 - 79.5	17.4 – 73.2
n-pentane	0.6 – 10.2	-	-	-	-	-	3 – 19	-	17.0 - 233.5	-
i-pentane	0.4 – 6.1	-	-	-	-	-	1.3 – 13	-	0.4 - 171.9	-
n-hexane	-	-	-	-	-	-	-	-	0.4 - 201.3	-
ethane	14.4 – 228	17 – 951	147 ± 110	107 ± 52	7 – 185	74.7 ± 29.9	-	107 ± 11	253.6 - 1610	23.1 – 126.2
propene	8.2 -77.0	13 – 330	73 ± 57	41 ± 16	4 – 159	28.2 ± 18.3	-	63 ± 11	112.9 - 656.3	8.6 – 62.2
1-butene	1.4 – 19.3	-	42 ± 30	30 ± 11	-	6.5 ± 2.3	-	-	22.3 - 232.6[c]	-
i-butene	4.6 -54.0	-	-	-	-	5.8 ± 3.2	2.7 – 16	-	-	22.1 – 60.6
c-2-butene	-	-	-	-	-	0.3 ± 0.2	0.7 – 14	-	-	-
t-2-butene	-	-	-	-	-	1.0 ± 0.2	-	-	-	3.9 – 17.7
1-pentene	2.5 – 19.6[a]	-	-	-	-	1.8 ± 1.0	-	-	17.0 - 219.6[c]	-
1-hexene	-	-	-	-	-	-	-	-	6.3 - 135.7	-
isoprene	0.7 – 54.3	-	-	-	-	-	-	-	-	-
acetylene	-	-	5.1 ± 2.9	10.3 ± 3.9	-	4.2	-	-	-	BDL – 1.5

Locations and sources in Table 1-2:

Air: **A1:** North Atlantic (53- ~70°N); **A2:** Fram Straight (Arctic) (80°N). Hopkins *et al.* [91] **B:** Mid-Atlantic (30°N-30°S). Koppmann *et al.* [79], **C1:** Central Pacific (20°N-14°S). Atlas *et al.* [14]; **C2:** Central Pacific (20°N-14°S). Donahue and Prinn. [92]
D: Tropical Pacific (Hao Atoll) (18°S, 140°W) Bonsang *et al.* [83] **E:** Western Indian Ocean (13°N-25°S). Bonsang *et al.* [85], **F:** Northwestern Indian Ocean (12°N-5°S). Warneke *et al.* [93] **G:** Southern Ocean (Kerguelen Island) (49°S, 70°E). Bonsang *et al.* [51], **H:** Southern Ocean (Cape Grim, Tasmania)(41°S, 145°E). Lewis *et al.* [94]

Seawater: **I:** North Sea (51-54°N). Minimum and maximum monthly means. Broadgate *et al.* [47] **J:** North Sea (coastal site) (54°N, 0.4°W). Annual minima and maxima. Gist and Lewis [90]. **K:** Mid-Atlantic (35°N-30°S). Plass *et al.* [88] **L:** Atlantic (50°N-35°S). Plass-Dülmer *et al.* [86] **M:** Beaufort Sea (69-71°N). MacDonald [95] **N:** Central Pacific (20°N-14°S). Donahue and Prinn [92]. **O:** South Pacific (10-54°S). 10^{th}-90^{th} percentiles. Pszenney *et al.* [87] **P:** North Pacific (13-21°N). Swinnerton and Lamontagne [96] **Q:** Western Indian Ocean (13°N-25°S). Bonsang [85] **R:** Southern Ocean (Kergeulen Island) (49°S, 70°E). Bonsang *et al.* [51]

mixing ratios when strong winds ventilated deeper waters, indicated a deeper marine source for alkanes. Whereas many studies regard acetylene as having a purely continental (combustion) origin [91], and regard its detection over the remote oceans as being due to its long tropospheric lifetime (see Table 1-1), a marine source has been postulated, based on supersaturation ratios in the Indian Ocean [85, 97]. Warneck [5] summarizes a number of sources to arrive at oceanic emission rates of 2.5 – 6 Tg $year^{-1}$ for light alkanes and alkenes, with a further >26 Tg $year^{-1}$ for C_9-C_{28} alkanes. Globally, total emissions of NMHCs from the oceans are small compared to terrestrial (primarily vegetation) and anthropogenic sources [5], constituting < 2-4 % of natural or biogenic emissions (which themselves are an order of magnitude larger than anthropogenic emissions). Nevertheless, they are likely to be locally important to the oxidant budget in large areas of the marine troposphere far removed from continental sources [49, 87].

1.3.2 Aldehydes and ketones

Fewer datasets for aldehydes and ketones in marine air and seawater have been reported than for NMHCs. Measurements of aldehyde and ketone concentrations in the marine atmosphere are generally also in the low ppbv – pptv range and are summarized in Table 1-3. In clean marine surface air (not subject to terrestrial inputs) over the Caribbean Sea [98] (Table 1-2), formaldehyde and acetaldehyde exhibited pronounced diurnal cycles in their concentrations with maxima in the afternoon, suggesting marine photochemical sources, while acetone and butanone, with longer atmospheric lifetimes, did not show these fluctuations. The acetone concentrations were comparable to those reported in surface air over the open tropical Atlantic and Pacific [99-100]; higher (1.16 ± 0.33 ppbv) concentrations were reported for the mid-latitude Pacific [99]. Singh *et al.* [101] reported from aircraft studies over the Northern Hemisphere Pacific that acetaldehyde and propanal concentrations were highest in the MBL (medians 205 pptv and 60 pptv, respectively), decreasing over the free troposphere to 60 pptv and 15 pptv, respectively, at 12 km altitude. Acetone was less abundant in the MBL (437 pptv) than in the free troposphere (636 pptv) (in contrast to previous measurements [102] in which acetone concentrations over the tropical Pacific in both hemispheres were no lower in the MBL than in the free troposphere up to 12 km). They calculated from these measurements that the ocean is a source of acetaldehyde (125 Tg yr^{-1}) and propanal (45 Tg yr^{-1}) but a sink for acetone (14 Tg yr^{-1}). In contrast, a modeling study by de Laat *et al.* [103], based on

measurements over the Indian Ocean, concluded an overall marine source of acetone of 15-20 Tg yr^{-1}. Formaldehyde concentrations over the tropical Pacific [102] decreased from 300 pptv in the MBL to 100 -150 pptv at 12 km altitude. Many of these authors call for further measurements of these substances in seawater to clarify the role of the oceans as sources or sinks.

Table 1-3. Concentrations of aldehydes and ketones reported in marine air. *surface air

Source	**Location(s)**	**Substances and concentrations reported (average or range)**
Shepson *et al*. [59]	Ice floes, Lincoln Sea (84 °N)*	formaldehyde: 193 pptv acetaldehyde: 93 pptv acetone: 1730 pptv
Williams *et al*. [100]	Tropical Atlantic (Longitudinal transect at 0-10 °N)*	acetone: 0.53 ppbv
Marandino *et al*. [99]	Tropical Pacific (0-25°N)* Mid-latitude Pacific (25-45 °N)*	acetone: 0.398 ± 0.130 ppbv acetone: 1.16 ± 0.33 ppbv
Zhou and Mopper [98, 104]	Caribbean Sea (23-10 °N)*	formaldehyde: 0.55 ppbv acetaldehyde: 0.50 ppbv acetone: 0.38 ppbv butanone: 0.03 ppbv C_3-C_{18} aldehydes and ketones (single sample only): 10-140 pptv
Wisthaler *et al*. [105]	Southern Indian Ocean (19 °N-13°S)*	acetaldehyde: 515 ± 31 pptv acetone: 178 ± 30 pptv

Table 1-3. (Continued)

Source	Location(s)	Substances and concentrations reported (average or range)
Singh *et al.* [101-102]	Pacific (10-45 °N, 100-230 °E), 0-12 km altitude [101]	acetaldehyde: 204 ± 40 pptv (MBL), 173 ± 45 (2-4 km) propanal: 68 ± 24 pptv (MBL), 60 ± 21 (2-4 km) acetone: 466 ± 97 pptv (MBL), 642 ± 207 (2-4 km)
	Pacific (30 °N-30 °S), 0-12 km altitude [102]	formaldehyde: 70 - 300 pptv acetaldehyde: 60 - 100 pptv acetone: ~ 300 - 650 pptv
Bottenheim *et al*. [106]	Barrow, Alaska (71 °N)*	acetaldehyde: 65 pptv acetone: 390 pptv
Fushimi and Miyake [107]	Western North Pacific (35-10 °N)* Indian Ocean (3 °N- 47 °S)*	formaldehyde: 0.8 - 3 ppbv formaldehyde: 0.8 - 7 ppbv
Sartin *et al*. [108]	Mace Head, Ireland (Atlantic) (53 °N)*	nonanal: 37 pptv decanal: 38 pptv geranyl acetone: 8 pptv

For seawater, studies by Mopper and co-workers [19-20, 109] reported individual C_1-C_9 carbonyl concentrations of 0.09 - 40 nM from tropical and subtropical waters from the Western Atlantic (Florida coast, Caribbean Sea, and

Sargasso Sea), with concentrations generally decreasing for greater carbon numbers. Concentrations down to 160 m depth were also determined for formaldehyde (~12 nM) and glyoxal (2-3 nM). Fluxes of formaldehyde, acetaldehyde and acetone of 0.76, -2.0 and -2.7 × 10^{-5} nmol cm^{-2} s^{-1} were calculated for the Sargasso sea [20] (fluxes greater and less than zero indicate air-to-sea and sea-to-air transfer, respectively). Variations in sea surface and air temperatures and irradiances presumably would not allow global fluxes to be calculated from these results. More recently, mean acetone concentrations of 17.6 nM have been reported for the tropical Atlantic [100] and 13.9 ± 11.7 and 13.6 ± 3.0 nM for the tropical and temperate Pacific, respectively [99]. These two studies simultaneously measured acetone concentrations in air and calculated net acetone fluxes out of the ocean and into the ocean. Based on the larger areas studied, Marandino *et al*. [99] extrapolate to give a global flux of 32.6 Tg yr^{-1} (ocean as a sink), while Williams *et al*. [100] suggest that the oceans are a global acetone source. These studies did not consider enrichment of carbonyl compounds in the sea surface microlayer, in contrast to Zhou and Mopper [20].

Abiotic processes acting on DOM are thought to be the source of much of the carbonyl compound budget of the surface oceans. Formaldehyde, acetaldehyde and glyoxal can be formed from the sunlight irradiation of tropical coastal surface water samples [110] and from open Atlantic waters [111], and acetaldehyde and acetone from Mediterranean waters [112]. Kieber *et al*. calculated these processes to be an appreciable sink for humic substances (chromophoric DOM, or CDOM) introduced to surface waters by major rivers

[113], since production rates were linearly related to loss of DOM absorbance and fluorescence. Formaldehyde, acetaldehyde and acetone were similarly produced from the irradiation of tetradecane in seawater [114], although the starting hydrocarbon was present at concentrations more relevant to polluted waters. In the latter study, the products were postulated to result from fragmentation of higher molecular weight methyl ketones. $C_6 - C_{13}$ aliphatic aldehydes in estuarine waters can result from the auto-oxidation of fatty acids of diatoms, dinoflagellates and green algae [115]. Marine microbes also produce low molecular weight aldehydes and ketones, including acetone by the bacterium *Vibrio* [116-117], formaldehyde by the algae *Skeletonema costatum* and *Heterocapsa pygmaea* as well as by natural plankton assemblages from the Carolina coast [118], and $C_7 - C_{10}$ dienals and trienals by diatoms upon cell damage [119]. Lastly, since formaldehyde is readily removed from the atmosphere by wet deposition [98, 120-121], and formaldehyde concentrations in rainwater are up to 3 order of magnitude greater than in surface waters [121], rain-out from the atmosphere may be an important source to surface ocean waters [120].

Sinks of aldehydes and ketones in seawater (Fig 1-3) include metabolism by marine microbes [122-123], transfer to the atmosphere [20, 100] and abiotic degradation processes such as photoinduced α-cleavage (Norrish Type 1 reaction), leading to alkene formation [45]. Loss by reaction with or condensation into higher molecular weight DOM is unlikely to be a significant sink for these compounds [110].

1.4 Analytical methods for VOCs in air and seawater

Since analytical method development or optimization constitutes a major part of this thesis, current methods for VOC analysis in ambient air and in seawater will be reviewed. Most methods for analyzing VOCs in seawater and in ambient air require some form of pre-concentration, due to the low concentrations at which these compounds are typically found, and some form of chromatographic separation, due to the complex mixture of compounds found in most environmental matrices. The latter is especially important when one wishes to determine numerous compounds or compound classes, rather than one or a few target compounds. A number of direct mass spectrometric or spectroscopic methods (see section 1.4.4) allow sensitive, real-time determination of VOCs but are typically restricted to a few molecules due to the lack of a separation step, and are often expensive and subject to interferences.

1.4.1 Sampling and preconcentration of VOCs

VOCs from air can be preconcentrated either directly from the ambient environment as a means of sampling, or from a discrete (grab) sample of air, which is most commonly drawn into a passivated (electropolished) stainless steel sampling canister [14, 37, 40, 124]. If the former approach is used, analysis may be on-site (at stationary field sites [38, 94, 125], on ships [14, 24, 79, 91], or on aircraft [40, 126]), with the pre-concentrated sample being immediately transferred to a chromatographic column. This approach allows data to be

obtained more rapidly, in real time, but requires chromatographs and other equipment to be suitable for field use and installation. Alternatively, if preconcentration is done on a sorbent (such as Tenax), the sorbent and sorbed VOCs may be transported for later analysis off-site [14, 51]. An advantage of canister sampling is that it allows for repeat analysis of a particular air sample. Many VOCs are stable in canisters for up to several years [127], although losses of some alkenes and styrene may occur through reactions with oxidants or sorption to the canister walls [124].

Sorbents- including Tenax (a 2,6-diphenyl-*p*-phenylene oxide polymer) [14, 38, 83, 128], activated carbon adsorbents [14, 51, 91, 94, 128], and carbon molecular sieves such as Carboxen [51]- can be used both for sampling and for preconcentration of VOCs in air previously obtained by grab sampling. VOCs are then thermally desorbed from the sorbent (or, occasionally, solvent-extracted, such as when analyzing alkyl nitrates [14]) for chromatography. Use of sorbents is associated with a number of problems, including the co-sorption of oxidizing gases which react with the analyte, low breakthrough volume (the volume sampled at which air exiting the sorbent bed still contains a significant concentration of the analyte), and incomplete desorption [129]. Tenax has been shown to lead to artifacts, including the formation of benzaldehyde and acetophenone due to reactions with oxidizing gases [130]. Furthermore, its adsorption capacity for very volatile NMHCs is poor. The sorption capacity of these sorbents may be increased by lowering their temperature [38, 51, 91, 125]. For NMHCs, sorbents may be selective, while canister (grab) sampling is

universal, each of which may be an advantage or drawback, depending on the analyte(s) of interest [124]. Sequential beds of different adsorbents may be used [128].

Cryogenic preconcentration is commonly used to enrich VOCs, especially NMHCs, from both canister samples and from air sampled directly. The air stream is passed through a trap filled with glass beads and cooled by liquid nitrogen [24, 40, 79] or argon [14, 37, 92, 131]. Subsequent heating of the trap introduces the analytes onto a GC column. Carbon dioxide and water vapour are typically removed from the air stream prior to the pre-concentration step to avoid clogging the trap [90, 131].

Analysis of VOCs in natural waters typically begins by purging the analyte from several liters of the sample with helium [30, 45, 51, 132] or nitrogen[47], or by allowing the analytes to equilibrate into a VOC-free headspace or through a semipermeable membrane [10, 92, 133]. Exceptions are analysis by solid-phase microextraction (section 1.4.1.1), and pre-concentration on C-18 silica solid phase extraction (SPE) cartridges impregnated with 2,4-dinitrophenylhydrazine (DNPH) [19-20], a method specific to carbonyl compounds which has also been used for air samples [128]. Preconcentration of the purged or equilibrated VOCs from the purge gas stream is generally similar to that used for air samples, involving glass bead-containing traps immersed in cryogens [10, 30, 47, 90, 134] or carbon- or polymer-based adsorbents [51].

1.4.1.1 Solid phase microextraction

In solid phase microextraction (SPME), analytes are directly preconcentrated from a gaseous or liquid sample onto/into a thin layer (7 – 100 μm) of sorbent coated onto a fused silica fibre, which can be retracted into a needle [135] (Fig 1-4). The process is typically an equilibrium, rather than exhaustive, extraction of the analyte (the number of moles, n) according to

$$n = \frac{K_{fs}V_fV_sC_o}{K_{fs}V_f+V_s} \qquad (1\text{-}29)$$

where K_{fs} represents the solution (s) to fibre (f) partition constant, V_f the volume of the fibre coating (sorbent), V_s the volume of sample and C_0 the analyte concentration in the sample. Generally, the volume of solution greatly exceeds that of the fibre coating and thus $V_s >> K_{fs}V_f$. Equation 1-29 then becomes

$$n = K_{fs}V_fC_0 \qquad (1\text{-}30)$$

i.e., for a non-exhaustive extraction, the quantity of analyte sorbed to the fibre is independent of sample volume, as well as being directly proportional to its concentration in the sample (C_0). Since the sorption-time profile (analyte sorbed vs. time) for a particular analyte is independent of concentration [135], pre-equilibrium sorption may be used for analytical purposes if the sorption time and conditions are carefully controlled [136-137].

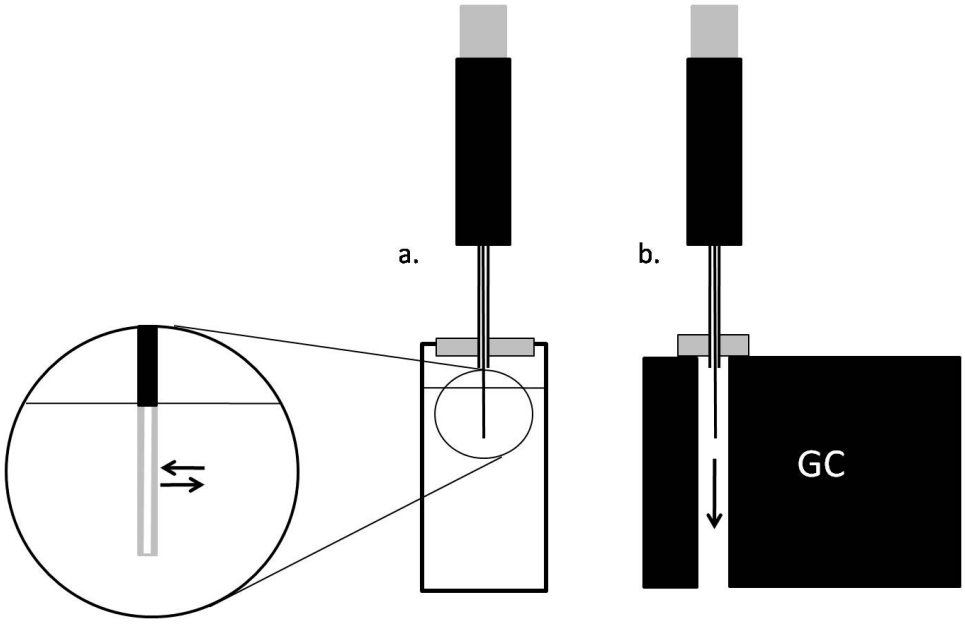


Figure 1-4. Process of solid phase microextraction (SPME), showing **a.** sorption (equilibration) of analytes with a sorbent layer on a fused silica SPME fibre (sorption from solution shown here), **b.** desorption and introduction of the analytes in the heated inlet of a GC.

After preconcentration, the analytes are thermally desorbed directly into the heated injector port of a gas chromatograph (GC) (Fig 1-4), thus avoiding the need for solvents, large sorbent traps, or cryogens. SPME methods generally require minimal sample preparation and small quantities of sample, and the SPME fibre is reusable many times. Sorbents covering a range of polarities, extracting by absorption or adsorption, from non-polar polydimethylsiloxanes (PDMS) to polar polyacrylate phases, are commercially available [137].

Whereas SPME has been used extensively to analyze environmental fresh waters [137-138], applications to seawater have been more limited, and fewer still

of these studies have analyzed seawater for VOCs by SPME. Notable examples include determination of DMS in open ocean surface waters and algal mesocosm experiments [139-141], the pollutant methyl *t*-butyl ether (MTBE)[142-143] in harbours, and a range of aromatics, C_1-C_3 halocarbons and C_5-C_{11} alkanes in coastal waters by SPME extraction of purge gas in the sample headspace [144-145]. SPME has not to date been used for the direct analysis of VOCs in marine air.

When SPME is combined with derivatization of VOCs, derivatization may take place in solution prior to SPME [146-148] or on the SPME fibre itself after it has been pre-loaded with the derivatization reagent [149-156].

1.4.2 Chromatography of VOCs

1.4.2.1 Non-methane hydrocarbons

Fused silica open tubular (FSOT) columns with common non-polar, liquid stationary phases, including 100 % polydimethylsiloxane (PDMS) (DB-1-type) and (5%-phenyl) polydimethylsiloxane (DB-5 type) are suitable for the analysis of NMHCs and other VOC classes, including some oxygenated VOCs (see section 1.4.2.2), but sub-ambient temperature programming is generally required [129]. Sin and co-workers [124] reported the preconcentration and chromatography of 143 NMHCs and halocarbons from urban air on a DB-1 column. Porous layer open tubular (PLOT) columns separate light molecules such as NMHCs by adsorption (gas-solid chromatography). Columns containing an alumina stationary phase allow the facile separation of low molecular weight

hydrocarbons [157-158] without the need for sub-ambient temperature programming and the cryogens it consumes, and have been widely used for NMHC separation (e.g., [25, 126]), but oxygenated VOCs are very strongly retained on such columns, precluding their analysis [158]. Furthermore, alumina-based PLOT columns, popular for NMHC analysis, are susceptible to damage by water vapour, requiring the sample to be dried before its introduction onto the column. This is typically undertaken by passing the sample past a Nafion (sulfonated fluoropolymer) membrane [47, 51, 92, 124], through anhydrous magnesium perchlorate [38, 48, 91, 94], or through a cryogenically cooled zone to freeze out water vapour [24-25, 33, 45, 90] prior to preconcentration.

Flame ionization detection (FID) and mass spectrometry (MS) are the most commonly reported detection methods in these studies. FID is well suited to NMHCs due to its sensitivity, near-universality and large linear dynamic range. MS detection for NMHCs alone may offer few advantages over FID, due to the very similar mass spectra of many species. A number of systems have been reported in which the pre-concentrated sample is split for chromatography on multiple columns for specific groups of VOCs (e.g., an Al_2O_3 PLOT column for C_2-C_5 NMHCs, a Cyclodex-B (cyclodextrin) column for C_6-C_{10} NMHCs and (non-polar) DB-5 and DB-1 columns for C_1-C_2 halocarbons and alkyl nitrates [82]) and/or for detection by multiple detectors [24-25, 82]. These sophisticated systems typically produce rich datasets involving numerous VOCs, but with attendant increases in apparatus cost and complexity of operation.

1.4.2.2 Aldehydes and ketones

Chromatography of aldehydes and ketones often follows some form of derivatization (see section 1.4.3), although these compounds may be cryogenically pre-concentrated and separated directly by GC on non-polar (DB-624) [159] or polar (Carbowax) [52, 102] GLC columns or polymer-based GSC (PLOT) columns [160-161]. These methods have generally targeted a narrow range of compounds, e.g., acetaldehyde and acetone [102], or acetone, methacrolein, methyl vinyl ketone and propanal [161]. Water vapour removal is generally required before preconcentration.

Means of detection have included reduction gas detection (RGD) [52, 102] (in which reaction of the analyte with mercuric oxide produces an equivalent amount of mercury vapour, quantified by absorbance at 254 nm) for acetaldehyde and acetone, FID [160], and MS [159, 161]. A number of these systems are automated and allow sampling and analysis every hour or less [159-160]. Derivatization can improve chromatographic (GC or High Performance Liquid Chromatography, HPLC) separation and allows identification of individual carbonyl compounds by mass spectrometry or, in the case of HLPC, by diode array detection.

1.4.3 Derivatization of carbonyl compounds

For aldehydes and ketones, bearing a reactive functional group (C=O) not present in NMHCs, various chemical derivatization methods can be used to convert them to forms more suitable for chromatography or which allow detection

by absorbance, fluorescence or chemiluminescence at characteristic wavelengths. Chemiluminescence methods are generally specific to a single compound. These derivatization methods are summarized in Table 1-4, with examples given in Figure 1-5, and include conversion of the aldehydes or ketone to substituted hydrazones [104, 162-166], oximes [146, 167-172], or thiazolidines [173-176], all suitable for gas or liquid chromatography, or formation of coloured complexes of specific aldehydes or ketones (e.g., with chromotropic acid [177], vanillin [178], or 3-methyl-2-benzothiazolinone hydrazone (MTBH) hydrochloride [179-181]) which can be quantified directly by optical absorbance or fluorescence. Most of these methods still require extraction/ preconcentration prior to the actual detection and quantification step, which may entail the use of organic solvents or non-reusable materials. By far the most commonly reported method involves conversion of carbonyls to 2,4-dinitrophenylhydrazones using DNPH. Detection limits of 0.01-0.02 ppbv have been reported for air [104] and < 0.5 nM (aldehydes; 0.05 nM for formaldehyde [20]) and <5 nM (ketones) for seawater [19]. Nevertheless, since 2,4-dinitrophenylhydrazones are generally unstable during GC, HPLC is used, with the attendant solvent use. Moreover, maximum sensitivity requires pre-concentration of the hydrazones and subsequent elution (typically with acetonitrile) [19, 104], with the associated sample contamination risk and, again, the environmental implications of solvent use. When carbonyl compounds are simultaneously extracted and derivatized to hydrazones, the process may be prone to artifacts or losses due to oxidizing gases including ambient levels of ozone. Carbonyl derivatives may also be pre-concentrated

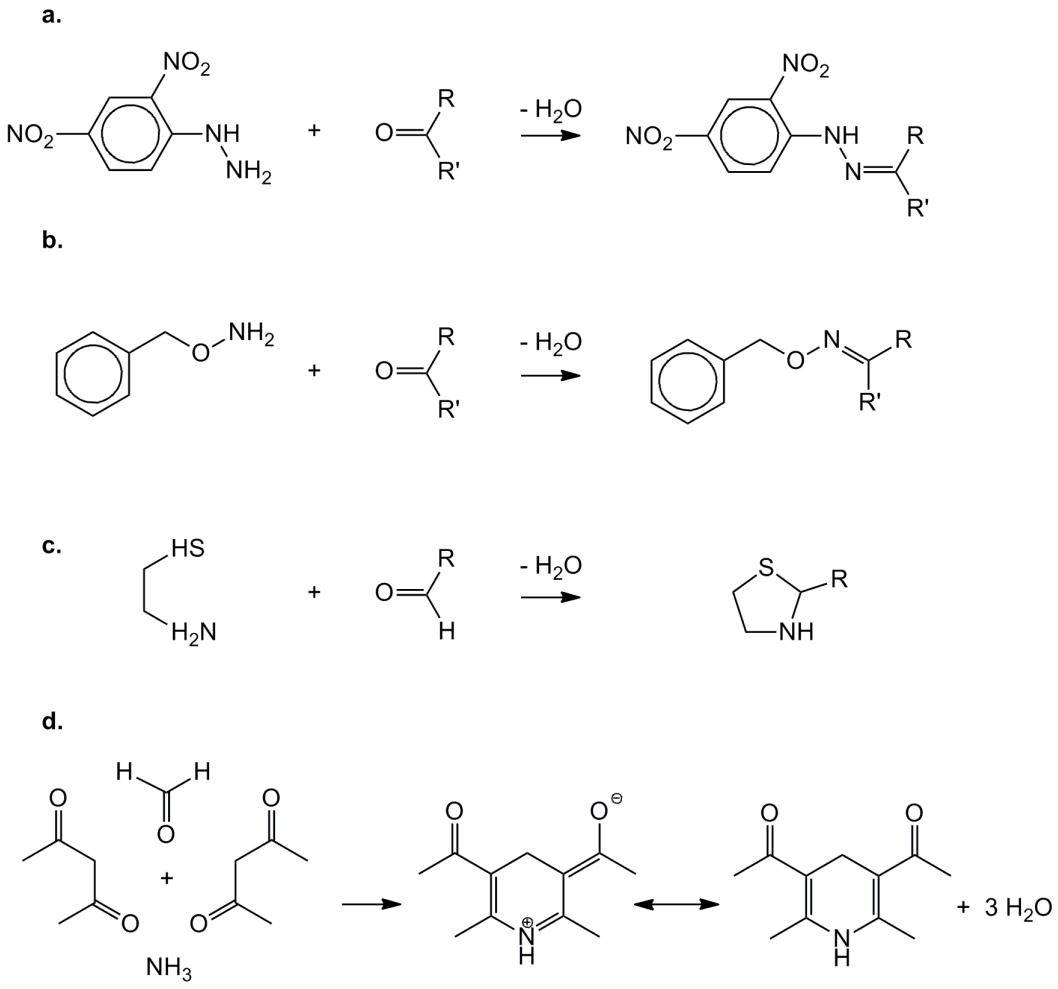


Figure 1-5. Selected examples of derivatization reactions reported for aldehydes and ketones in environmental samples **a.** hydrazone formation (here, 2,4-dinitrophenylhydrazone) **b.** oxime formation (here, benzyloxime) **c.** thiazolidine formation (shown for aldehydes only) **d.** Hantzsch reaction to form 3,5-diacetyl-1,4-dihydrolutidine (after Jones *et al*. [182])

Table 1-4. Derivatization methods reported for aldehydes and ketones in ambient or polluted air and natural waters.

Name / Derivatization Reagent	*Applicable compounds*	*Derivative(s) formed*	*Detection/separation method*	*Matrix*
Vanillin	Acetone	Yellow-orange dye (structure not reported)	Spectrophotometry (430 nm)	Air [178], biological fluids [178]
Hantzsch reaction: Acetylacetone and ammonia/ammonium acetate (Nash method) [182-184] or dimedone (5,5-dimethylcyclo-hexane-1,3-dione) [185]	Formaldehyde; C_1-C_6 aldehydes	3,5-diacetyl-1,4-dihydrolutidine (DDL)	HPLC with spectrophotometric detection (412 nm) [182]; flow injection with fluorescence detection (λ_{ex} 410 nm, λ_{em} 502 nm) [184]; HPLC with fluorescence (λ_{ex} 385 nm, λ_{em} 460 nm)[185]	Rainwater [182-183], seawater [184], air [185-187]
Chromotropic (4,5-dihydroxynaphthalene-2,7-disulfonic) acid	formaldehyde	(Purple condensation product)	Colourimetry (555 nm)	Urban air [177], marine air [107]
2,4-dinitrophenyl-hydrazine	C_1-C_{10} aldehydes and ketones; oxoacids	2,4-dinitrophenyl-hydrazones	HPLC with UV detection;	Urban air [163], remote/marine air [59, 104, 188-190], seawater [19-20, 110], rainwater [121]
N-(5-dimethylamino-1-naphtalenesulphonamido)-3-oxapentane-1,5-dioxyamine (dansyloxyamine, DNSOA)	C_1-C_5 aldehydes, acetone	DNSOA oxime ethers	HPLC with fluorescence detection (λ_{ex} 330 nm, λ_{em} 530 nm) [191]	Snow [192-193]

Table 1-4. (Continued)

O-2,3,4,5,6-pentafluorobenzyl hydroxylamine (PFBHA) hydrochloride	C_1-C_{10} aldehydes and ketones;	Pentafluorobenzyl oximes	GC with MS, FID or ECD	Air [169, 194] fresh waters [146, 167-168], seawater (for C_4 aldehydes) [195]
Cysteamine ($HS(CH_2)_2NH_2$)	Formaldehyde [174, 176], acrolein [173], C_1-C_7 aldehydes [175]	Thiazolidine	GC with nitrogen selective detector [173-175] or isotope ratio MS [176]	Ambient air [173-174, 176], exhaust air [175]
Pentafluorophenyl-hydrazine	C_1-C_{11} aldehydes	Pentafluoro-phenylhydrazones	GC	Urban air [164] Rural air [162]
Methyloxyamine and benzyloxyamine hydrochlorides [170]; benzyloxyamine hydrochloride followed by bromination [171-172]	C_1-C_9 aldehydes [170]; crotonaldehyde and acrolein [171-172]	*O*-methyl- and *O*-benzyl oximes [170]; brominated *O*-benzyl oximes [171-172]	GC with MS, nitrogen-selective detection [170] or ECD [171-172]	Automotive exhaust [170, 172], rainwater [171]
Dansylhydrazine (5-dimethylaminonaphthalene-1-sulfohydrazide)	C_1-C_6 aldehydes and ketones [196], acrolein [197-198]	dansylhydrazones	HPLC with fluorescence detection (λ_{ex} 240 nm, λ_{em} 470 nm)	Air [196-198]
N-alkylated 1,3,5-triazine-2-hydrazines	C_1-C_7 aldehydes	Alkylated triazine-2-hydrazones	HLPC with UV/fluorescence detection	Mineral water [166], air [165]
3-methyl-2-benzothiazolinone hydrazone (MTBH) hydrochloride, $FeCl_3$	Formaldehyde; total aldehydes as formaldehyde equivalents	(Blue complex)	Spectrophotometry (635 nm [179] or 626 nm [181])	Bacterial cultures, seawater [179], air [180-181]

by solid phase microextraction (SPME) [147, 156], potentially alleviating some of the aforementioned problems.

1.4.4 Direct Mass Spectrometric and Spectroscopic Methods for VOCs

Measurements by differential optical absorbance spectroscopy (DOAS) [199-200] have been reported in marine air for a limited number of VOCs, including formaldehyde [187, 201] and glyoxal [202], with detection limits down to 50 pptv [34], and in urban air for monoaromatic NMHCs [203]. DOAS is based on measuring the ultraviolet or visible absorption intensity (in a narrow-wavelength, distinct 'fingerprint' absorption region) against a slowly varying background which is due to other absorbing or scattering species [34]. Thus, the *differential* optical absorption (with respect to other absorbing species in air) is measured [34]. The differential absorption coefficient of the absorbing species, as determined in the laboratory, can be used to calculate its concentration directly. Since DOAS constitutes a signal processing method as much as an instrumental method [200], the technique can be applied to satellite data [204], allowing atmospheric column-integrated measurements of certain VOCs over large areas. Conversely, the satellite approach limits vertical resolution.

Proton Transfer Reaction-Mass Spectrometry (PTR-MS) is a form of chemical ionization mass spectrometry employing H_3O^+, created from water vapour in a hollow cathode discharge, to ionize VOC molecules (here designated M) to protonated adducts MH^+, via

$$M + H_3O^+ \rightarrow MH^+ + H_2O \qquad (1\text{-}31)$$

The adducts MH^+ are detected by quadrupole [205] or time-of-flight [206] mass spectrometry without further fragmentation. (Atmospheric Pressure Chemical Ionization-Mass Spectrometry, as used by Marandino *et al.* [99] for acetone in seawater and marine air, operates on similar principles.) Any gas-phase molecule with a proton affinity greater than water can thus be detected [207]. This includes numerous VOCs, and real-time monitoring with high time resolution is possible. PTR-MS has been used to determine selected VOCs in marine air including methanol, acetone, acetaldehyde, DMS, acetonitrile, isoprene and methyl vinyl ketone [100, 105, 208-210] (methyl vinyl ketone is typically reported together with methacrolein as a result of their indistinguishable molecular masses [209]). PTR-MS may also analyze for VOCs by sparging a seawater sample with helium, which is passed through a cryogenic trap [100] prior to introduction into the mass spectrometer. Sparging and cryotrapping with PTR-MS detection has been used to monitor methanol, acetaldehyde, acetone, isoprene and DMS in marine algal mesocosm experiments [205]. While characterized by low detection limits, and high time resolution, PTR-MS is subject to mass interferences (e.g. propanal with acetone, methyl vinyl ketone with methacrolein [209, 211]), although de Gouw *et al.* [212] address this shortcoming by coupling PTR-MS to VOC separation by GC. Furthermore, VOCs with low proton affinities (including ethene, ethyne, propane and isobutene) [207] cannot be analyzed, calibration is often difficult (for example,

due to the exponential decline in sensitivity over the instrument's mass range [213]) which limits accuracy to 20-25% [207, 212] and the instrumentation is currently expensive, limiting its accessibility.

1.5 Objectives

The acquisition of data sets in the immediate future for a variety of VOC species with diverse geographical, climatic, seasonal and temporal resolutions will clarify the relationships between VOCs in surface ocean waters, in the MBL and in other reservoirs of the marine and atmospheric carbon cycles. To this purpose, VOC measurements must become routine, through the development of readily accessible, facile, field-ready and low-cost analytical methods. Thus, the work presented in this thesis aimed to develop methods for the analysis of specific classes of VOCs (NMHC's, low molecular weight carbonyl compounds) in seawater and in marine air, and to apply these to open ocean areas of the North and Northwestern Atlantic, accumulating data sets which would help clarify the biogeochemistry of these compounds. Specifically, the aims were:

- To optimize a cryogenic pre-concentration system, built in-house and based on readily accessible columns and instrumentation, for the determination of NMHCs in discrete air samples from remote locations,
- To characterize time-and-space matched samples of atmospheric NMHCs, size segregated aerosols and surface water DOC concentrations and chemistry over the Nordic Seas (Greenland and Norwegian Seas, Fram Strait)

- To develop and optimize a compact, mobile, solvent-less, facile method for determination of low molecular weight carbonyl compounds specifically in seawater, based on derivatization and solid phase microextraction, and fully characterize the derivatization methodology and associated contamination and blank suppression issues
- To assemble a data set for selected carbonyl compounds for selected areas of the North Atlantic using this solid phase microextraction method, and to elucidate the biogeochemistry of these carbonyl compounds in the area, including estimating selected sea-air fluxes.

1.6 Structure of the Thesis

This thesis takes the form of four manuscripts. They are presented as they were published or submitted, except for the numbering of figures to make these distinguishable throughout the thesis (thus, 'Figure 1' in the manuscript constituting Chapter 2 becomes 'Figure 2-1') and the addition of section numbers within these chapters.

Chapter 2, published as *Hudson, E. D.; Ariya, P. A., Measurements of non-methane hydrocarbons, DOC in surface ocean waters and aerosols over the Nordic seas during Polarstern cruise ARK-XX/1 (2004), Chemosphere* ***2007,*** *69, (9), 1474-1484*, details concentrations of non-methane hydrocarbons over the Nordic Seas during summer, concentrations of dissolved organic carbon in corresponding surface seawaters, the properties of size-fractionated marine aerosols in the region, and the isolation and identification of a bacterium from

these aerosols. It also describes our initial identification of selected VOCs in these surface seawaters using solid phase microextraction, leading to further development of SPME methods in subsequent chapters.

Chapter 3, published as *Hudson, E. D.; Okuda, K.; Ariya, P. A., Determination of acetone in seawater using derivatization solid-phase microextraction*, *Analytical and Bioanalytical Chemistry* ***2007,*** *388, (5-6), 1275-1282*, describes the development and optimization of a solid-phase microextraction method, specific to seawater, for the analysis of acetone. It further contains the application of this method to selected surface water samples from the Nordic seas during the sampling cruise undertaken in the context of chapter 2. The work was done in collaboration with Kadek Okuda, a summer research assistant in our laboratory.

Chapter 4 has been submitted to *Environmental Science and Technology* as *Hudson, E. D.; Ariya, P. A.,Gélinas, Y., A method for the simultaneous quantification of 23 C_1-C_9 trace aldehydes and ketones in seawater.* It generalizes the derivatization-solid phase microextraction method described in Chapter 3 to a range of low molecular weight carbonyl compounds in seawater, and contains the results of the analysis of surface waters from the St. Lawrence Estuary. It also describes ongoing efforts to identify and eliminate carbonyl compounds and their pentafluorobenzyl oximes from blanks associated with the use of PFBHA. Finally, it outlines the modeling of the effects of contamination of seawater samples by atmospheric carbonyl compounds, or their loss from seawater samples to clean, inert atmospheres used to protect these samples.

Chapter 5 is a manuscript in preparation for submission to *Environmental Chemistry* as *Hudson, E. D.; Ariya, P. A., Aldehydes and Ketones in Surface Waters of the North-western Atlantic.* It reports concentrations of selected aldehydes and ketones in surface seawaters from the Labrador Sea and the Scotian Shelf, sampled in May 2009, as well as nonanal in waters from a depth profile in the central Labrador Sea. It discusses the implications of these concentrations for the sources, sinks and biogeochemistry of carbonyl compounds in the oceans and provides estimated air-sea fluxes for selected compounds.

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Chapter 2

Measurements of Non-Methane Hydrocarbons, DOC in Surface Ocean Waters, and Aerosols over the Nordic Seas during *Polarstern* cruise ARK-XX/1 (2004)

This paper documents our initial attempts to explore relationships between the dissolved organic matter in surface ocean waters and volatile organic compounds in the lower marine troposphere, especially by what processes and to what extent the former may be a source of the latter. We also aimed to identify what other analytical methods may need to be developed (and for which classes of compounds) to address these questions. The work was undertaken in the context of our involvement in C-SOLAS, the Canadian component of the Surface Ocean-Lower Atmosphere Study. We investigated marine boundary layer air, surface seawaters, and aerosols of marine origin in an attempt to determine patterns linking organic or carbonaceous compounds in these three compartments, with supporting meteorological data being used to support the marine origin of certain air masses. The particular emphasis on non-methane hydrocarbons (NMHCs) stemmed from our interest in these compounds as both contributors to and indicators of tropospheric oxidative capacity. Several analytical and sample preparation techniques were used and/or optimized, due to the diverse nature (gases, liquids, solids) of the samples; some of these analytical approaches led to further method development as described in Chapters 3 and 4. For the first time, a culturable bioaerosol was isolated from an aerosol impactor sample taken at sea.

Further details on the set-up of the pre-concentration system for NMHC analysis, on the methods for bioaerosol cultivation and identification, and on air mass origin during the sampling period appeared in on-line supplementary information for the published article and are appended to this chapter. Additional information on the pre-concentration system (not published) appears in Appendix A of this thesis.

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Measurements of Non-Methane Hydrocarbons, DOC in Surface Ocean Waters, and Aerosols over the Nordic Seas during *Polarstern* cruise ARK-XX/1 (2004)

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2.1 Abstract

To explore processes leading to the formation of volatile organic compounds at the sea surface and their transfer to the atmosphere, whole air, marine aerosols, and surface ocean water DOC were simultaneously sampled during June-July 2004 on the Nordic seas. 19 C_2-C_6 non-methane hydrocarbons (NMHCs) in the air samples are reported from nine sites, spanning a range of latitudes. Site-to-site variability in NMHC concentrations was high, which suggests variable, local sources for these compounds studied. Total DOC in surface waters sampled ranged from 0.84 mg L^{-1} (Fram Strait) to 1.06 mg L^{-1} (East Greenland Current), and decreased 6-8% with 24-hour UV-A irradiation. Pentanes and hexanes, as well as acetone and dimethylsulfide were identified in the seawater samples using solid-phase microextraction/GC-MS. All these compounds are volatile enough that exchange with the atmosphere can be expected, and the detection of the hydrocarbons in particular is consistent with a marine source for these in the air samples. Size-fractionated aerosols from the same sampling regions were analysed by SEM-EDX and contained sea salt, marine sulfates, and carbonates. A culturable bacterium was isolated from the large (9.9 – 18 μm) fraction at one site, and identified by 16S rRNA PCR analysis as *Micrococcus luteus*, raising the possibility that marine bioaerosols could transfer marine organic carbon to the aerosol phase and thus influence formation of VOCs above the remote oceans.

Keywords: volatile organic compounds, marine aerosols, bioaerosols, dissolved organic matter, marine boundary layer

2.2 Introduction

Non-methane hydrocarbons (NMHCs) are ubiquitous in the remote marine troposphere at trace levels, ranging from parts-per-trillion (pptv) to low parts-per-billion by volume (ppbv) (1 ppbv = 2.45×10^{10} molecule cm^{-3}). They may impact the oxidative capacity of the lower troposphere (Donahue and Prinn, 1990; 1993), therefore affecting the lifetime, transport and fate of pollutants. Furthermore, measurements of the relative concentrations of NMHCs may be used to determine the relative importance, or even absolute concentrations, of different oxidants (such as OH and halogen radicals) in the troposphere (Jobson et al., 1994; Rudolph et al., 1997; Ariya et al., 1998; 1999; Wingenter et al., 1999). These so-called 'hydrocarbon clock' techniques to evaluate oxidant concentrations rely on an understanding of the sources, and degree of homogeneity, of the NMHCs that are used as probes.

Many studies (Rudolph and Ehhalt, 1981; Bonsang et al., 1988; Plass-Dülmer et al., 1993; 1995) have reported that C_2-C_6 NMHCs are supersaturated in surface ocean waters, and inferred that the remote oceans are therefore a source of these NMHCs to the remote marine troposphere. This implies that studies employing NMHCs as indicators of oxidant activity must take into account local variability in emission source strength for different hydrocarbons. Dissolved organic carbon (DOC) is thought to be the source of many of these light NMHCs (Wilson et al., 1970; Lee and Baker, 1992; 1993; Ratte et al., 1998; Riemer et al., 2000). Isoprene is also produced directly by marine algae and emitted to the

atmosphere (Bonsang et al., 1992; Broadgate et al., 1997; Shaw et al., 2003). However, few studies have examined the chemical processes by which NMHC may be produced from DOC. Ratte et al. (1993; 1998) determined that ethene, propene and 1-butene are photochemically produced from DOC, and determined quantum yields for ethene and propene production over the 300-420 nm wavelength range. The processes leading to the formation of ethane, propane and isoprene in the same system could not be clarified. Riemer et al. (2000) measured rates and wavelength- and oxygen dependence of C_2-C_4 alkene formation in sunlit surface seawater, and speculated on mechanisms of NMHC formation. None of these studies have sought to link the profile of NMHCs produced in surface waters with atmospheric observations of NMHCs at the same sites.

It is also conceivable that NMHCs or other volatile organic compounds could originate indirectly from marine organic matter through reactions occurring in the carbonaceous component of marine aerosols, rather than through bulk reactions in surface seawater. Blanchard (1964; 1989) observed that jet drops produced by bursting gas bubbles at the sea surface were enriched in organic material relative to bulk seawater, and that this could lead to organically enriched marine aerosols. Matsumoto et al. (1998; 2004) reported that much of the organic matter in aerosols at island sites in the Northwestern Pacific was of marine origin. Fatty acids may be enriched and localized on the surfaces of sea-salt aerosols (Tervahattu et al., 2002).

During a month-long sampling campaign in the summer of 2004, and in the framework of the Canadian Surface Ocean Lower Atmosphere Study (C-SOLAS), we aimed to concomitantly characterize NMHCs, size-segregated aerosol composition, and surface water DOC in/over the Nordic seas (Fig. 2-1) such that these measurements would be matched in time and location. To our knowledge, this is the first study that examines whole air, surface seawater, and aerosols sampled at the same sites and times, and assembling a coherent data set on these three environmental compartments will aid our ongoing investigation of the relationships between surface water DOC and volatile organic compounds in the marine boundary layer.

2.3 Methods

2.3.1. Study area

All samples were taken during a month-long (June 16-July 15, 2004) cruise (cruise ARK-XX/1) on the *FS Polarstern* from Bremerhaven, Germany to Longyearbyen, Svalbard (Fig. 2-1), which aimed to cover a range of environments, from populated/coastal (North Sea) to remote marine, and from temperate to high Arctic.

2.3.2 Air

Whole air was sampled using electropolished SUMMA canisters (AeroSphere, LabCommerce Inc., San Jose, CA); these allow for repeat analyses and sample storage. Canisters were prepared by evacuating them (10^{-4} Torr, 2 hours) at 100 °C - 120 °C, flushing them with ultra-high purity (UHP) helium three times, and subsequently re-evacuating them. 26 whole air samples were taken at sites over a variety of latitudes, of which nine (Fig. 2-1) are discussed in this paper. Samples were taken 20 m above the sea surface, forward of ship exhaust, when relative wind speed and direction were from the forward sector. Canisters were pressurized to 300 kPa over 15 min with a Teflon diaphragm pump (KNF-Neuberger, Trenton, NJ), through a 0.45 μm PTFE membrane filter to lessen contamination by aerosols.

Hydrocarbons in whole air samples were pre-concentrated at -196 °C (see Supplementary material). Interferents (CO_2 and water vapour) were removed using K_2CO_3 and by routing the sample stream over dry ice (-60 to -50 °C), respectively (Jobson, 1994). Subsequently heating the pre-concentration loop to 120 °C (5 min) released the hydrocarbons for gas chromatography (GC) (HP 6890 Series II GC, Agilent, Palo Alto, CA) on an Al_2O_3/Na_2SO_4 porous layer open tubular (PLOT) column (HP AL/S 50 m × 0.32 mm id × 8 μm porous layer thickness; Agilent). A Model 691 Cryo-trap (cryofocuser) (Scientific Instrument

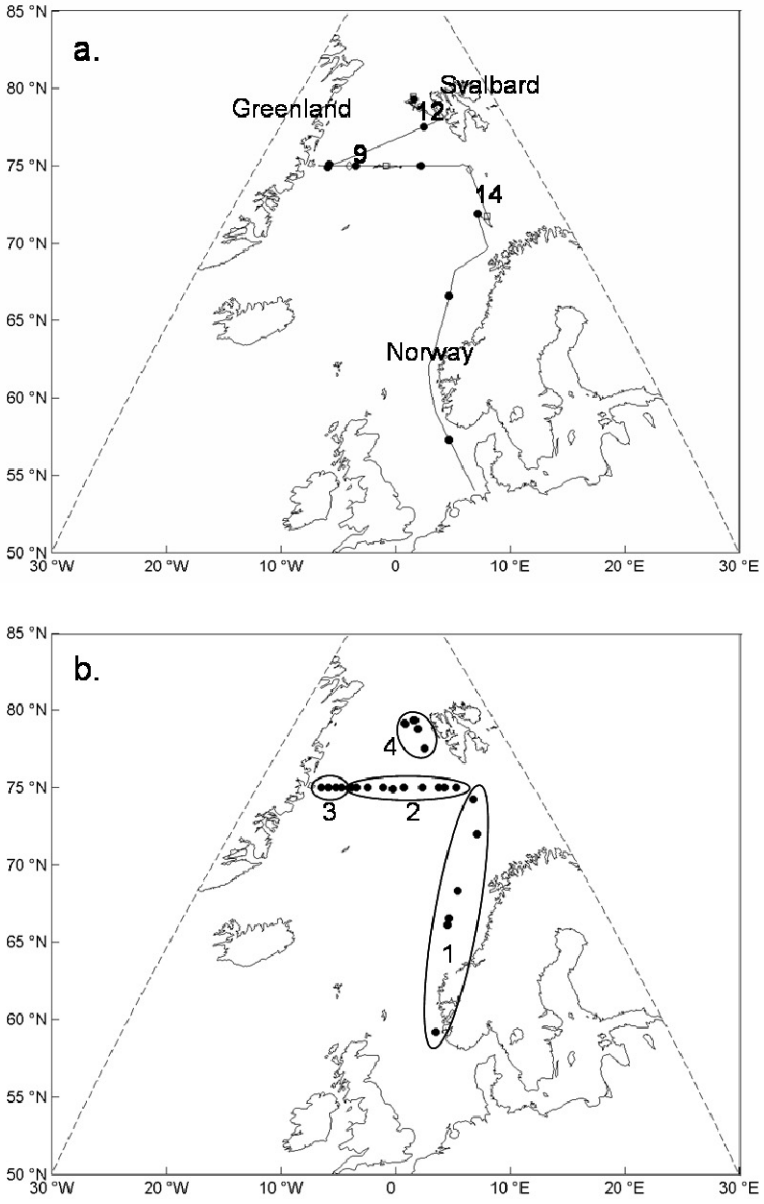

Figure 2-1. Map of the study area, indicating **a.** Track of FS *Polarstern* cruise ARK-XX/1, and the location of air sampling sites (●) and aerosol sampling regions (start: □, end: ◊, number indicates length of sampling in hours) described in this paper, **b.** Locations for seawater sampling 1. North Sea/Norwegian Sea, 2. Greenland Sea transect (75 °N), 3. East Greenland Current (sea ice), 4. Fram Strait. Note that at many locations, more than one water sample was taken. Maps are sinusoidal equal-area (Sanson-Flamsteed) projections.

Services, Inc., Ringoes, NJ), operated at -180 °C, refocused hydrocarbons at the head of the column. GC conditions were: splitless mode, He carrier gas (3.5 mL min^{-1} constant flow), injector at 200 °C; GC oven 50 °C (2 min hold), then 8 °C min^{-1} to 80 °C, 22 °C min^{-1} to 130 °C, 15 °C min^{-1} to 200 °C (5 min hold), and 15 °C min^{-1} to 220 °C (5 min hold); flame ionization detector at 220 °C. Calibration standards were prepared in SUMMA canisters by injecting pure compounds (for C_5 and larger) and Scotty gas mixes 54 and 55 (Scott Specialty gases, Plumsteadville, PA) diluted in UHP He, and humidified by adding 100 µL ultra-pure (MilliQ) water through a heated transfer line to simulate 83% relative humidity.

2.3.3 Seawater

Most seawater samples were taken using a Teflon-lined inlet line leading directly from the ship's keel (11-m depth) into the laboratory. This allowed for sampling while the ship was in motion, which is consistent with how air was sampled. At several sites, samples were also taken at 10-m depth with standard 12-L Niskin bottles. Water samples were immediately filtered (0.22 µm PTFE membrane), transferred to pre-cleaned amber glass bottles (Environmental Sampling Supply, Oakland, CA), and stored frozen until analysis.

For total DOC determination, 10 mL aliquots were acidified to pH <2 by adding 0.1% hydrochloric acid (trace metal grade, Sigma-Aldrich, St.-Louis, MO) by volume and analyzed by high-temperature catalytic oxidation using a TOC-V

total organic carbon analyzer (Shimadzu, Tokyo, Japan). Typical analytical error was 2 – 4%. Samples from three locations were also UV-irradiated for 24 hours in a box with a reflective interior and containing eight 15-W black light bulbs ($350 \leq \lambda \leq 400$ nm, emission maximum at 370 nm) (F15T8 BL, Hitachi) to simulate the UV component of solar radiation. Samples were irradiated in pre-combusted glass vials with custom-made quartz-window caps. The irradiance over the vial surface was estimated to be 50 W m^{-2}.

To determine which volatile organic compounds might best be used to characterize the organic matter in the seawater, a limited number of samples were analyzed using solid phase micro-extraction (SPME) (Lord and Pawliszyn, 2000). Four different SPME sorbents (100 μm polydimethylsiloxane (PDMS), 75 μm Carboxen/PDMS, 65 μm PDMS/divinylbenzene (DVB) and 65 μm Carbowax/DVB) (Supelco, Bellefonte, PA) were tried; 75 μm Carboxen/PDMSwas found to be most suitable. 10-mL aliquots of seawater in pre-combusted glass vials were extracted by immersing SPME fibres, with stirring, for 30 minutes at ambient temperature. A 3.5% (w/v) solution of pre-combusted (450 °C) sodium chloride in ultra-pure (MilliQ) water, as well as MilliQ water filtered and bottled during sampling in the same manner as the seawater samples, were used as blanks. Analytes were desorbed (1 min) and analyzed by gas chromatography/mass spectrometry (GC/MS) (HP 6890 GC with 5973 MSD, Agilent) on a HP 5-MS (5%-Phenyl-methylpolysiloxane) column (30m × 0.25 mm id × 0.25 μm film) under the following conditions: splitless injection (vent time 1 min), He carrier gas (1.5 mL min^{-1}, constant flow), injector

270 °C, oven 35 °C for 6 min, then 7 °C min^{-1} to 80 °C, then 15 °C min^{-1} to 250 °C, 5 min hold, MS in scan mode beginning at m/z 35, with 70 eV electron ionization, transfer line temperature 280 °C, MS source temperature 230 °C, quadrupole temperature 150 °C.

2.3.4. Aerosols

Aerosols were collected on polished aluminum foil impactor substrates (previously baked at 450 °C overnight) using a Micro-orifice Uniform Deposit Impactor (MOUDI, MSP Corporation, St. Paul, Minnesota), a cascade impactor which fractionates the aerosols into nine nominal size classes: > 18 μm, 9.9 – 18 μm, 6.2 – 9.9 μm, 3.1 – 6.2 μm, 1.8 – 3.1 μm, 1.0 – 1.8 μm, 0.55 – 1.0 μm, 0.31 – 0.55 μm, and 0.19 – 0.31 μm. Impactor substrates were sealed into Petri dishes, protected from light, and stored frozen (-18 °C) until analysis. Collection times varied (6 - 40 hours), but were typically ca. 12 hours (corresponding to 19 m^3 air). Wherever possible, samples were collected without interruption. However, during periods of station work, the MOUDI pump was stopped and the inlet covered whenever the ship was not in motion, or when contamination by ship exhaust might otherwise be anticipated. Blanks were loaded into the MOUDI as were normal foil substrates, and left there for 12 hours with the inlet covered and the pump switched off.

Preliminary work showed the quantity of aerosol material on each stage to be insufficient for specific compound analysis by chromatography. Samples

were therefore analyzed for morphology and elemental composition using a Hitachi S-4700 field emission scanning electron microscope (FE-SEM) with an Inca Pentafet Energy Dispersive X-ray (EDX) detector (Oxford Scientific). Samples were introduced into the SEM on excised sections of the aluminum foil MOUDI substrates, attached to aluminum sample stubs using double-sided carbon tape. Images were obtained using a 2 keV beam voltage and 10 μA current by imaging secondary electrons, while X-ray spectra were obtained at 5 - 10 keV. These lower voltages were selected so that lower atomic mass elements such as carbon could be detected, but they precluded the analysis of elements heavier than calcium (or occasionally, iron). Samples were not sputter-coated or otherwise pre-treated.

2.3.5 Aerosols- microbiology

To explore whether any viable micro-organisms present in marine aerosols might have been collected intact by the MOUDI, sub-samples from three size fractions (9.9 – 18 μm, 1.8 – 3.1 μm, and 0.19 – 0.31 μm) from each of three sampling periods (June 23, 2004, 14-hour sample; July 1, 2004, 9.4-hour sample; July 14, 2004, 12-hour sample) were incubated, separately, on growth media suitable for bacteria and for fungi. Blanks for each size fraction were also incubated in duplicate. DNA from the bacterial isolates was lysed and purified. 16S rDNA was sequenced and identified according to standard microbiological methods (see Supplementary Material).

2.3.6. Meteorological data

Air mass back trajectories were supplied by the German Weather Service (DWD), and were calculated using the DWD Globalmodell (GME) (Kottmeier and Fay, 1998) with 60 km resolution. Standard meteorological information (air temperature and pressure, relative humidity, wind speed and direction, global radiation) were updated continuously from onboard facilities.

2.4 Results and Discussion

2.4.1 Meteorology

108-hour air mass back trajectories (see Supplementary material) indicated that for whole air and aerosol sampling periods, with one exception (air sampled June 22), air masses encountered had spent the previous 4.5 days over marine areas. These back trajectories also indicated largely laminar air flow which would, for the greater part of the trajectory, be in close proximity to the ocean surface.

2.4.2 Air samples- non-methane hydrocarbons

Concentrations of NMHCs in air from nine sites, spanning the full range of latitudes, are shown in Figure 2-2. We were cautious in our use of the canister samples, and excluded from the reported data set any which, despite precautions

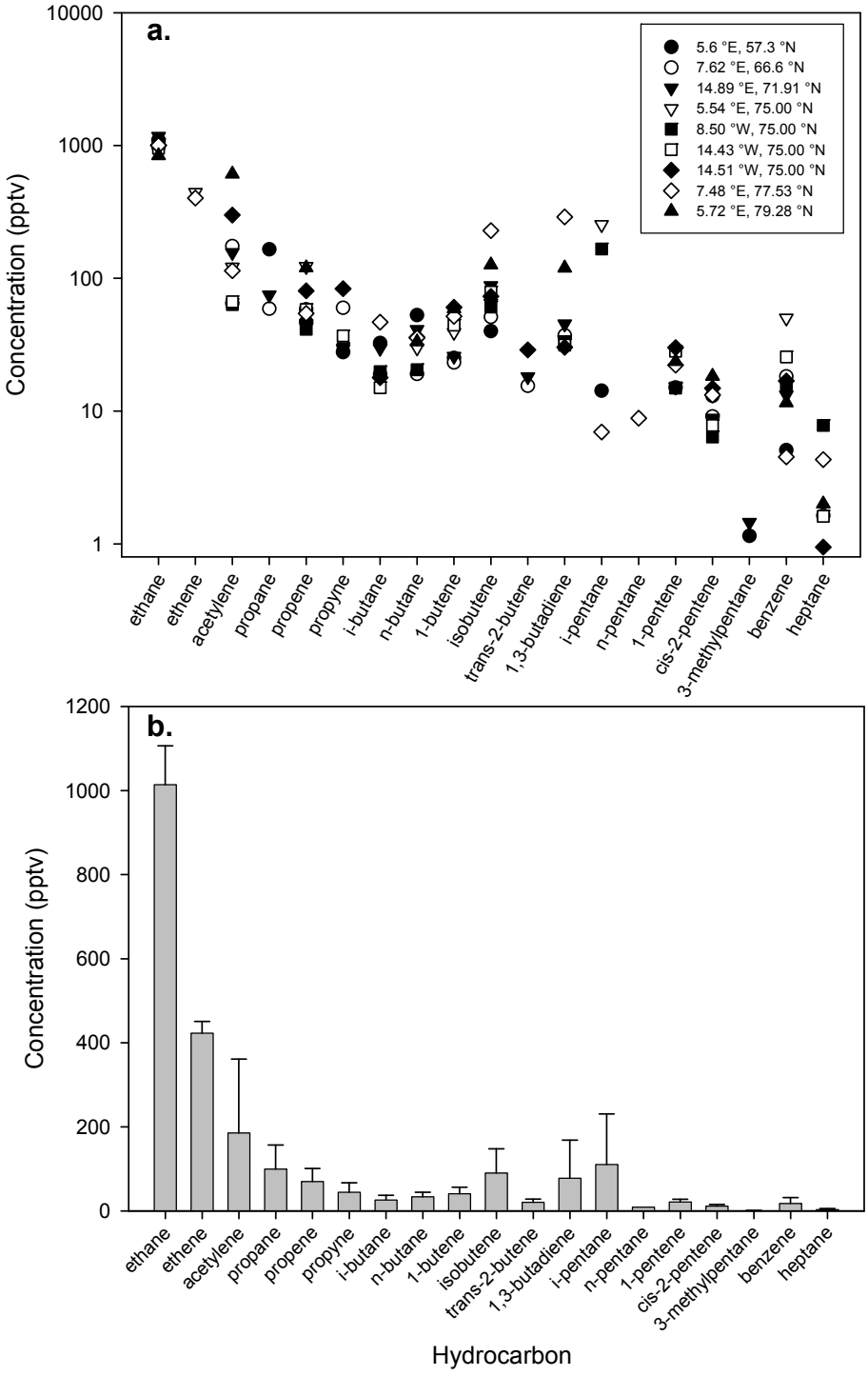

Figure 2-2. **a.** Individual non-methane hydrocarbon concentrations at sites representing a range of latitudes. **b.** Non-methane hydrocarbon concentrations averaged over the sites above (mean ± SD, n = 9)

taken during sampling, showed any possibility of contamination (for example, those containing anomalously high levels of benzene) and also those for which all compounds were below their detection limits. High detection limits for certain alkenes (e.g., ethene) were due to a highly variable blank for these compounds. Artifacts leading to increases in concentration have been noted for certain alkenes in canisters, making their quantification

less reliable. Certain C_6 and C_7 compounds (n-hexane, toluene) are not reported due to similar concerns about the quality of blanks.

Ethane was consistently present at around 1 ppbv (1.01 ± 0.09 ppbv), while propane, propene and ethyne (acetylene) displayed mean concentrations roughly 10-fold lower (100, 70 and 185 pptv, respectively). Ethane concentrations were expected to be quite consistent from site to site, given its long photochemical lifetime (39-56 days) (Jobson, 1994; Warneck, 2000). C_4 - C_7 hydrocarbons were detected at still lower mean concentrations. Site-to-site variability increased with increasing molecular weight. The data are consistent with other published data sets over the remote ocean, including those reported by Rudolph and Ehhalt (1981) and Hopkins et al. (2002) for the Nordic Seas in spring and summer, although our values for C_2 – C_4 compounds are somewhat higher than those in the latter study.

Propyne, detected at six of nine sites, has not previously been reported in surface air samples over the remote ocean. Its C_2 homologue, ethyne, has a long photochemical lifetime (τ) of 18 days (Warneck, 2000) (assuming removal by OH

oxidation only, and [OH] = 8×10^5 molecule cm^{-3}, $k_{OH} = 8 \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1}), and is often taken to be of anthropogenic (or at least continental) origin (Hopkins et al., 2002). Certainly, the unusually high (610 pptv) ethyne mixing ratio at the northernmost site, in Fram Strait (Fig. 2-2), may reflect that the ship was operating in that area over an extended period (Fig. 2-1a), leading to elevated background concentrations of this long-lived compound, even if air sampling was conducted away from direct ship exhaust. However, Bonsang et al. (1988) found ethyne to be supersaturated in Indian Ocean waters and postulated a marine source. If this is the case, propyne may also be of marine origin, although with a limited number of samples, we cannot currently confirm this.

The back trajectories indicate air which had spent 4-5 days over the marine environment and suggest that, with the possible exception of long-lived hydrocarbons (such as ethane, ethyne and benzene), the NMHCs analyzed have marine sources. We regressed (linear least-squares) concentrations of all NMHCs against each other, expecting that this might suggest which NMHCs might have similar origins, or the emissions of which NMHCs might be influenced by the same factors. Also, concentrations of each hydrocarbon were regressed against selected meteorological and oceanographic variables which might be expected to influence their formation, emission or breakdown: O_3 mixing ratio, wind speed, global radiation, air temperature, surface water temperature, surface chlorophyll fluorescence, and total DOC concentration. Few correlations were detected. The data contrast with those from our previous studies (Ariya et al., 1998; 1999) in spring and winter in the Arctic, in which all NMHCs co-vary to a large degree.

For those data, a homogeneous source and largely static "smog chamber"-type conditions could be assumed, in which radical oxidation alone changed the concentrations of NMHCs over time. Those studies considered a largely stagnant air mass over the polar ice cap, while meteorological conditions in the current study did not allow for such an assumption. Thus, while a kinetic analysis on hydrocarbon trends to determine oxidizing radical concentrations was attempted, it was not successful.

The data suggest highly variable sources for NMHCs, most likely influenced by local emission and chemistry, in addition to being influenced by transport. Notably, surface water DOC concentrations do not appear to correlate significantly with measured atmospheric NMHC concentrations, although differences in the origin and thus nature of DOC at different locations during the cruise may explain this observation. Pszenny et al. (1999) noted that for a few observations in South Pacific, higher concentrations of dissolved NMHCs were associated with higher DOC levels.

2.4.3 Surface waters- dissolved organic carbon

To examine concentrations of dissolved organic carbon, surface water samples were grouped into four different cruise sections (Table 2-1). DOC concentrations were highest (1.06 ± 0.13 mg L^{-1}) in the East Greenland Current, where waters flowed south, were consistently -1 to -2 °C, and were typically ice-covered. The data are consistent with other published data sets for the Nordic

Seas (Opsahl et al., 1999; Amon et al., 2003). The East Greenland Current carries much of the riverine DOC which is exported from the Arctic into the Atlantic (Amon et al., 2003), and thus higher DOC concentrations are expected. Furthermore, much of this additional DOC is terrestrial, resulting in a

Table 2-1. DOC concentrations for various water masses/ sectors of the cruise, and effect of UV-A irradiation (λ_{max} 370 nm) on DOC concentrations of selected samples. The quantities marked* differ significantly from each other at P = 0.05 (Student's t-test).

Region or location	**[DOC] (mg L^{-1}) (mean ± SD; n)**	
Norwegian Coast/Norwegian Sea	0.92 ± 0.34 (6)	
Greenland Sea transect (75 °N)	0.88 ± 0.24 (22)	
East Greenland Current (ice cover)	1.06 ± 0.13 (7)	
Fram Strait	0.84 ± 0.13 (10)	
	before irradiation	*after irradiation*
75.00 °N, 5.94 °W	0.775 ± 0.006* (2)	0.729 ± 0.005* (2)
75.00 °N, 14.49 °W	1.11 ± 0.04 (2)	1.04 ± 0.02 (2)
79.33 °N, 5.58 °W	0.85 ± 0.01 (2)	0.78 ± 0.03 (2)

heterogeneity in DOC structure and chemistry, which may influence processes by which NMHCs are formed from DOC. DOC concentrations were lower along the 75 °N transect and in the southern Norwegian Sea/off the Norwegian coast, as well as in Fram Strait where both Atlantic and Arctic surface waters would have been sampled (Opsahl et al., 1999). Considerable variability in [DOC] was noted along the 75 °N transect, presumably reflecting the algal blooms which were periodically encountered.

[DOC] appeared to decrease 5-8% after 24 hours of UV irradiation, although for only one site (75.00 °N, 5.94 °W) was the decrease (6%) statistically significant (Table 2-1). This is consistent with the generation and loss of volatile compounds on irradiation. Other studies on NMHC evolution from seawater have either employed much longer irradiation times (Ratte et al., 1998) or tropical, coastal waters which are much richer in DOC than those used here (Riemer et al., 2000). In the study by Ratte et al. (1998), [DOC] in some samples decreased by 75% after 41 days of irradiation.

Using the 75 μm Carboxen/PDMS SPME fibre, C_5 and C_6 hydrocarbons (pentane, hexanes), dimethylsulfide (DMS) (a product of marine phytoplankton (Andreae et al., 2003)) and acetone were detected in samples from the 75 °N transect (1.80 °E, 0.60 °W, 8.47 °W and 11.68 °W), and in a sample from the East Greenland Current (75.00 °N, 14.49 °W). The detection of C_5 and C_6 alkanes in these waters is consistent with the marine source of the higher molecular weight hydrocarbons suggested by the whole air data (section 3.2). The variability in DOC concentrations and in the nature of DOC (terrestrial or marine) noted above

would thus be consistent with the variability in the higher molecular weight hydrocarbon concentrations in the air samples. We note that the process by which alkanes (in particular) may be formed in surface seawater is unclear (Ratte et al., 1998; Riemer et al., 2000) and our results suggest that for hydrocarbons greater than $C_{4,}$ this would be a fruitful area for further investigation. On the topic of acetone, measurements of this compound in seawater are relatively rare in the literature, with only figures from the tropical Atlantic (mean 17.6 nM (Williams et al., 2004); 3.0 nM (Zhou and Mopper, 1997)) and tropical and sub-tropical Pacific (10 nM (Singh et al., 2003); 12 – 14 nM (Marandino et al., 2005)) reported, and its role in/contribution to the oxidative potential of the marine troposphere is still unclear. Thus, a straightforward method for its analysis in seawater by SPME is potentially valuable. Further studies are required to optimize the method for quantification of these and other volatile organics in the remaining seawater samples.

2.4.4 Aerosols

For characterization by SEM-EDX, aerosol samples were chosen representing the early, mid and latter parts of the cruise (June 23, 2004, 14-hour sample; July 1, 2004, 9.4-hour sample; July 14, 2004, 12-hour sample) (Fig. 2-1), and larger, smaller and mid-range size fractions (9.9 – 18 μm, 1.8 – 3.1 μm, and 0.19 – 0.31 μm) were selected from each. Aluminum is present in many of the EDX spectra as a result of the aluminum substrate, and therefore this element itself could not be analyzed. Figure 2-3 shows an overview of some of the

particles collected. A great variety of particle morphologies were observed, with no distinguishable site-to-site differences in their distribution. Predictably, most forms could be ascribed to marine sources, although aerosols of crustal mineral origin have been detected in the remote tropical Atlantic and Pacific (Posfai et al., 1994; 1995). Particles in our samples include sea salt (Fig. 2-3a), sulfate (Fig. 2-3f), and mixtures of these phases (Fig. 2-3c,d). We attribute the sulfate to marine sources, due to the remote, marine nature of the air masses (Section 3.1), in contrast to studies where correlation with black carbon particles indicated sulfate aerosol from continental pollution sources (Andreae et al., 2003). Forms such as that in Figure 3b were commonplace, and are interpreted as resulting from the evaporation of droplets or highly deliquescent aerosols that impacted the substrates. Calcium sulfate (Fig. 2-3h), although not common, has also been reported in aerosols in marine air masses by Hoornaert et al. (1996). Particles with elemental ratios consistent with calcium carbonate were observed in the 0.8 – 3.1 μm fraction (Fig. 2-3i). Besides carbonates, little carbonaceous matter was detected in any size fraction, although one particle observed (Fig. 2-3e) contained (47 ± 5)% carbon (mean ± SD, n=3) and (33 ± 1)% oxygen, and may be fresh diatomaceous material (silicon was also detected). The general paucity of carbon detected may be due to the use of EDX which, for lighter elements, is often semi-quantitative at best (Posfai et al., 1994). Furthermore, despite the relatively low electron beam voltages, ablation of fragile areas of the sample was occasionally observed, and lighter elements such as carbon are particularly prone to such

volatilization. Thus, while we have been unable to definitively establish the prevalence of organic carbon in these

aerosols, we cannot rule out a contribution as the method used is not particularly suitable for organic carbon compounds. Preferred methods for carbonaceous aerosols would be thermal techniques such as evolved gas analysis (Novakov et al., 2000; Mayol-Bracero et al., 2002), which allows total carbon to be determined and is largely able to distinguish black carbon from organic carbon, although these techniques do not yield the information on morphology or elemental composition obtainable by SEM. It is also not well known whether these techniques would be sufficiently sensitive for the quantities of material collected on MOUDI substrates under pristine conditions.

SEM also allowed us to verify the efficacy of size-fractionation by the MOUDI. The 0.8 – 3.1 μm and 0.19 – 0.31 μm size fractions contained a number of particles larger than these stage cut-off sizes (Fig. 2-3g, h, f). Large particles may bounce from impactor plates, resulting in larger particles appearing in fractions corresponding to smaller sizes (Wittmaack et al., 2002; 2005) and certain kinds of particles (e.g., sulfates) may grow in impactors by accretion from the gas phase (Wittmaack et al., 2002). Larger particles shattering on impact may be responsible for smaller particles being present on larger stages (Fig. 2-3a).

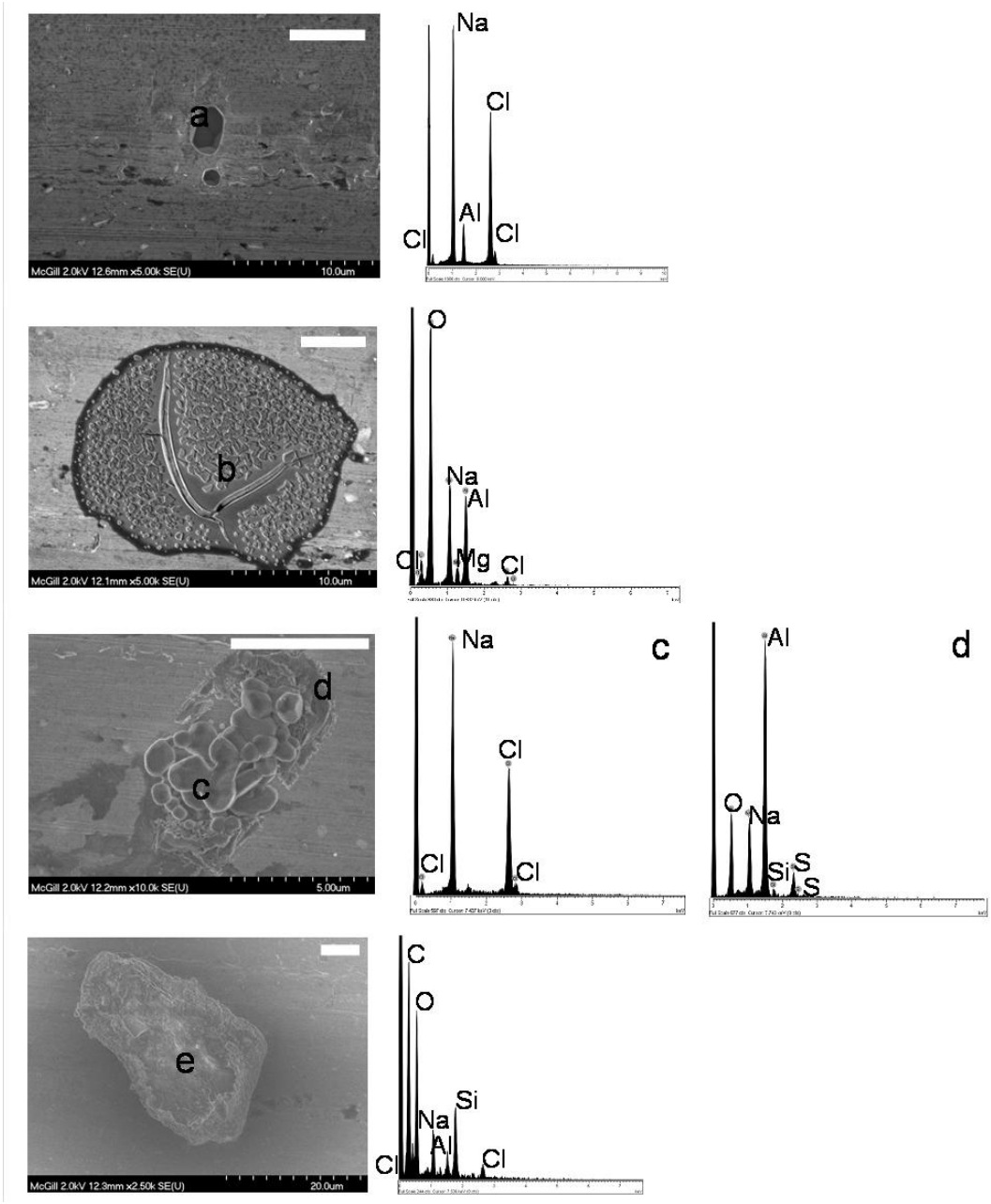

Figure 2-3. Overview of typical aerosol forms (with energy dispersive X-ray spectra) observed in Nordic Sea samples. **a-e.** Particles from the largest (9.9-18 μm) fraction; **f-h.** Particles from 1.8 – 3.1 μm fraction; **i,j.** Particles from the 0.18-0.31 μm fraction. The horizontal white bar in each image represents 5 μm length.

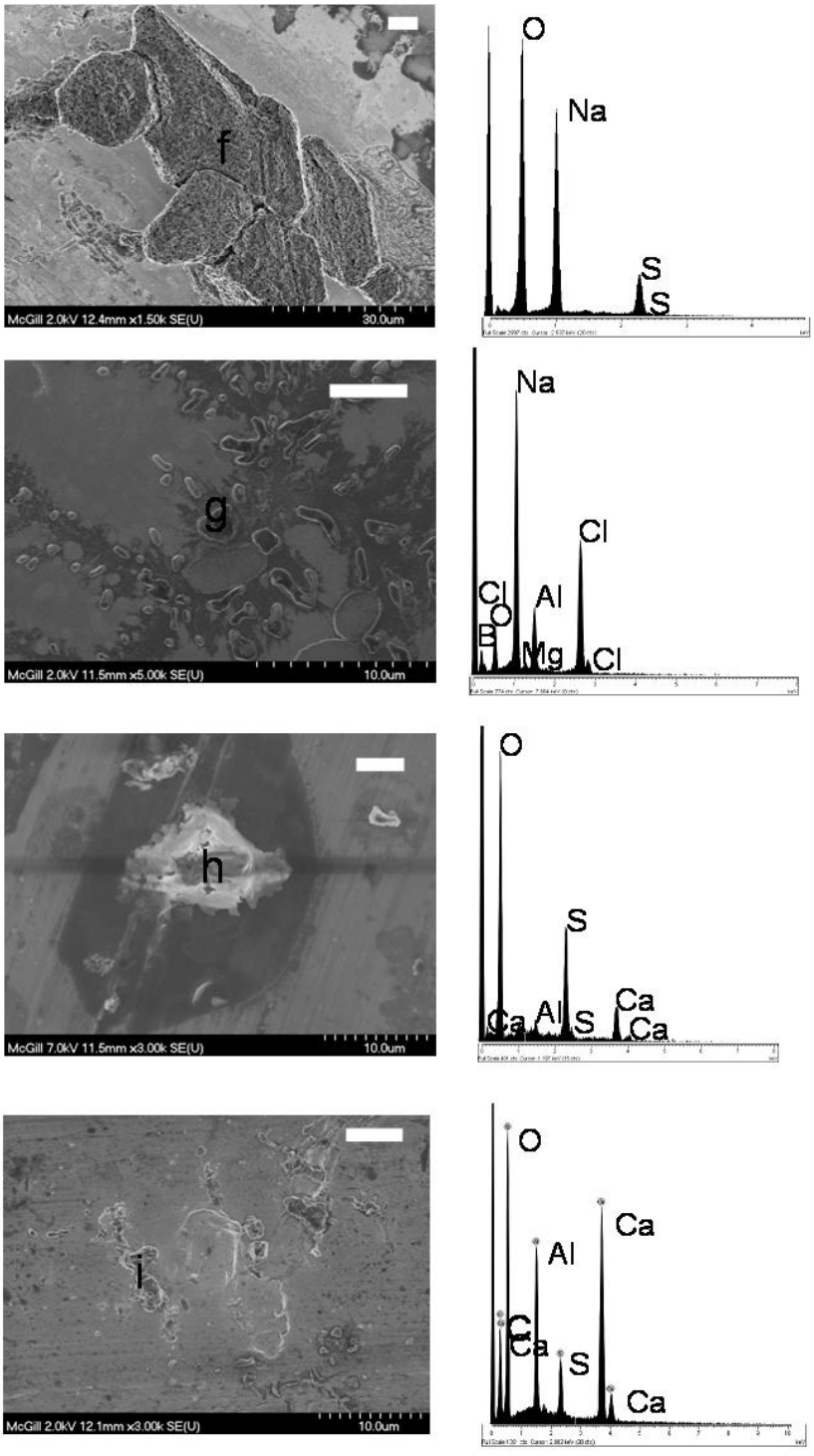

Figure 2-3 (continued)

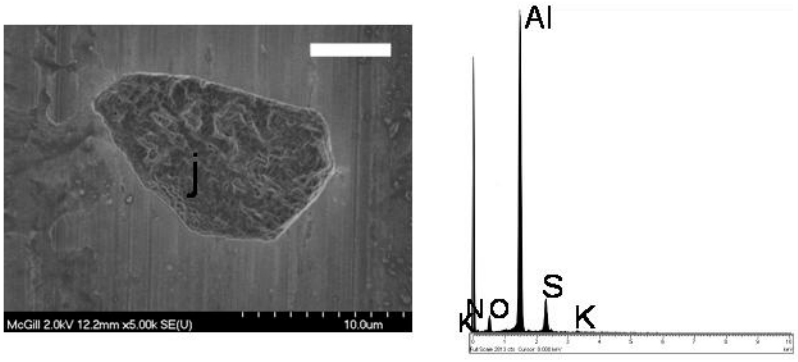

Figure 2-3 (continued)

2.4.5 Bioaerosols

For most of the 11 aerosol samples which were incubated (including all of the blanks), no observable micro-organisms grew under the culture conditions used here. However, on one of the duplicates on bacterial agar from the large (9.9-18 μm) aerosol fraction from June 23, 2004, circular, yellow colonies formed, reaching approximately 3 mm diameter after five days. It is noteworthy that SEM did not detect any recognizably biological material in this size fraction, though as noted previously, it may not have been observed due to the fragility of soft material under the strong electron beam.

The sequence obtained for the 16S rRNA gene isolated from this colony was rich in C and G and was 99% identical to the gram-positive bacterium *Micrococcus luteus*. While *M. luteus* is widespread in the environment (Bultel-Ponce et al., 1998), certain strains have been found in marine biofilms (Kwon et al., 2002), and associated with marine sponges (Bultel-Ponce et al., 1998), and a

marine origin is therefore plausible. Though bacteria in marine aerosols are subject to harsh conditions such as increased UV irradiation, they may be imbedded in gel-like organic particles originating in the sea-surface microlayer (Aller et al., 2005) allowing them to remain viable for longer. This result suggests that cultures should be attempted from other size fractions and sites, or that bioaerosol-specific samplers might be used in future marine field campaigns. Posfai et al. (2003) found that bacteria constituted 1% of aerosol particles sampled over the Southern Ocean, yet found no bacteria in similar samples from the Atlantic and Pacific (Posfai et al., 1994; 1995). They suggest that numbers of microorganisms in the marine atmosphere are highly variable, and the apparent variability may be enhanced by collection using impactors (Posfai et al., 2003). A cascade impactor will likely bias the sampling in favour of mechanically hardier species (Li and Lin, 1999). Furthermore, it is known that only a small fraction of viable marine bacteria (indeed, environmental bacteria in general), are culturable (Aller et al., 2005; Sun and Ariya, 2006). Lastly, while the standard microbiological methods we used do not match the temperature at which the aerosols were samped, psychrotolerant bacteria from cold environments can be cultured over a wide range of temperatures (up to 45 °C in some cases) (Morita, 1975; Xiang et al., 2005). These findings all suggest that our single observation of a culturable bacterium is an underestimate, and that more taxa of culturable microbes might be found in marine aerosols if less mechanically harsh sampling apparatus and cold-room culture conditions are used in future studies.

2.5 Conclusions

A data set of 19 non-methane hydrocarbons across a range of latitudes in surface air over the Nordic seas was obtained. The data are very heterogeneous, particularly for short-lived (C_4 and C_5) hydrocarbons, which supports the idea of a possible localized marine origin for these compounds. Underlying surface ocean waters have also been analyzed for total DOC, with higher concentrations (1.06 ± 0.13 mg L^{-1}) detected in the surface waters of the East Greenland Current than those from the Norwegian coast, the Norwegian-Greenland Sea transect and Fram Strait. These DOC concentrations decreased 6-8 % on 24-hour UV-A irradiation in selected samples. A number of low molecular weight organic compounds were also identified in these waters using SPME, among them C_5 and C_6 hydrocarbons, which again supports the notion of marine sources of NMHCs. While aerosols from the same sites appeared, from SEM-EDX results, to contain little carbonaceous material, the isolation of a culturable bacterium for the largest aerosol fraction suggests that microorganisms may be contributing organic material to the boundary layer through aerosols in this region. However, it is as yet unclear whether this biological material contributes appreciably to the VOC content of the marine boundary layer, either through photodegradation or direct emission. This study suggests that further work is needed on exactly how much organic and biological material is typically present in remote marine aerosols and how readily this material is converted to or emits VOCs. It further supports the idea that DOC in bulk surface ocean waters is a source of low molecular weight

hydrocarbons to the marine troposphere, and that a more quantitative understanding of the processes responsible for this VOC formation is needed.

2.6 Acknowledgements

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Appendix. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.chemosphere.2007.04.056.

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2.8 Appendix to Chapter 2. Supplementary Material

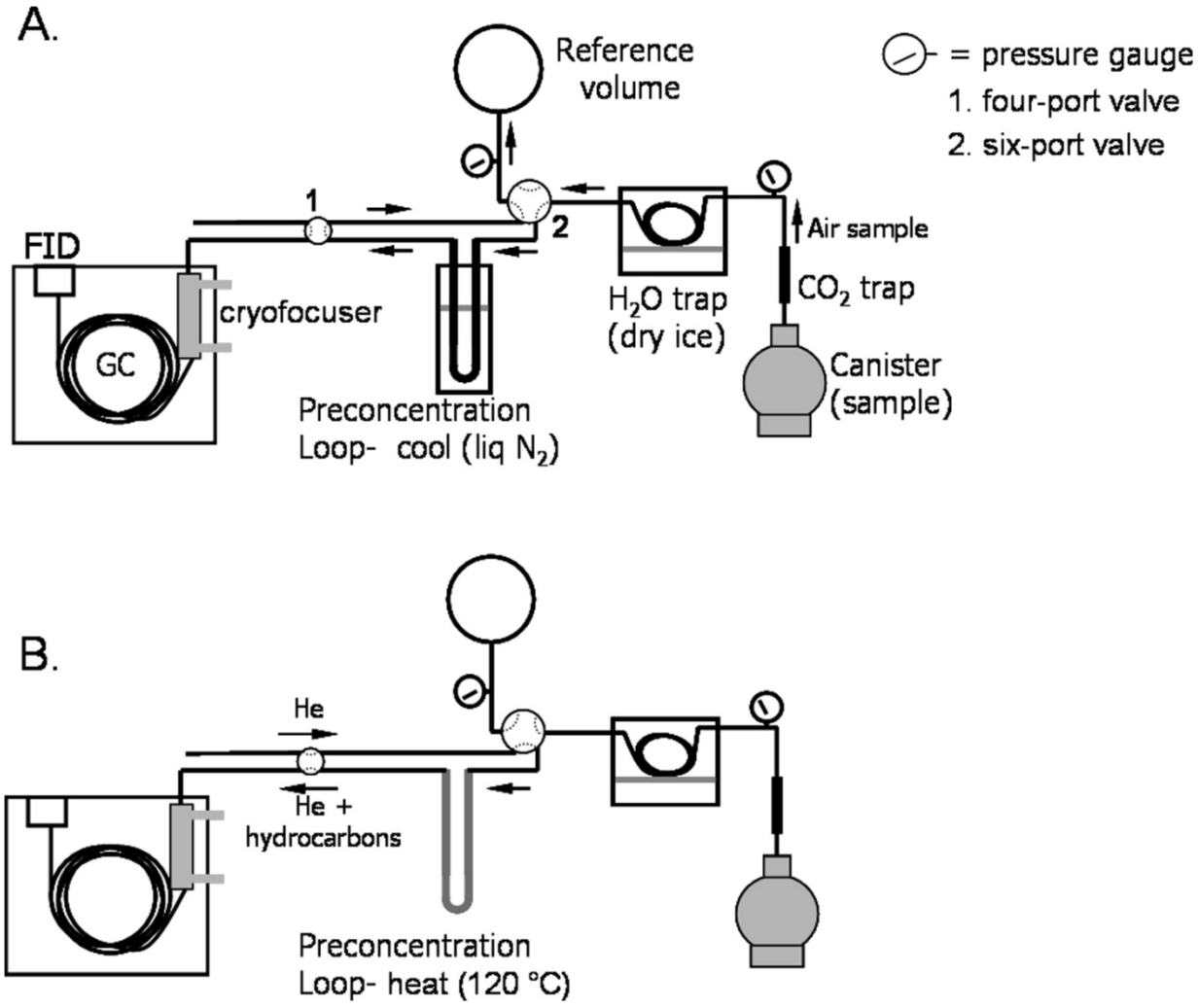

Figure 2-4. Analysis of non-methane hydrocarbons (NMHCs) in whole air samples. All surfaces in contact with the sample were chromatographic-grade stainless steel **A.** Air sample passes through traps for CO_2 and water vapour removal, and NMHCs are preconcentrated on a liquid nitrogen-cooled trap packed with glass beads; remaining air flows into (pre-evacuated) reference volume. **B.** Trap is heated rapidly and a helium flow transfers NMHCs to a gas chromatograph for separation and detection.

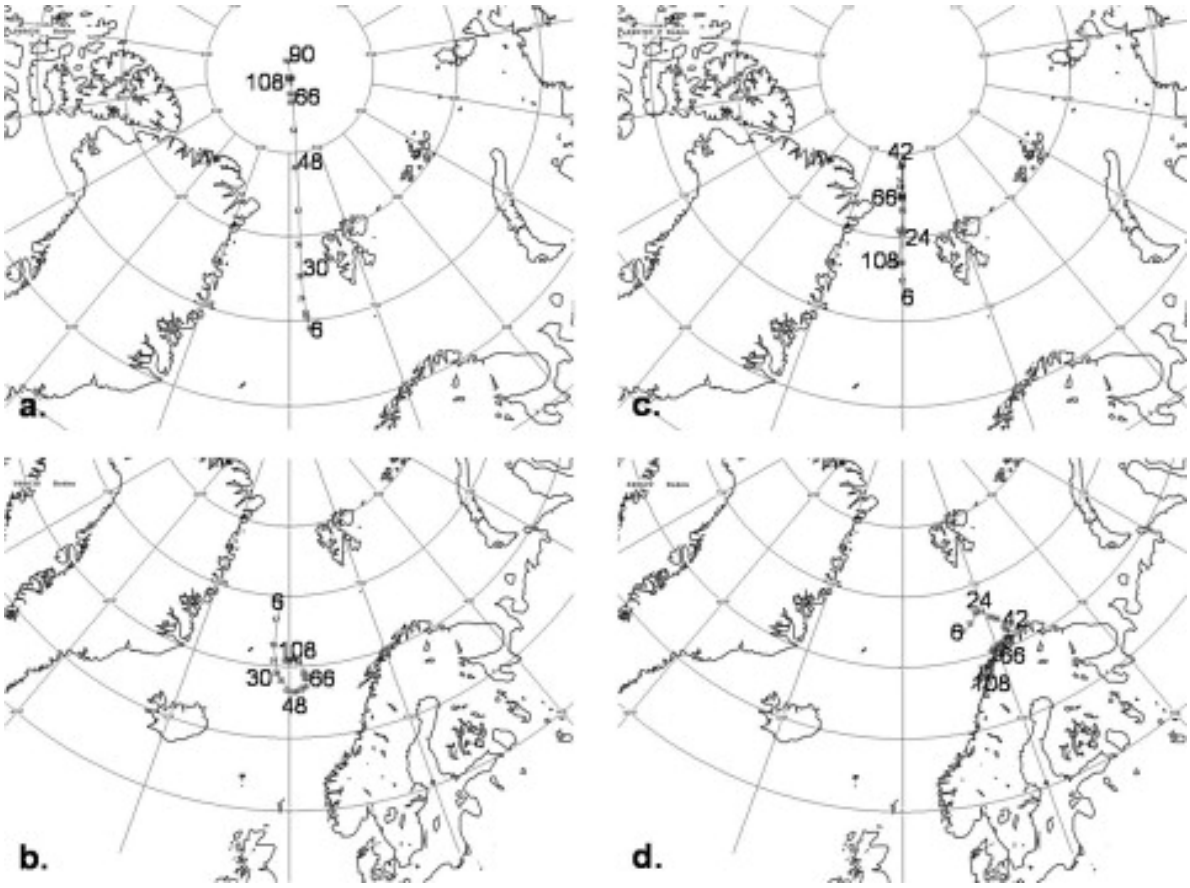

Figure 2-5. 108-hour air mass back trajectories for selected, representative air sampling locations on FS *Polarstern* cruise ARK-XX/1. **a.** Air originating at extreme high latitudes (earlier sections of the cruise) (June 26) **b.** Southerly oceanic air masses (June 30) **c.** Air masses originating over the Greenland Sea/Fram Strait (July 5- last third of the cruise). **d.** Air mass static near remote Norwegian coast (June 22). With the exception of d., all air sampled had spent at least the preceding 108 hours over the oceans. Maps are polar azimuthal equidistant projections.

2.8.1 Methodology for bioaerosol culture, isolation and identification

Subsamples of aerosols sampled by MOUDI were incubated on growth media suitable for bacteria (Trypticase Soy Agar, spiked with cycloheximide to suppress fungi) and fungi (Sabouraud Dextrose Agar, spiked with streptomycin sulfate to suppress bacteria). Each sub-sample was incubated in duplicate at 37 °C, as per standard microbiological culture methods. DNA from the bacterial isolates was lysed and purified using Ready-Lyse Lysozyme and the Master Pure DNA purification kit (Epicentre Technologies, Madison, WI) according to the manufacturer's instructions. Extracted DNA was amplified using the Polymerase Chain Reaction (PCR) in a final volume of 50 μL using the 16S forward primer (5'-AGAGTTTGATCCTGGCTCAG-3') and reverse primer (5'-ACGGCTACCTTGTTACGACTT-3') (Integrated DNA Technologies, Coralville, IA). PCR included 35 cycles of denaturing at 94 °C for 1 min, annealing at 55 °C for 1 min, and extending at 72 °C for 2 min, followed by a 7 min final extension at 72 °C. The PCR product was separated and analyzed by gel electrophoresis in 1.5% agarose gel stained with ethidium bromide.

The PCR product of the 16S rDNA gene obtained from the above culture was purified using a QIAquick PCR Purification Kit (QIAGEN, Mississauga, Canada) and sequenced at the Sheldon Biotechnology Center, McGill University, Montreal. The 16S rDNA sequence was aligned and compared with those available in the GenBank databases using BLASTN software through the National

Center for Biotechnology Information server. Only 16S rDNA database sequences containing <1% undetermined positions were retained for analysis.

Chapter 3

Determination of Acetone in Seawater Using Derivatization-Solid Phase Microextraction

In this chapter, we aimed to address an overarching problem that arose from the work shown in chapter 2: the need for accessible methodology to readily perform quantitative measurements of volatile organic matter in the ocean. Chapter 2 described the measurement a number of compound classes in marine air and surface seawater, sampled simultaneously, as a first step in investigating the links between organic carbon in these two environmental compartments. Solid phase microextraction (SPME) was used to identify a number of volatile compounds in seawater. These included compound classes besides hydrocarbons, one of which was the carbonyl compound acetone, and highlighted the need to measure volatile as well as bulk (non-volatile) organic carbon in seawater. The potential for its detection by SPME was highlighted, but the results indicated that there would be challenges to its separation from other compounds and its quantification. Acetone links the surface oceans and the marine troposphere through its volatility and its effect on tropospheric oxidant chemistry, and which is furthermore though to be formed in part from the photochemistry of higher molecular weight DOC. We therefore set out to develop methodologies which would specifically allow the better separation and quantification of this key compound. We also considered this a first step in developing methods which would potentially be applicable to the same

compound, and carbonyl compounds generally, in marine air as well as seawater, allowing both sides of the interface to be studied with the same methods at the same time.

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Determination of Acetone in Seawater Using Derivatization-Solid Phase Microextraction

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3.1 Abstract

Acetone plays an important role in the chemistry of both the atmosphere and the ocean, due to its potential effect on the tropospheric HO_x (= HO + HO_2) budget, as well as its environmental and health effects. We discuss the development of a mobile, sensitive, selective, economical, and facile method for the determination of acetone in seawater. The method consists of derivatizing acetone to its pentafluorobenzyl oxime using 2,3,4,5,6-pentafluorobenzylhydroxylamine (PFBHA), followed by solid phase micro-extraction (SPME) and analysis by Gas Chromatography/Mass Spectrometry (GC/MS). A detection limit of 3.0 nM was achieved. The buffering capacity of seawater imposes challenges in using the method's optimum pH (3.7) on seawater samples, requiring calibration standards to be made in buffered salt water and the acidification of seawater samples and standards prior to extraction. We employed the technique for analysis of selected surface seawater samples taken on the Nordic Seas during the ARK-XX/1 cruise (R.V. *Polarstern*). 5.5 –9.6 nM acetone were observed in these waters, the first acetone measurements reported for far North Atlantic and Arctic waters.

Keywords: ketones, volatile organic compounds, Gas Chromatography/Mass Spectrometry, dissolved organic carbon

3.2 Introduction

Acetone in the atmosphere is produced by the oxidation of propane and other larger molecular weight hydrocarbons or through direct emission by various species of plants [1,2]. It may also be transferred to the atmosphere from surface seawater [3], where it is thought to be derived from the photodegradation of dissolved organic matter (DOM) [4,5]; it has also been suggested to be produced directly by certain algae [6] and bacteria [7]. It can be readily exchanged between natural waters and air due to its low molecular weight and volatility. Interest in acetone, along with many other low molecular weight (LMW) carbonyl compounds, has increased due to their potential adverse health effects in drinking water [8]. Moreover, acetone can potentially alter the oxidizing potential of the troposphere through the production of HO_2 [1,9]. One of the main sources of hydroxyl (OH) radicals in the troposphere is the reaction of water vapor with $O(^1D)$ (Reactions 3-1 and 3-2).

$$O_3 + h\nu\ (\lambda \leq 320\ nm) \rightarrow O_2 + O^{\cdot}\ (^1D) \qquad (3\text{-}1)$$

$$O^{\cdot}\ (^1D) + H_2O \rightarrow 2\,^{\cdot}OH \qquad (3\text{-}2)$$

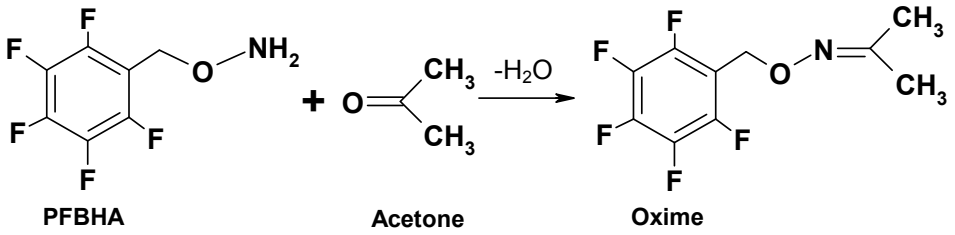
Since the upper troposphere is much dryer than the lower troposphere, the above pathway for the production of hydroxyl radicals is less efficient [10]. In this region of the troposphere, acetone contributes to the production of HO_x [10].

Indeed, by considering acetone photochemistry (photolysis and OH-initiated reactions) in HO_x calculations, better agreement between experimental and observed values is obtained [11]. Additionally, acetone, along with other LMW carbonyl compounds, can lead to the production of peroxyacetylnitrate (PAN), a reservoir species that allows for long range transport of NO_x [1] and thus impacts the atmospheric HNO_3 budget. Major sinks of atmospheric acetone are photolysis, oxidation (leading to the production of acetic acid, peroxyacetic acid, and methyl glyoxal), and wet deposition [1].

It is not well known whether the oceans are a net source or sink for acetone. Past studies have surmised that the ocean is a net source [3,12], although more recent studies have obtained data pointing to the contrary [9]. The few reported measurements of acetone in surface seawater show concentrations between 3 and 55 nM [3,9,12,13] with lower concentrations occurring in the bulk water and the higher concentrations occurring in the sea surface microlayer [12]. In the atmosphere the concentration of acetone varies with height and latitude but average mixing ratios are typically 0.3 – 2.3 ppbv [1,9,13].

Acetone quantification in the atmosphere and the oceans is challenging due to its low concentrations and its volatility. In recent years, proton transfer reaction mass spectrometry (PTR-MS) [3] and atmospheric pressure chemical ionization mass spectrometry (API-CIMS) [9] have allowed for on-site measurement of acetone in seawater and marine air; however, the instrumentation is expensive and not widely available. Derivatization-chromatographic methods

are those most frequently found in the literature as they are selective, relatively inexpensive, and widely available. The most commonly reported derivatizing agent for the determination of acetone in both fresh water and seawater is 2,4-dinitrophenylhydrazine (DNPH) [4,5,13-16]. The reaction of acetone with DNPH creates a hydrazone, which can be analyzed using Liquid Chromatography (LC) with detection by Ultraviolet-Visible (UV/Vis) absorbance. Dansyloxyamine (DNSOA) has also been used to derivatize ketones in aqueous samples [17]; the derivatives are separated by LC and quantified by fluorescence. For gas chromatography (GC), derivatization has been accomplished using O-(2,3,4,5,6-pentafluorobenzyl)-hydroxylamine (PFBHA) hydrochloride [8,18-20] (Reaction 3-3).



(3-3)

Acetone has also been quantified photometrically by its reaction with vanillin, which produces a yellow-orange dye which absorbs at 430 nm [21], and by its reaction with alkaline salicylaldehyde [22].

DNPH derivatization can provide low detection limits since it is possible to obtain low blank measurements [16]. However, the use of DNPH also limits the separation techniques available due to the decomposition of several hydrazones at higher temperatures [23]. Derivatization using PFBHA results in the formation of an oxime that is amenable to GC since, unlike hydrazones produced by DNPH derivatization, oximes do not decompose at the high temperature used for GC [24]. Furthermore, the DNPH derivative must be solvent-extracted or otherwise pre-concentrated [16], a step which may be environmentally detrimental (if solvents are needed) or lead to sample contamination.

Solid phase microextraction (SPME), a method developed by Pawliszyn and co-workers [25,26] is an attractive alternative for sample preparation, since it requires no solvents and the SPME fibres are readily portable and easy to use. SPME has been used to extract PFBHA derivatives of a range of carbonyl compounds (primarily aldehydes) from both air and water [8,23,24].

In the current work, we aimed to develop a routine method for the analysis of acetone in seawater using a SPME-GC-MS technique, which would be sensitive, rapid, facile, environmentally benign, and use readily available equipment. To date, SPME has been used to a limited extent to analyze acetone in fresh waters only [8] and the present study represents its first published use for seawater. The use of this technique for analysis of selected surface waters from

the Nordic seas, taken during the ARK-XX/1 cruise (R.V. *Polarstern*, 2004), is herein presented, and advantages and limitations of the technique are discussed.

3.3 Experimental

3.3.1 Materials

Acetone (HPLC grade, 99.5+ %) was purchased from Fisher Scientific (Nepean, ON), and PFBHA hydrochloride from Fluka (St. Louis, MO). Ultrapure water (MilliQ QPAK-1 system, Millipore, Billerica, MA) was used throughout. NaCl was baked overnight at 450 °C to remove any organic contaminants. SPME fibres and holders were purchased from Supelco (Bellefonte, PA). Fibres were initially conditioned as per the supplier's instructions, and re-conditioned daily (15 min, 250 °C) prior to first use.

Glassware was cleaned by rinsing with ultrapure water, followed by baking overnight in a muffle furnace at 450 °C to remove organic contaminants. Where this was not possible (e.g., volumetric glassware), it was rinsed with ultrapure water and ethanol and dried overnight at 125 °C.

3.3.2 Solutions, procedure and instrumentation

PFBHA was prepared daily as a 12 mg/mL (0.0476 *M*) aqueous solution. Blanks and standard solutions for initial tests were made in a 3.5 % w/w (0.6 *M*) NaCl solution to simulate the salinity of seawater. To additionally simulate the

buffering capacity of seawater, buffered salt-water solutions were made using 34.78 g NaCl, 0.193 g $NaHCO_3$ and 0.026 g H_3BO_3 per L of solution. This solution was used for calibration purposes (see Results and Discussion).

Figure 3-1 shows a schematic of the derivatization and extraction procedure. Derivatizations and extractions were carried out in 20-mL screw-capped vials with Teflon-faced silicone septa. The vials were wrapped in aluminium foil to inhibit any photochemical reactions. 10-mL samples of acetone standards or seawater were used. 50 μL of PFBHA solution was added to the vials using an Eppendorf pipette and the samples were derivatized with stirring for two hours, at which point the septum was pre-pierced with a clean syringe needle, 12.7 μL 0.2 *M* HCl added if necessary (see Results and Discussion) and the SPME fibre was inserted into the vial for 30 minutes of adsorption. The use of a 30-minute adsorption was based on other published studies [8], which indicated that for lower molecular mass PFBHA ketone oximes, maximum adsorption was achieved in 20-50 minutes, depending on the ketone. Furthermore, it has been shown [27,28] that as long as the adsorption time is constant, full equilibration of the analyte onto the SPME fibre is not necessary for reproducible quantification.

After solid phase microextraction, the acetone PFBHA oximes were analyzed by Gas Chromatography-Mass Spectrometry (GC/MS). The fibre was desorbed (250° C) in splitless mode for 5 minutes before the split vent was re-opened. The fibre was then left in the inlet for an additional 10 minutes to ensure that it was fully clean before re-use. GC-MS (HP 6890 GC with 5973 MSD,

Agilent, Palo Alto, CA) was performed on a HP 5-MS (5%-Phenyl-methylpolysiloxane) column (30m × 0.25 mm id × 0.25 μm film) under the following conditions: splitless injection, He carrier gas (1.5 mL/min, constant flow), injector 250 °C, oven 50 °C for 2 min, then 5°C /min to 140 °C , then 20 °C /min to 260 °C (no final hold), MS in scan mode (m/z 25 to 400), with 70 eV electron ionization, transfer line temperature 280 °C, MS source temperature 230 °C, quadrupole temperature 150 °C. The acetone-PFBHA oxime was identified by comparison of its mass spectrum with previously published electron ionization mass spectra [18,29] and in the NIST 5.0 mass spectral database, and by its presence and retention time in the chromatograms of acetone standards. Peaks were autointegrated using HP Chemstation (version B-01.00) software on the total ion chromatograms.

3.3.3 Seawater sampling and analysis

The method was applied to selected samples of surface seawater taken from the Norwegian and Greenland Seas during June/July 2004 (cruise ARK-XX/1, RV *Polarstern*). Samples were taken from 11 m depth by means of a direct inlet line in the ship's keel, and were immediately suction-filtered though a 0.22-μm PTFE membrane filter (across a pressure drop of no greater than 300 mbar). Samples were stored frozen in amber glass bottles with Teflon-lined caps (pre-cleaned for EPA Procedure 2 for purgeable volatile organic compounds) (Environmental Sampling and Supply, Oakland, CA) until analysis. 10-mL aliquots of these samples were derivatized and analyzed as described previously.

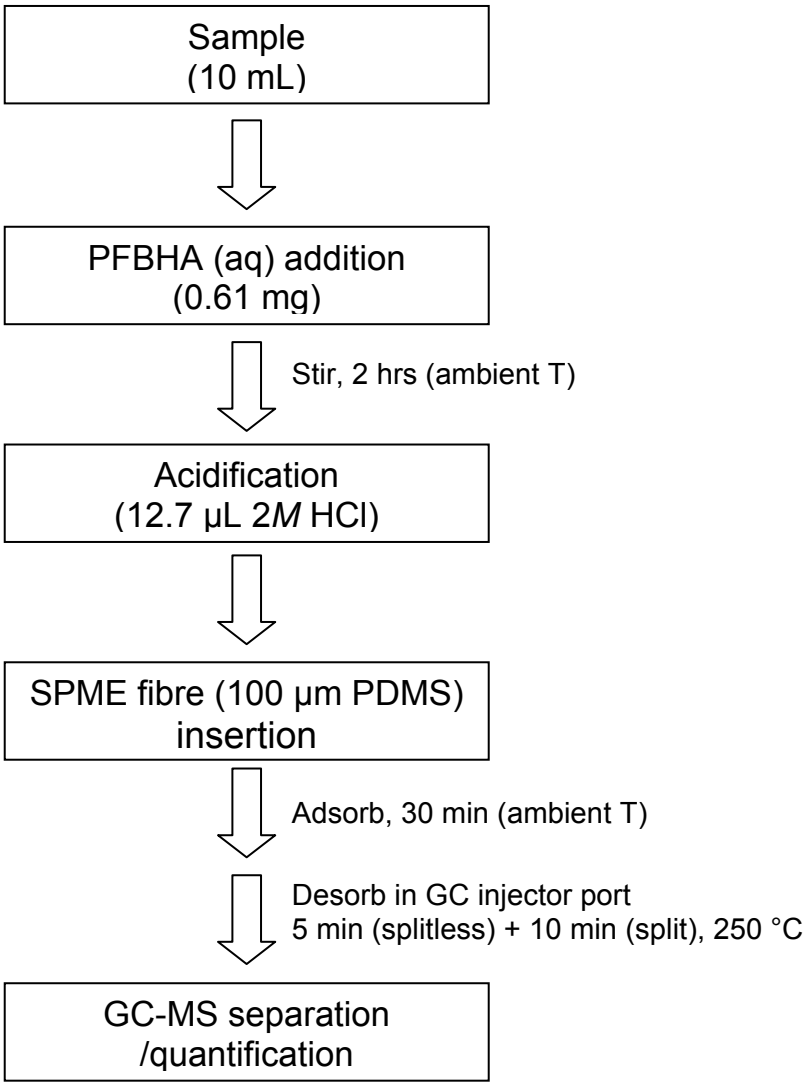


Figure 3-1. Schematic of the derivatization/SPME procedure used here for acetone analysis in seawater.

3.4 Results and Discussion

Figure 3-2 shows a typical chromatogram and mass spectrum for the analysis of acetone in seawater as its PFBHA oxime. Throughout this study, reported peak areas are from the integration of the total ion chromatogram.

3.4.1 Comparison of SPME fibres (adsorbents)

Derivatized and underivatized acetone were compared on three different SPME fibres: 100 μm Polydimethylsiloxane (PDMS), 65 μm Polydimethylsiloxane/ Divinylbenzene (PDMS/DVB), and 75 μm Carboxen/ Polydimethylsiloxane (CAR/PDMS) (Fig 3-3a). Underivatized acetone (0.27 μM) was only detected by the CAR/PDMS fibre. The peak for underivatized acetone in the total ion chromatogram on this fibre was small and eluted before the split vent had closed, where the baseline of the total ion chromatogram was considerably higher. By comparison, the peak due to the acetone oxime on the CAR/PDMS fibre was larger, exhibited less tailing, and eluted later (after the re-opening of the split vent), resulting in more reliable integration. All three fibres detected the acetone oxime at this same concentration (0.27 μM), whereas only the CAR/PDMS fibre detected underivatized acetone. We thus concluded that derivatizing the acetone had the ability to provide a superior method for acetone analysis.

Figure 3-3a shows the acetone oxime peak areas on all three fibres, based on duplicate measurements. The measurement on the CAR/PDMS fibre was the least sensitive and least reproducible (34 % RSD) and consequently this fibre was not employed in any further experiments. Furthermore, Fig. 3-3a indicates that the

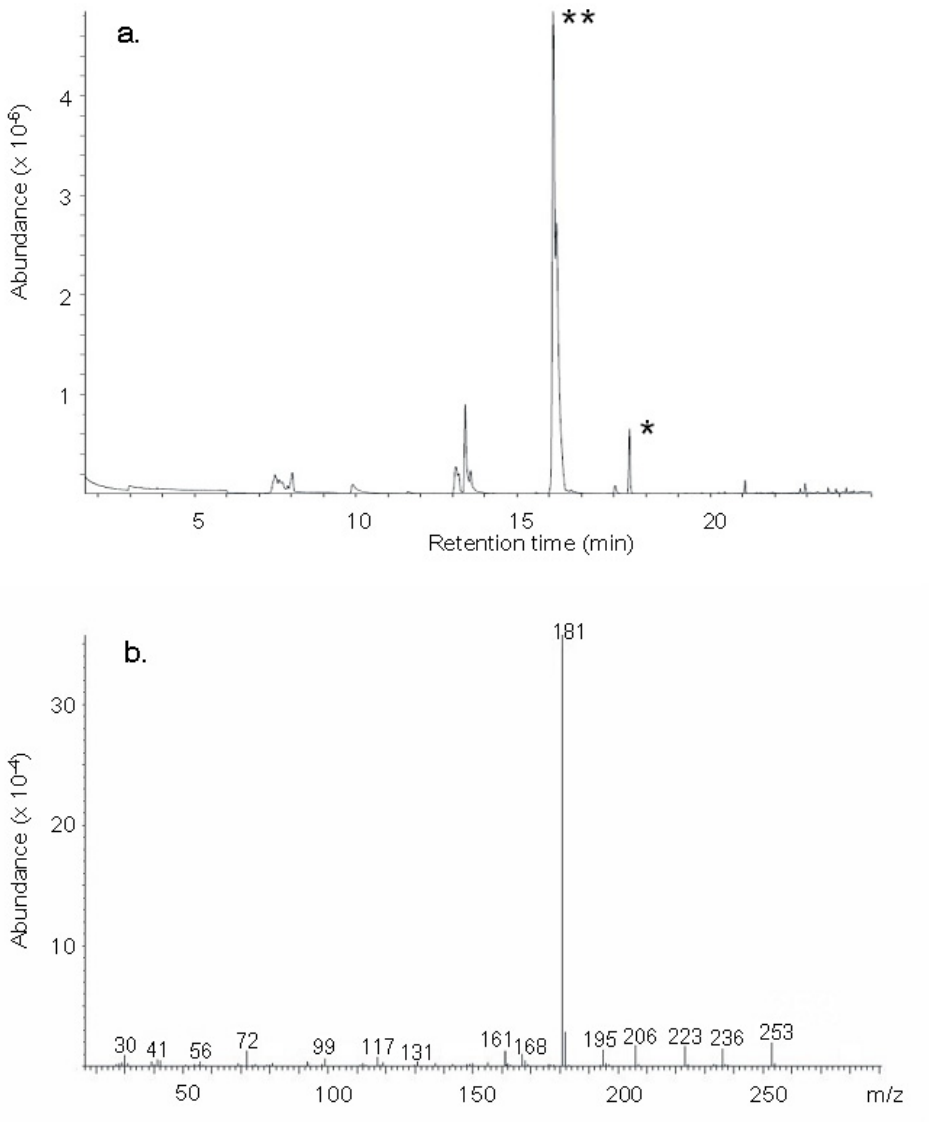


Figure 3-2. **a.** Typical gas chromatogram of a PFBHA-derivatized seawater sample, showing the acetone PFBHA oxime (*) as well as unreacted PFBHA (**). **b.** Mass spectrum of peak * in a., above.

PDMS/DVB fibre shows greater sensitivity while the PDMS fibre shows greater reproducibility under these conditions (0.27 μM acetone, derivatized). Further comparisons between the PDMS/DVB and PDMS fibre were performed, using acetone concentrations of 67 nM and 13 nM, in triplicate. Again, the PDMS fibre showed greater reproducibility and the PDMS/DVB fibre showing better sensitivity (Fig. 3-3b). The PDMS fibre was thus selected for future experiments due to its greater reproducibility coupled with its adequate significant sensitivity.

3.4.2 Sample and headspace volume

While the fibre comparisons were done using a sample size of 10 mL, a comparison was performed between 10-mL and 20-mL sample volumes to determine if the headspace had significant effects. For duplicate samples containing 0.34 μM acetone, the blank-corrected acetone oxime peak areas for the two volumes were 5.7 % greater for the 20-mL than for the 10-mL sample volume. A 10-mL sample size was used for all other experiments. This smaller sample size reduced the amount of sample and derivatizing agent required while still providing substantial peak areas for acetone analysis.

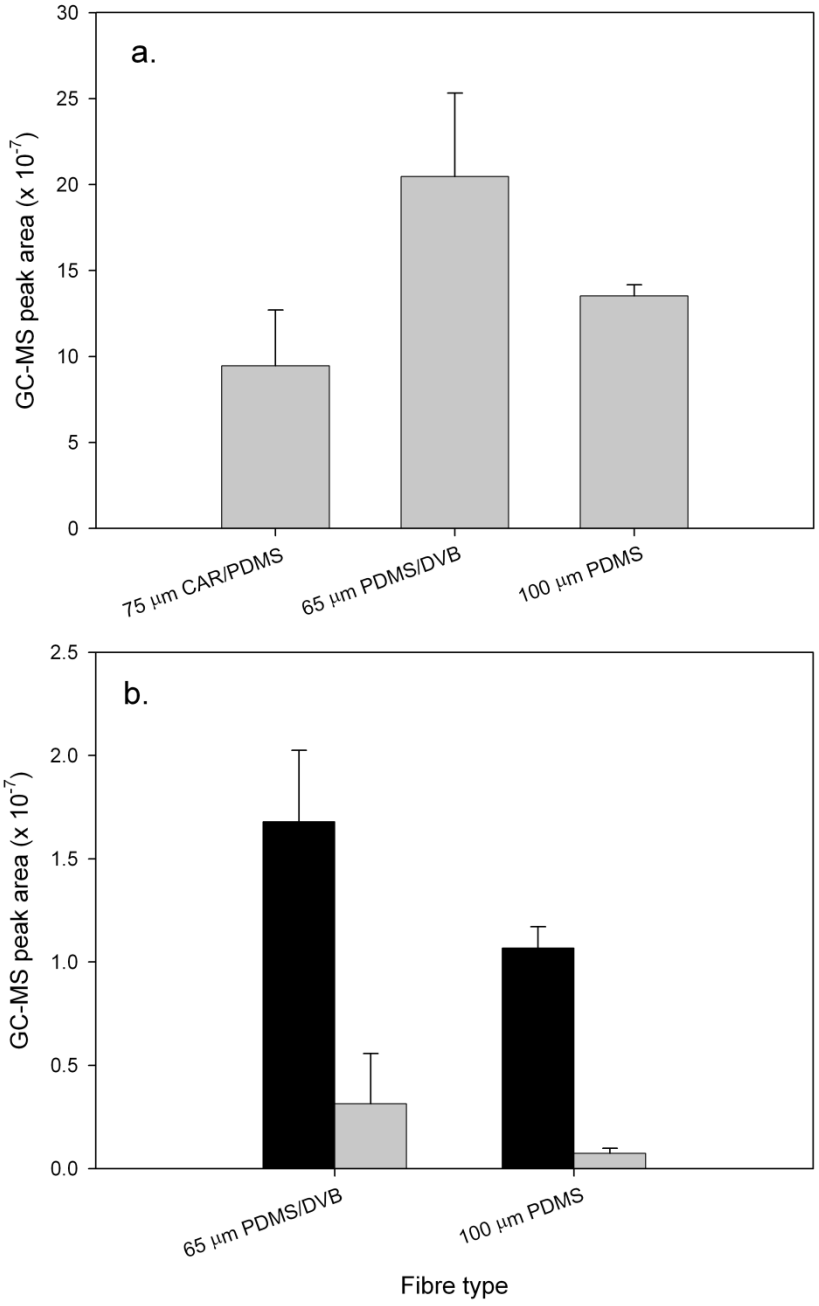


Figure 3-3. **a.** Comparison of three different SPME adsorbents for sensitivity and reproducibility for acetone PFBHA oxime (0.27 µM acetone), mean ± SD, n=2. **b.** Further comparison of the two best adsorbents in a. Black bars- 67nM acetone; grey bars- 13 nM acetone; mean ± SD, n=3.

3.4.3 Effect of pH and of buffering in seawater

To determine the optimum pH for the SPME extraction step, the pH of derivatized 34 nM acetone solutions was modified immediately prior to extraction using small quantities of trace metal grade hydrochloric acid (2 M or 0.2 M) or ammonia (0.08 M). These 40 -50 μL additions changed the volume negligibly. The unmodified solutions of PFBHA and the acetone oxime consistently produced a pH of 3.7 ± 0.1. Over the pH range tested, the pH of the unmodified solution (pH 3.7) was optimal both in terms of peak area and reproducibility (3 % RSD) (Fig. 3-4a), although the peak areas did not differ greatly over the range studied. This contrasts with the work of Bao *et al*.[8], who acidified the sample between derivatization and extraction, although they did not explain the purpose of this procedure. Basic pH values were not tested because of the difficulty in obtaining them reproducibly.

It was subsequently noted that the final pH of seawater after derivatization and extraction was between 7 and 8, in contrast to that of salt water standards (pH 3.7, above). This is due to the buffering of seawater by the carbonate and, to some extent borate, systems. Thus, the optimum pH for SPME extraction (pH 3.7) could not be achieved on seawater without modification. We found that the addition of 12.7 μL of 0.2 *M* HCl brought the pH of seawater and PFBHA to 3.7 ± 0.1 (Table 3-1), and all seawater samples were therefore acidified this way

Table 3-1. pH behaviour of surface seawater from 75.00 ° N, 16.06 ° W and of the salt water solution buffered by $NaHCO_3$ and H_3BO_3. Mean ± SD, n=2. The pHs obtained after acidification did not differ significantly at the 5 % confidence level.

	Seawater	**Buffered salt water**
Original pH	7.83 ± 0.05	7.66 ± 0.05
pH after addition of 50 µL PFBHA solution	7.53 ± 0.07	7.00 ± 0.04
pH after further addition of 12.7 µL 0.2 *M* HCl solution	3.59 ± 0.08	3.75 ± 0.09

immediately prior to insertion of the SPME fibre for extraction. For calibration purposes, a buffered salt water was devised (as described in the Experimental section) with which we aimed to replicate the salinity and buffering capacity of seawater. The pH behaviour of this solution on addition of PFBHA·HCl and of 0.2 *M* HCl was the same as that of natural seawater (Table 3-1). Tests on seawater from 75.00 °N, 16.06 °W (Site 4, Table 3-2), derivatized as described

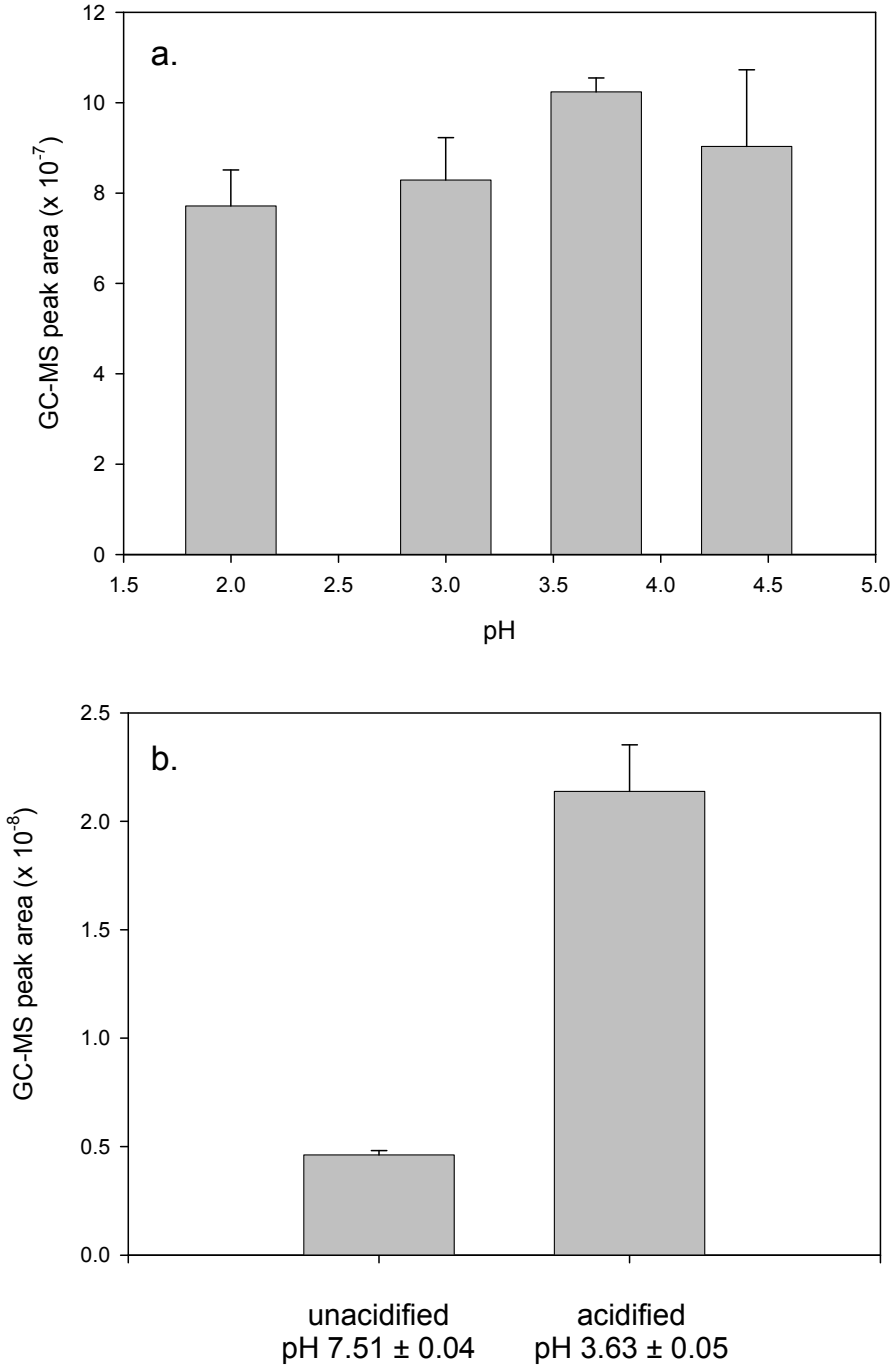


Figure 3-4. **a.** Effect of pH on the adsorption of acetone PFBHA oxime on a 100 µm PDMS SPME fibre. **b.** Effect on seawater (75.00 °N, 16.06 °W) of acidification prior to SPME extraction. Both plots: mean ± SD, n=2

previously, demonstrated that the acidification step led to more of the acetone oxime being extracted and detected (Fig. 3-4b).

3.4.4 Acetone in salt-water blanks

Throughout the experiments described, a notable acetone oxime peak area ($1 - 1.5 \times 10^7$ GC-MS peak area counts) was detected in blanks (buffered or unbuffered salt water), as well as in standards and samples. We aimed to identify the source of acetone in these blanks to see if it could be reduced, since method detection limits are currently constrained by this blank measurement. We considered two possibilities: that acetone in the blanks was coming from the laboratory air during preparation or transfer of standards and samples, or that it was present in the purified water used to make the salt water solutions (and therefore the standards).

On the assumption that the water was the source of this contamination, further purification was attempted. A second purification of the water, already purified as described, was undertaken using a Milli-Q Simplicity 185 water purifier fitted with a Simpak 2 cartridge and a final UV oxidation cell (Millipore, Billerica, MA), and salt water was prepared using this re-purified water. Further batches of salt-water solution, prepared using the original (QPAK-1) purified water, were subjected to UV oxidation to attempt to destroy any remaining organic contaminants. Solutions were enclosed in a 3-L cylindrical glass vessel fitted with a 7-cm circular quartz window and irradiated with a 75-W mercury arc

lamp (λ_{max} 254 nm; Oriel, Stratford, CT). As a final treatment, the solution and the headspace were sparged/purged with UHP Helium prior to irradiation.

Further purification using the Simpak 2 cartridge/final UV oxidation cell did not result in a significantly different (Students' t-test, $P<0.05$) acetone oxime peak area in the blanks (Fig. 3-5, A vs. B). Batchwise UV irradiation resulted in higher acetone oxime peak areas in the blanks (Fig. 3-5, C-E) than in non-irradiated salt water, even after 71 hours of irradiation (Fig. 3-5, D), or after purging/sparging with UHP helium and 17 hours irradiation (Fig. 3-5, E). These results suggest *de novo* formation of acetone from UV oxidation of higher molecular-weight contaminants, rather than acetone destruction, although this conclusion is tentative due to limited experimentation.

In an attempt to prevent contamination of samples via laboratory air, the use of acetone anywhere in the laboratory was avoided on days when any of the experiments described in this work were performed. However, to further investigate this air as a potential contamination source, all operations during the preparation, dispensing and derivatization of buffered salt water blanks (except the weighing of the dry salts) were performed in a Plexiglas chamber of ca. 1 m^3 volume with a front face of heavy, flexible, clear polyethylene and flushed with UHP Helium, or later, UHP Nitrogen. This included enclosing the Milli-Q Simplicity 185 water purifier in the chamber; however, the 2-hour stirring and 30-minute SPME extraction steps, during which time the samples were isolated from the laboratory atmosphere in vials, were still done on the open bench. In each

case, acetone oxime peak areas in buffered salt water solutions prepared in these clean atmospheres did not differ significantly ($P<0.05$) from those in buffered salt water solutions prepared contemporaneously on the laboratory bench. These results suggest that the laboratory air was not the source of traces of acetone in blanks.

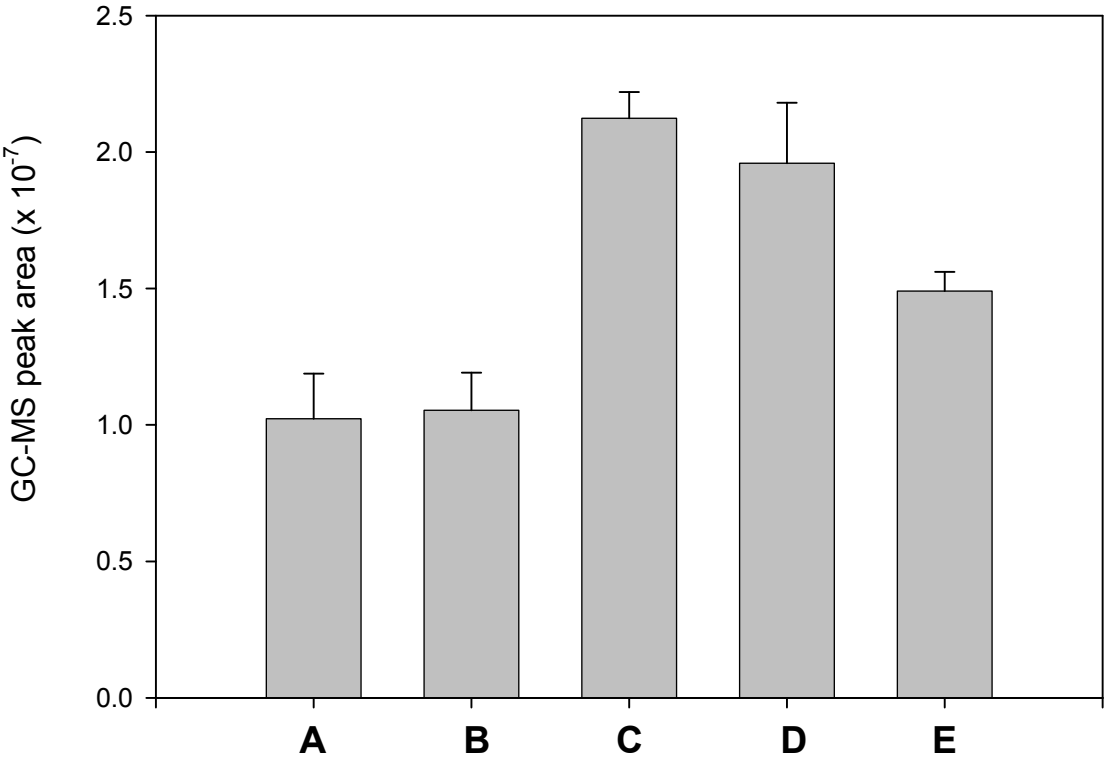


Figure 3-5. Acetone PFBHA oxime peak areas in salt water blanks prepared with different purified water sources or irradiated. *A.* Salt water prepared with Milli-Q (QPAK-1) water *B.* Saltwater prepared after further purification of Milli-Q water (Simpak 2, UV oxidation) *C.* Water from *A.*, UV-irradiated 20 hours *D.* Water from A., irradiated 71 hours *E.* Water from A., sparged with UHP Helium and irradiated under Helium, 17 hours. Mean ± SD, n=2

3.4.5 Derivatization time

Bao et al. [8] report that, for the PFBHA derivatization of ketones (in contrast to aldehydes) in fresh waters, longer derivatization times (up to 20 hours) are needed. Other studies also indicate an increasing yield of PFBHA oximes with longer reaction time for selected ketones, including acetone [18,19]. We wished to ascertain whether the length of derivatization could be shortened to a more practical time without sacrificing sensitivity and reproducibility, as well as to determine the stability of the acetone PFBHA oxime over time. A series of 10-mL aliquots of surface seawater from 75.00 °N, 16.06 °W (Site 4, Table 3-2) was derivatized for differing lengths of time before being acidified, adsorbed and analyzed as described previously. The peak area from the oxime increased in a near-linear fashion (r^2 = 0.93) over the first 25 hours of derivatization. The increase appeared to continue for up to 66 hours, although with more scatter in the data (r^2 = 0.86); the peak area measured after 68 hours was less than that at 66 hours. Earlier experiments with acetone standards in NaCl solution had indicated a more rapid degradation or loss of the oxime once 50 hours had elapsed. The data suggested that better sensitivity could be obtained using a longer derivatization time, but at a cost of reproducibility, and that sensitivity after a relatively short derivatization time was adequate. Hence, all further samples were derivatized for 2 hours.

3.4.6 Calibration

Given previously reported acetone concentrations in seawater [3,9,12,13], we analyzed calibration standards over the range 4.3 – 150 nM, made in buffered salt water. Calibration samples were analyzed with two different SPME fibres of the same type (100 μm PDMS), one for each calibration curve, on separate days (Fig. 3-6). For both curves, r^2 exceeded 0.99. The two different SPME fibres gave calibration curves with different slopes. This may reflect differences in age and degree of use, and underlines the need to use a single fibre when comparing samples and standards. For the lower calibration curve in Figure 3-6, the calculated detection limit (3 × the standard deviation of the blank divided by the slope of the calibration curve) was 3.0 nM. This same SPME fibre was used in seawater analysis. Bao *et al.* [8] reported a detection limit of 1.4 nM for acetone in fresh water by PFBHA derivatization followed by SPME, although that study employed an electron capture detector, highly sensitive to the polyfluorinated derivative, as the GC detector.

3.4.7 Analysis of seawater

Acetone concentrations in selected surface seawater are reported in Table 3-2, and range from 5.5 – 6.9 nM. These are the first acetone concentrations reported for far North Atlantic and Arctic waters (Fig. 3-7). They are lower than the mean reported for the tropical Atlantic (17.6 nM) [3], although within the range of values reported from both the Atlantic and Pacific (<3 – 70 nM) [3,9,12]. The

values are also surprisingly uniform, given the area covered, and lower than might be expected given that sampling took place during the season of greatest biological activity, that algal blooms were observed in the waters traversed by the

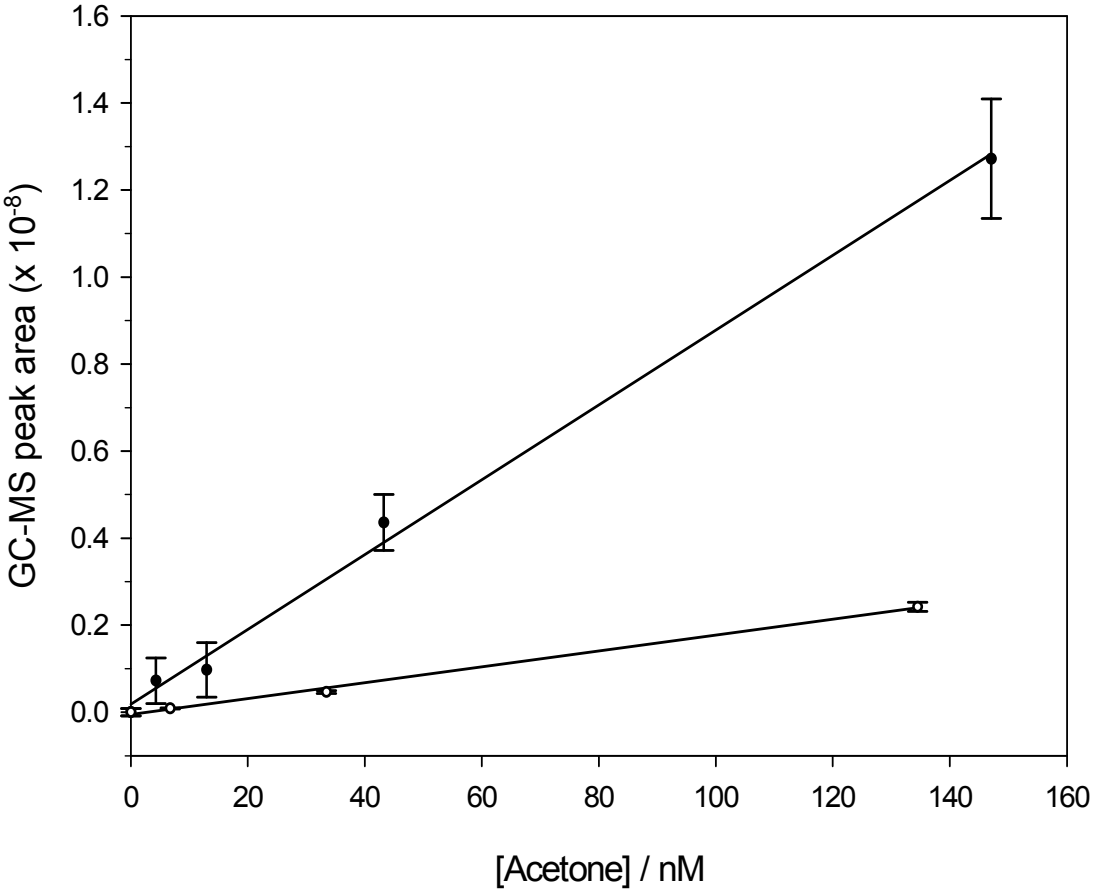


Figure 3-6. Calibration curves for acetone, as its PFBHA oxime, using 100 µm PDMS SPME fibres. The upper and lower curves represent calibrations performed on different days and with different fibres. Error bars are standard deviations.

Table 3-2. Acetone concentrations in surface waters from selected sites in the Nordic seas. Location numbers refer to Figure 3-7. BDL = below detection limit.

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Location, sampling date	Measured [acetone] /nM (mean ± SE, n=2)
1. 68.30 ° N, 9.46 ° E, June 19/04	6.7 ± 3.6
2. 75.00 ° N, 5.77 ° E, June 25/04	6.3 ± 3.6
3. 75.00 ° N, 1.80 ° E, June 26/04	9.6 ± 3.6
4. 75.00 ° N, 16.06 ° W, July 3/04	5.5 ± 3.6
5. 79.34 ° N, 5.92 ° W, July 12/04	BDL

cruise at the time of sampling, and that certain marine algal and bacterial species are known to produce acetone [6,7]. Furthermore, Whelan *et al.* [6] noted that filtering the sample can lead to additional acetone formation or release. Thus, the reported values must be considered upper limits, and concentrations in these waters may be lower still. Analysis of a greater number of samples from this area should elucidate the degree of uniformity, or patterns of variability, in acetone concentrations. Based on the current data set, it is not yet possible to ascertain whether surface waters of the Nordic Seas are a source or sink of tropospheric acetone, especially considering the paucity of atmospheric acetone measurements

for these regions and further considering that acetone may be 18 × more concentrated in the sea surface microlayer than in underlying bulk seawater [12].

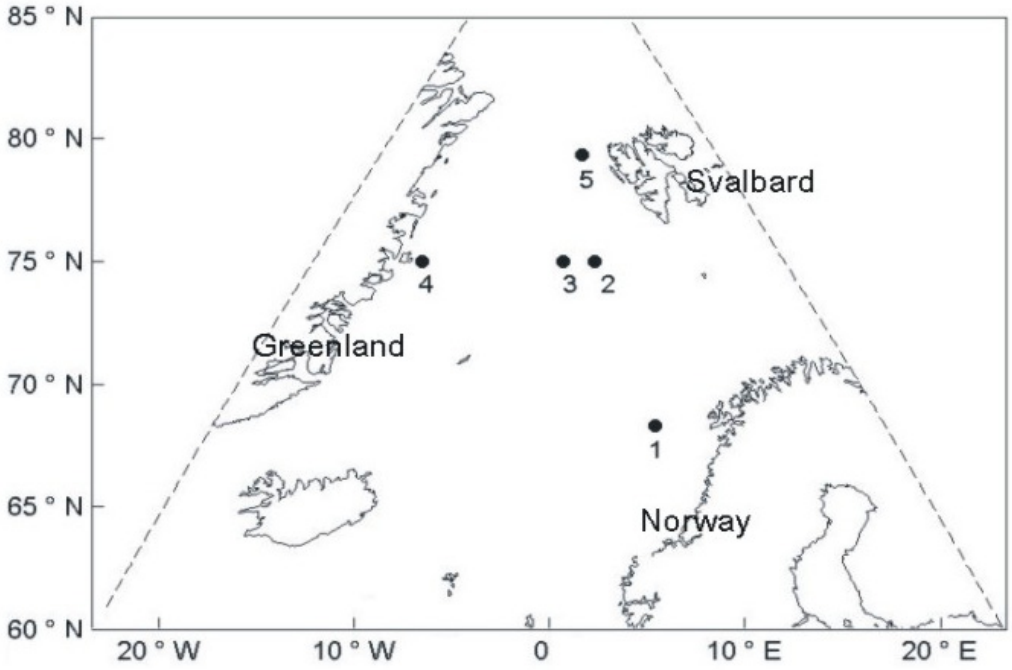

Figure 3-7. Sampling locations of seawater samples reported in Table 3-2. All samples were taken at 11 m depth. Map is a sinusoidal equal-area (Sanson-Flamsteed) projection.

3.5 Conclusions

A variety of factors which affect the SPME analysis of acetone in seawater (SPME adsorbent, pH, derivatization time) have been identified, explored and optimized. While further work is needed to improve detection limits by lowering

signals in salt-water blanks, results to date indicate a promising, low cost, easy-to-use method that could be applied to large-scale studies of acetone and other carbonyl compounds in seawater. Initial results from the analysis of North Atlantic/Arctic surface seawater indicate an upper limit of 5.5 – 9.6 nM acetone in these waters. More extensive analysis of Nordic Sea surface waters will better indicate the spatial pattern of acetone concentrations. SPME fibres are readily portable, and no solvents are required. Therefore, through the use of portable GC and/or GC-MS instrumentation (e.g., [30,31]) the method could be used at sea, thus avoiding the risk of contamination or artifacts associated with the filtration, transport or storage of seawater samples.

3.6 Acknowledgements

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Chapter 4

A method for the simultaneous quantification of 23 C_1-C_9 trace aldehydes and ketones in seawater.

In our study of the determination of acetone in seawater by derivatization and solid phase microextraction (Chapter 3), we developed a low-cost, facile, solventless method applicable to nanomolar concentrations of acetone. In this chapter, we further developed this method for 22 additional carbonyl compounds, ranging from 1 to 9 carbons. This paper thus expands on and generalizes the methods developed and reported in the previous paper, including re-optimizing critical method parameters such as sample volume, choice of adsorbent, and pH, considering the greater variety of carbonyl compounds being analyzed. Furthermore, we explored additional means for lowering method blanks, one of the problems identified in Chapter 3 as constraining the detection limits of the method. Unlike the approaches investigated in the previous paper, these means focused mainly on the derivatization agent, PFBHA, itself. Lastly, we previously commented (Chapter 3) that it is preferable to avoid storage and transport effects for seawaters intended for carbonyl analysis and proposed to address this by using the method at sea. The cryogenic storage experiment in this chapter investigates an alternative means of avoiding these effects by storing derivatized carbonyl compounds on a SPME fibre for later analysis, such as in a shore-based laboratory.

Further details on modelling of potential contamination of samples by carbonyls in air, and of the half-factorial optimization experiment, have been submitted to appear as on-line supplementary information for the manuscript. They are appended to this chapter. Additional experiments or information which would be pertinent to those building on this work appear in Appendix B of this thesis.

The manuscript constituting this chapter has been submitted to *Environmental Science and Technology.*

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A method for the simultaneous quantification of 23 C_1-C_9 trace aldehydes and ketones in seawater.

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4.1 Abstract

Low molecular weight aldehydes and ketones in the surface oceans are produced by dissolved organic matter photochemistry or by biology, and can be transferred to the atmosphere, affecting its oxidative capacity. They thus link the organic carbon biogeochemistry of the atmosphere and the oceans. We have developed and optimized a mobile, economical and facile method which allows for the simultaneous quantification of 23 $C_1 - C_9$ low molecular weight aldehydes and ketones in seawater. The compounds are derivatized using O-(2,3,4,5,6-pentafluorobenzyl)-hydroxylamine (PFBHA), pre-concentrated by solid phase microextraction (SPME), and analyzed by gas chromatography with mass spectrometric (GC/MS) or flame ionization (GC-FID) detection. Detection limits range from 0.01 nM to 23.5 nM, with sub-nanomolar detection limits achieved for most compounds. The method was applied to surface waters from the Lower St.-Lawrence Estuary (Quebec, Canada) and revealed the presence of a variety of $C_2 - C_6$ carbonyl compounds, including the dicarbonyls glyoxal, methylglyoxal and 2,4-pentanedione, at concentrations of up to 7.5 nM. High process blanks were observed for C_1-C_3 carbonyl compounds, but sparging with UHP argon, and C-18 solid phase extraction of the dissolved PFBHA to remove pre-existing carbonyl PFB oximes, were found to be the most effective blank reduction methods.

Keywords: volatile organic compounds, SPME, Gas Chromatography/Mass Spectrometry, dissolved organic carbon, chemometrics

4.2 Introduction

Low molecular weight carbonyl compounds (aldehydes and ketones) typically occur in surface seawaters at low nM to high pM concentrations [1-5]. They may originate from the photochemical breakdown of dissolved organic matter (DOM) [6], direct production by marine algae [7-10] or bacteria [11] or by transfer from the atmosphere [2, 5] if concentrations in the marine boundary layer exceed equilibrium concentrations with respect to the sea surface. Thus, they are of interest as sinks of DOM and in studies of the metabolism, abundance or state of marine algal communities. Furthermore, high mixing ratios of certain carbonyl compounds, including acetone, acetaldehyde and formaldehyde, occur over parts of the remote oceans [12-13], even in the upper troposphere, where they may produce a significant fraction of tropospheric odd hydrogen (HO_x) [12, 14] and otherwise influence tropospheric oxidative capacity and aerosol formation, consequently affecting climate. It is unclear whether, globally, the oceans are a source or a sink of carbonyl compounds with respect to the atmosphere [2, 4]. More spatially and temporarily varied measurements of these compounds in surface seawaters would allow for stronger conclusions about their global budgets and an improved understanding of their roles in lower tropospheric oxidation processes and in climate.

Carbonyl compounds in seawater have to date been determined by derivatization or direct mass spectrometric methods. Formaldehyde in Antarctic coastal waters has been determined by flow injection analysis of a fluorescent

derivative formed by reaction with 2,4-pentanedione and ammonia [15]. Derivatization of carbonyl compounds to dinitrophenylhydrazones for HPLC using 2,4-dinitrophenylhydrazine (DNPH), one of a number of derivatization-based HPLC methods for carbonyl compounds in waters, has largely been optimized for seawater by Mopper and co-workers [1, 5, 16-18]. These HPLC methods allow simultaneous analysis of many C_1-C_{10} carbonyl compounds, with sub-nanomolar detection limits, although the use of solvents has negative environmental impacts and increases the risk of sample contamination. Atmospheric Pressure Chemical Ionization Mass Spectrometry [2] and Proton Transfer Reaction Mass Spectrometry [4, 8] allow rapid, real-time analysis of certain carbonyl compounds, with excellent sensitivity, but the required equipment is often costly, and certain mass spectrometric interferences [2, 19] add uncertainty. Published measurements of carbonyls in seawater by these mass spectrometric methods have been restricted to acetone [2, 4, 8] and acetaldehyde [8].

Solid Phase Microextraction (SPME) is a small-scale, solventless, non-exhaustive extraction method developed by Pawliszyn and co-workers [20]. Sample requirements are minimal, and the freedom from solvents and re-usability of the SPME fibre make the method environmentally friendly. To date, derivatization of carbonyl compounds by O-(2,3,4,5,6-pentafluorobenzyl)-hydroxylamine (PFBHA) followed by SPME and gas chromatography (GC) has been developed for fresh waters [21-22] and some physiological fluids [23-25], but has not been optimized for seawater. GC is a widely available technique,

robust enough for field use. We have developed a method based on readily available and relatively inexpensive columns, detectors and SPME sorbents which would be readily accessible to the scientific community.

We have identified optimum analytical conditions for the simultaneous quantification of a wide range of low molecular weight aldehydes and ketones in seawater, and demonstrated their applicability to samples from the St. Lawrence Estuary (Quebec, Canada). Furthermore, we addressed issues which hamper the use of PFBHA [26] by systematically studying the factors affecting blanks obtained with this reagent.

4.3 Experimental section

4.3.1 Materials

Carbonyl compounds were purchased as neat compounds (purities 95.0-99.5%) or as aqueous solutions (formaldehyde - 37% w/v, glyoxal - 40% w/v, methylglyoxal - 40% w/v, glutaraldehyde - 25% w/v) from Fisher Scientific (Nepean, ON) (acetone), from Caledon Laboratories (Georgetown, ON) (formaldehyde, glyoxal), or Sigma-Aldrich/Fluka (St. Louis, MO) (all other carbonyls), and used as received, except for methacrolein and *trans*-2-hexenal, which were purified by percolation through basic alumina before use. PFBHA hydrochloride was purchased from Fluka (St. Louis, MO). Ultrapure water (Milli-Q QPAK-1 system and Simplicity Plus 185 system, Millipore, Billerica, MA) was used throughout. Sodium chloride was baked overnight at 450 °C (723

K) to remove organic contaminants. SPME fibres and holders were purchased from Supelco (Bellefonte, PA). Solid phase extraction cartridges (Strata C8 and C18, 100 mg and 200 mg, 1 mL) were obtained from Phenomenex (Torrance, CA).

Glassware was cleaned by rinsing with ultrapure water, followed by baking overnight in a muffle furnace at 450 °C to remove organic contaminants. Where this was not possible (e.g., volumetric glassware), it was rinsed multiple times with ultrapure water and ethanol and dried overnight at 125 °C.

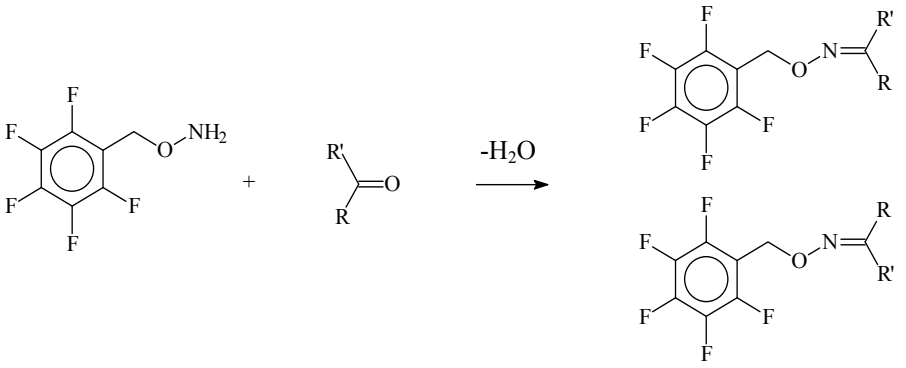
4.3.2 Solutions, procedure and instrumentation

PFBHA was prepared daily as previously described [27]. Stock solutions of carbonyl compounds were made in HPLC-grade methanol and stored at 4 °C, and diluted to working solutions in Milli-Q water, with the final standards made as described below. Compounds were selected to include a variety of structural motifs including saturated and unsaturated aliphatic aldehydes and ketones, aromatic aldehydes, and dialdehydes/diketones. Initial optimization was conducted on the 18 compounds shown in Figure 4-1, while a further 5 compounds (methacrolein, methyl vinyl ketone, crotonaldehyde (2-butenal), glutaraldehyde (1,5-pentanedial), *trans*-2-hexenal) were included in later calibrations due to their potential biogeochemical interest.

Nitrile rather than latex gloves, and polypropylene vial caps rather than those made of phenolic resins, were used throughout, since it has been reported

that latex and phenolic resins may contaminate samples with aldehydes [28].

Blanks and standard solutions were made in an artificial seawater, prepared as described previously [27], and sparged with UHP argon for 45 min to attenuate levels of carbonyl compounds observed in blanks. This artificial seawater had a final pH of 8.1-8.2 and a salinity of 34.2 ‰ (w/w), and simulated both the salinity and pH behavior of seawater. Derivatizations and extractions were carried out in 20-mL screw-capped vials with Teflon-faced silicone septa. The vials were amber glass, or were wrapped in aluminum foil, to inhibit photochemistry. Hydrochloric acid (0.2 M, *ca.* 28 µL, to achieve the desired pH - see Results and Discussion) and 100 µL of a PFBHA solution (for 20 mL samples) were added to the vials and the samples were derivatized according to equation (4-1),



(4-1)

with magnetic stirring at 550 rpm (Horizon Multi-stirrer, Brinkmann Instruments) for two hours. The SPME fibre was then inserted into the vial for 30 minutes of sorption (by direct immersion in the liquid) with continued stirring at 550 rpm. All SPME was conducted manually. Other studies [21] have indicated that maximum sorption of lower molecular mass carbonyl pentafluorobenzyl (PFB)

oximes from fresh waters onto an SPME fibre was achieved in 20-50 minutes, depending on the oxime. However, full equilibration of the analyte onto the SPME fibre is not necessary for reproducible quantification if the sorption time is constant [29-30]. Lastly, a 30-minute sorption was the maximum time which corresponded roughly with the time needed for gas chromatography, leading to most efficient sample throughput.

After SPME, the carbonyl PFB oximes were analyzed by Gas Chromatography-Mass Spectrometry (GC/MS) or Gas Chromatography with Flame Ionization Detection (GC-FID). The oximes were desorbed at 270° C in splitless mode for 5 minutes before the split vent was re-opened. The fibre was then left in the inlet for an additional 10 minutes to ensure that it was fully clean before re-use. GC-MS or GC-FID (HP 6890 GC, with 5973 MSD for GC-MS, Agilent, Palo Alto, CA) was performed on a HP 5-MS (5%-phenyl-methylpolysiloxane) column (30 m × 0.25 mm i.d. × 0.25 μm film thickness) as follows: He carrier gas (2.5 mL/min, constant flow), injector 270 °C, oven 50 °C for 2 min, then 50°C /min to 125 °C , then 8 °C /min to 210 °C, then 15°C /min to 275 °C with a 5 min final hold. The FID was operated at 300 °C, with 40 mL/min H_2, 300 mL/min air, and 15 mL/min He (make-up gas). While the carrier gas flow rate was considerably higher than that which would minimize the Height Equivalent to a Theoretical Plate under the Van Deemter equation, it allowed faster chromatography while maintaining acceptable resolution [31]. The MS instrument was operated in scan mode (m/z 45-400 until 13.5 min and 50-550 after 13.5 min), with 70 eV electron ionization, transfer line temperature 280 °C,

MS source temperature 230 °C, and quadrupole temperature 150 °C. The MS scan mode was used, allowing identification of unanticipated carbonyl compounds using their mass spectra. The PFB oximes were identified by comparison of their mass spectra with previously published data [32-33], with spectra in the NIST 5.0 mass spectral database, and with the spectra and retention times of standard compounds derivatized and extracted individually. GC-MS peaks were integrated using HP Chemstation (version B-01.00) software on the extracted ion chromatograms for m/z = 181 (the base peak in the mass spectra of all the PFB oximes).

4.3.3 Cryogenic storage experiment

To determine whether carbonyls in samples might be immediately derivatized and SPME-extracted in the field and the PFB oximes stored for later analysis in the laboratory [34], standard carbonyl solutions in artificial seawater (14-54 nM) were derivatized, extracted and analyzed as described above. Identical samples were immediately derivatized and extracted using the same SPME fibres. The retracted SPME fibres were capped with a silicone GC septum and stored on dry ice (–78 °C) for one week, before gas chromatography in the same manner.

4.3.4 Seawater sampling and analysis

Selected coastal water samples from the Lower St. Lawrence Estuary were analyzed using the same method. Surface water samples (2-3 m below the air-

water interface) were taken in June 2009 using standard Niskin bottles from the RV *Coriolis II*. Samples were not filtered since filtration may result in increased carbonyl compound concentrations [1, 17], likely due to the bursting of algal cells. They were stored in combusted 125-mL amber glass bottles with Teflon-lined caps, leaving no headspace, at 4 °C. Aliquots (20 mL) of these seawater samples were analyzed as described for standards using GC-MS. Samples were also analyzed for total dissolved organic carbon (DOC) using a Shimadzu TOC5000A Total Organic Carbon Analyzer. β-Alanine, at concentrations between 0.48 and 2.6 mg/L, was used as a DOC calibration standard; instrument precision was ± 2%.

4.4 Results and discussion

We considered key factors in the SPME determination of carbonyl compounds as PFB oximes both individually and on the possibility that factors may interact with each other. A 2^{4-1} half-factorial experiment (see on-line Supplementary Information, Table 4-3 and Figure 4-6), examining four parameters simultaneously (SPME sorbent, pH, sorption time, and sample volume), detected no significant ($P<0.05$) two-factor interactions which were antagonistic to the main effects (Supplementary Figure 4-6), suggesting that our individual optimization experiments were not missing any optima resulting from two-factor interactions. The optimal set of conditions eventually chosen for determination of carbonyl compounds in seawater considered both maximizing

yield of carbonyl PFB oximes and consistency of oxime formation, and practical considerations related to SPME fibre stability, sample throughput, and method ruggedness.

4.4.1 Comparison of SPME fibres (sorbents)

We had previously determined [27] that 75 μm Carboxen/polydimethylsiloxane (CAR/PDMS) SPME fibres absorbed PFBHA-derivatized acetone to a lesser extent and less reproducibly than either 65 μm polydimethylsiloxane/divinylbenzene (PDMS/DVB) or 100 μm polydimethylsiloxane (PDMS) fibres. Therefore, sorbent choice in the current work focused only on the latter two sorbents.

PFB oximes of carbonyl compounds are more efficiently extracted by PDMS/DVB fibres than by PDMS fibres (Fig. 4-1), with an extraction efficiency of up to five times greater (for formaldehyde PFB oxime). However, reproducibility of the extractions was often poorer for the PDMS/DVB fibres (Fig. 4-1). Furthermore, despite the greater intrinsic sensitivity of the PDMS/DVB fibres, calculated detection limits determined with these fibres were not necessarily lower than those determined with the PDMS fibres, due to the lower precision in measurements with the PDMS/DVB fibres (e.g, for formaldehyde, 9.9% (PDMS-DVB) vs. 1.9% (PDMS) RSD for the blank). We also observed that the PDMS fibres are considerably less prone to discoloration, cracking of the stationary phase, and other wear with repeated long term use; their mechanical robustness was confirmed by Pawliszyn [20]. Lastly, bleed of siloxane peaks

from the fibres themselves was greater for PDMS/DVB fibres, increasing the risk of peak co-elutions when a non-specific detector (FID) is used, and more unreacted PFBHA was sorbed on PDMS/DVB fibres, decreasing the resolution between the PFBHA peak and that of the acetaldehyde PFBHA oxime. Therefore, the 100 μm PDMS fibres were chosen for all future use/optimization.

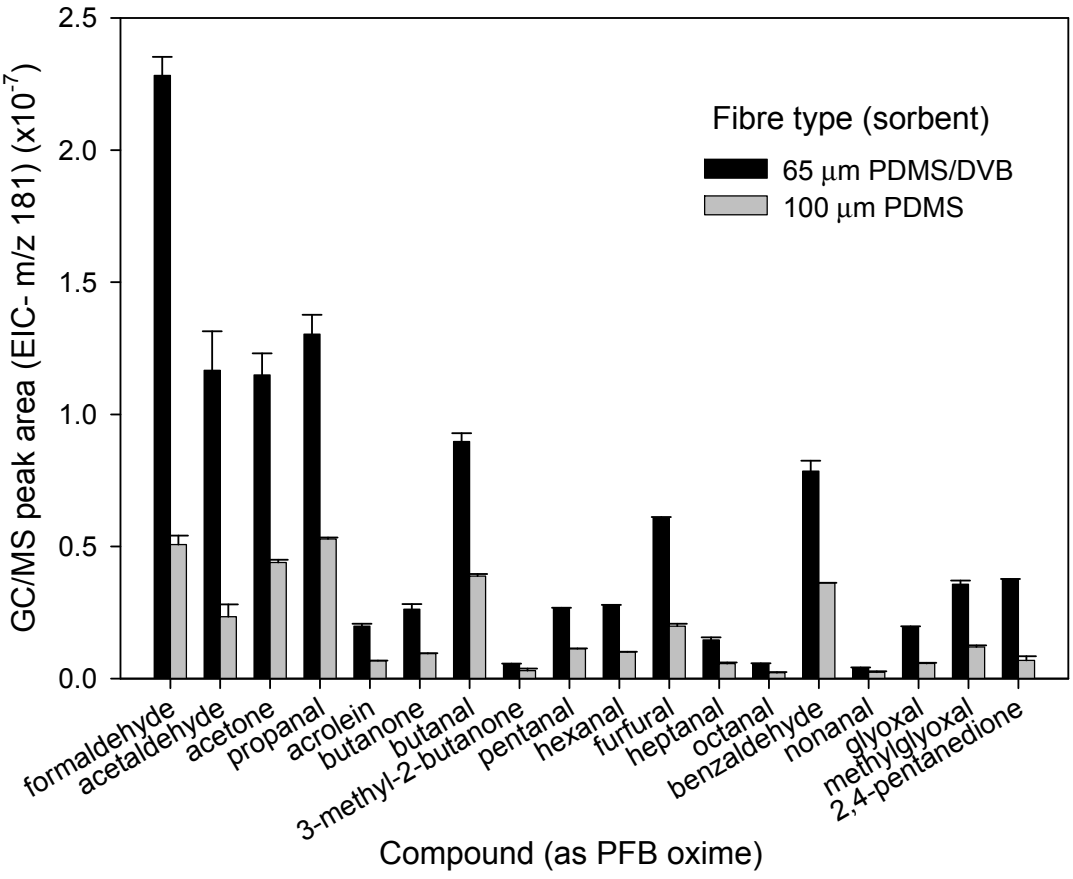


Figure 4-1. Comparison of SPME fibres (sorbents) for a range of aldehydes and ketones standards in artificial seawater. Concentrations range from 22.0 nM (nonanal) to 80.6 nM (formaldehyde). Points are mean ± SD; n = 2.

4.4.2 Derivatization time

For aldehydes, including dialdehydes, the maximum yield of PFB oximes was reached within 30 minutes of starting the derivatization (Fig. 4-2a), and the amount of oxime extracted decreased over the following 24 hours, presumably as the oxime degraded. For ketones as well as for furfural, maximum yield was reached after approximately 16 hours, with a decrease thereafter (Fig. 4-2b). This agrees with the trend observed in other studies [21, 32, 35], in which aldehydes derivatized much faster than ketones, although Baba *et al*. [36] reported that 5 hours were needed to fully derivatize methacrolein and crotonaldehyde in aqueous solution. Steric effects (a bulkier substituent) and inductive effects (addition of electron density to the carbonyl centre, making it less prone to the initial nucleophilic addition by the hydroxylamine $-NH_2$ moeity) can hinder oximation of carbonyl compounds [37]. We attribute the slower derivatization of ketones to steric effects (it was particularly pronounced for acetophenone and 1,3-dichloroacetone, two ketones with bulky substituents which were not studied further). We selected 2 hours as a derivatization time best suited to a wide variety of carbonyl compounds, giving both adequate and reproducible yield.

4.4.3 Effect of pH and acidification time

Previous studies have indicated that both SPME extraction [38] and oxime formation[33, 39] can be pH-dependent. In our study on acetone PFB oxime extraction [27], we optimized the pH for extraction by SPME only, and chose a

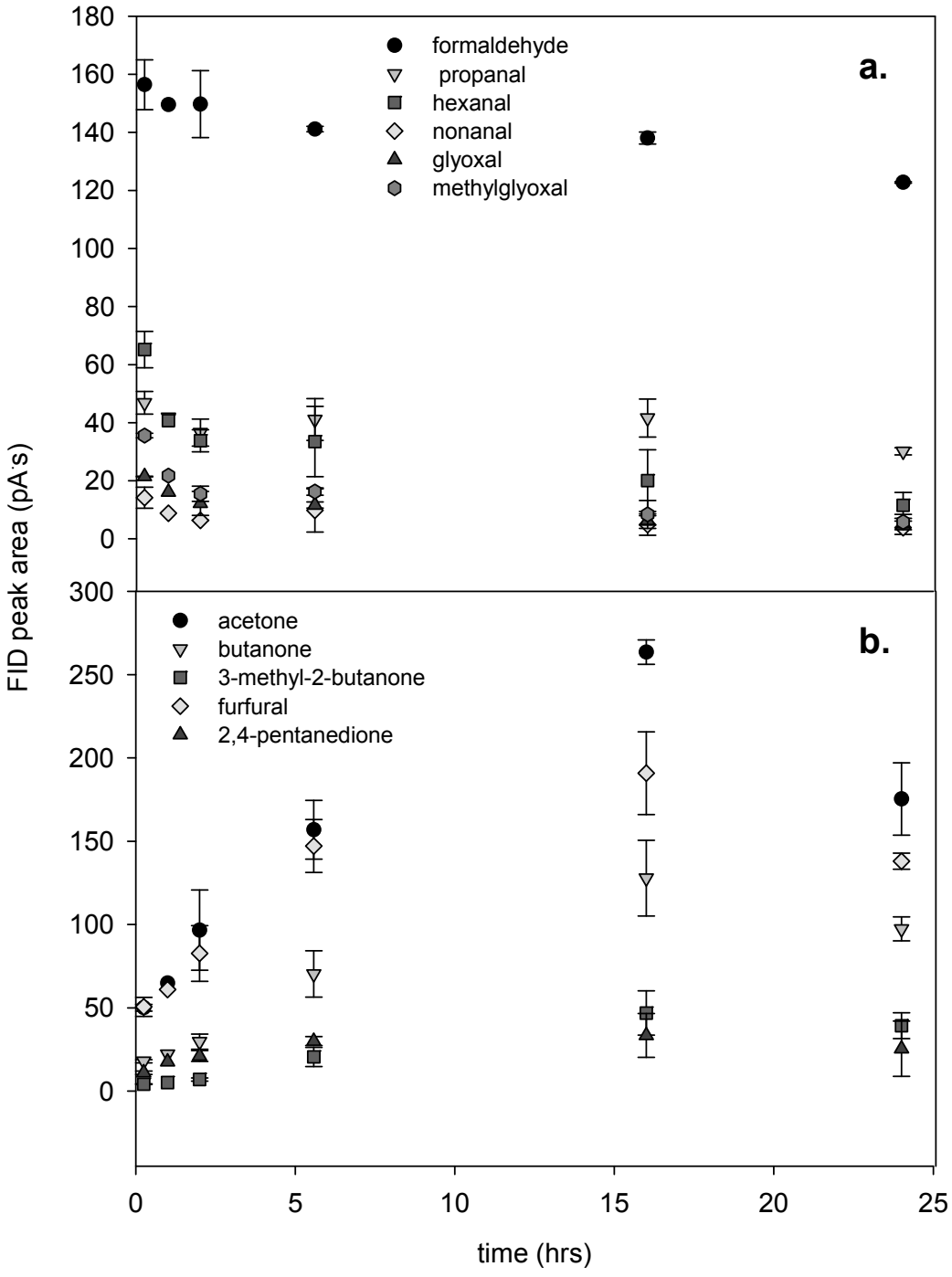


Figure 4-2. Yield of PFB oximes *vs.* derivatization time for selected aldehydes and ketones in artificial seawater at pH 3.7. Points are mean ± SD; n = 2.

pH of 3.7 as most suitable for the method. In this study, we revisited the issue of pH, and aimed to optimize pH for the derivatization and extraction simultaneously. Oxime formation with unsubstituted hydroxylamine occurs optimally at *circa* pH 4 [40]; Ojala e*t al*. [33] found a pH of 4.5 to be most suitable for carbonyl PFB oxime formation in beer samples. Cancilla *et al*. [39] reported that, in fresh water, formaldehyde and acetaldehyde PFB oxime formation was not very sensitive to pH over a wide range, differing only in reproducibility, whereas for higher molecular weight aldehydes, yields increased at pH < 3.

Yields/extracted quantities of carbonyl PFB oximes formation at four pHs (2.2, 3.2, 3.7 and 4.4) are shown in Figure 4-3. One-way analysis of variance (ANOVA) [41] indicated that the total peak area for the 18 oximes differed significantly across the pH range ($P<0.05$), with an apparent maximum at a pH of 3.7. ANOVA also indicated a significant effect ($P<0.05$) of pH on the individual peak areas for all ketones, furfural, benzaldehyde, glyoxal and all straight-chain aldehydes up to C_6 (hexanal) except acetaldehyde; for most of these compounds, the apparent maximum occurred at pH 3.2 or 3.7, with glyoxal (maximum at pH 4.4) as a notable exception.

While ANOVA can indicate a significant difference across means for a range of treatments or conditions, further statistical treatment is necessary to distinguish which individual means among them differ from each other [41]. We therefore conducted Newman-Keuls multiple rank tests [41] at $\alpha = 0.05$ for oximes for

which ANOVA had indicated a significant pH effect. For most aldehydes (propanal, butanal, pentanal, hexanal, benzaldehyde, furfural), these tests were able to distinguish the pH (4.4) giving the lowest peak areas. Nevertheless, only

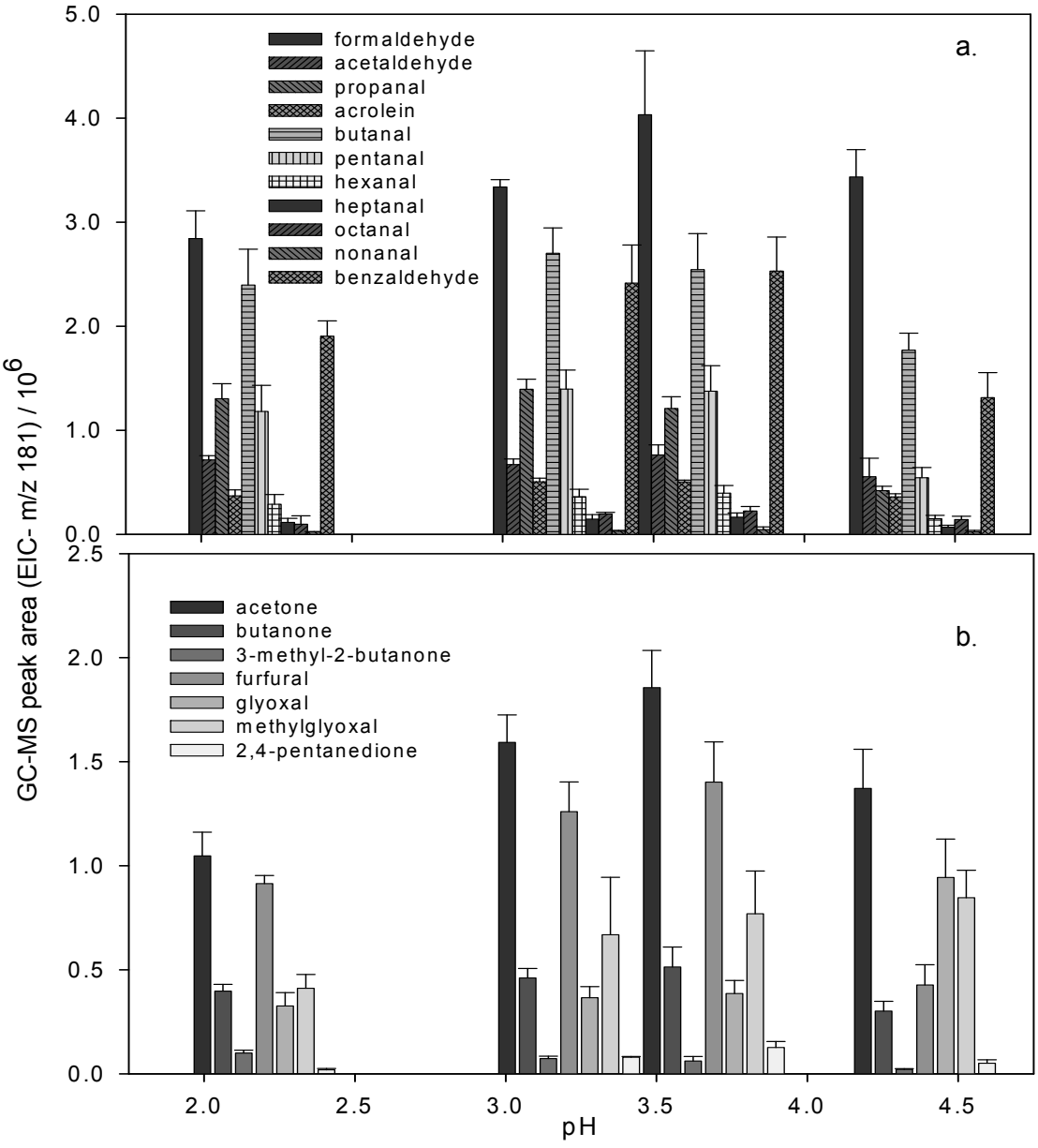


Figure 4-3. Effect of pH on yield of PFB oximes (PDMS fibre). Points are mean ± SD; n = 3.

for 2,4-pentanedione (pH 3.7), 3-methyl-2-butanone (pH 4.4) and glyoxal (pH 4.4) could the pH giving the highest mean peak areas be clearly distinguished from the next-highest mean; for acrolein and furfural, yields at pHs 3.7 and 3.2 could be differentiated from those of the other 2 pHs. We also tested whether acidifying prior to derivatization or prior to extraction led to significantly different oxime yields. Acidification prior to extraction was not optimal for any of the compounds used; acidification prior to derivatization was optimal ($P < 0.05$) only for furfural, benzaldehyde, acetone and butanone. These four compounds are among those slower to derivatize, suggesting that pH effects are exerted primarily during derivatization rather than sorption.

Overall, we conclude that the method is sensitive enough to pH for many compounds of interest to warrant careful pH control, and that a pH of 3.7 is optimal. This is consistent with the greater availability of the unprotonated hydroxylamine (necessary for the first step) as pH increases, and the ease of removal of the protonated carbonyl oxygen (second step) as pH decreases. As noted previously, these effects combine for an optimum pH of 4 for unsubstituted hydroxylamine [40]; O-substitution with an electron-withdrawing moiety such as pentafluorobenzyl might be expected to lower this pH slightly by reducing the basicity of PFBHA amine. We also found that pHs above 4 were difficult to maintain at a consistent level throughout the derivatization and extraction, presumably due to some acidity being consumed during the derivatization reaction. A pH of 3.7 was subsequently adopted, and was achieved by the addition of 2M HCl at the start of derivatization with the PFBHA.

4.4.4 Investigation and reduction of blank signals

The achievable detection limits for most analytes in this study are ultimately constrained by signals due to carbonyl compounds detected in artificial seawater blanks, especially for common carbonyl compounds ubiquitous in the laboratory and urban environments (e.g., formaldehyde, acetaldehyde, acetone, and glyoxal). Our previous study [27] suggested the Milli-Q water as a source of these impurities. We here considered this in greater detail, re-examined the possible effect of contamination from laboratory air using calculations, and examined the PFBHA reagent itself as a potential source of contamination [26, 42-43].

a) Purification of reagent water or artificial seawater. UV irradiation reagent water, for up to 70 hours (75 W Hg arc Lamp , λ_{max} 254 nm, Oriel, Stratford, CT), led to formation of several-fold greater formaldehyde, glyoxal, and acetaldehyde blank concentrations, as had occurred with acetone in previous work [27]. It is known that UV irradiation ($\lambda > 290$ nm) of high molecular weight DOM [16] or hydrocarbons [44-45] in aqueous solution can produce carbonyl compounds. Addition of 2 mM H_2O_2 before irradiation (as an additional source of oxidative radicals) was also undertaken, having been used successfully to reduce organic contaminant levels in Milli-Q water blanks [46], but this failed to reduce carbonyl levels in our blanks; indeed, propanal concentrations in blanks also increased several-fold.

Sparging the prepared artificial seawater with UHP argon led to some decrease in carbonyl compound concentrations, lowering formaldehyde PFB oxime detected by 10% and acetone PFB oxime by over 50%. This effect is shown in Figure 4-4 (bars furthest to left), in which argon sparging alone (no treatment of the PFBHA) is one of the treatments compared (normalized) to unsparged artificial seawater/untreated PFBHA. Argon was used in preference to nitrogen due to its density (greater than air), which allowed it to remain in place in containers and over solutions, and due to our experience that concentrations of trace impurities in UHP argon are lower than those in UHP nitrogen.

b) Effect of exposure to air or inert gas. We sought to minimize contact of samples with laboratory air to avoid contamination by aldehydes and ketones in the latter. Samples were transferred to SPME vials using an all-glass syringe with a stainless steel needle, which pierced the septum on the cap, expelling the 20 mL of gas present in the vial through a second needle piercing the same septum. Such transfers were as far as possible performed under UHP argon, but this led to a further concern of analyte losses to this argon. We therefore modeled the amounts of analyte which might be lost to argon, or contaminants which might be acquired from laboratory air, using temperature-dependent apparent partition coefficients for carbonyl compounds in seawater, K* (M/atm), published by Zhou and Mopper [5], where

$$C_{aq} = K^* P \qquad (4\text{-}2)$$

with C_{aq} being the compound's concentration in seawater (in M), and P its partial pressure in air (or headspace) (in atm). The temperature-dependence of K* can be described by

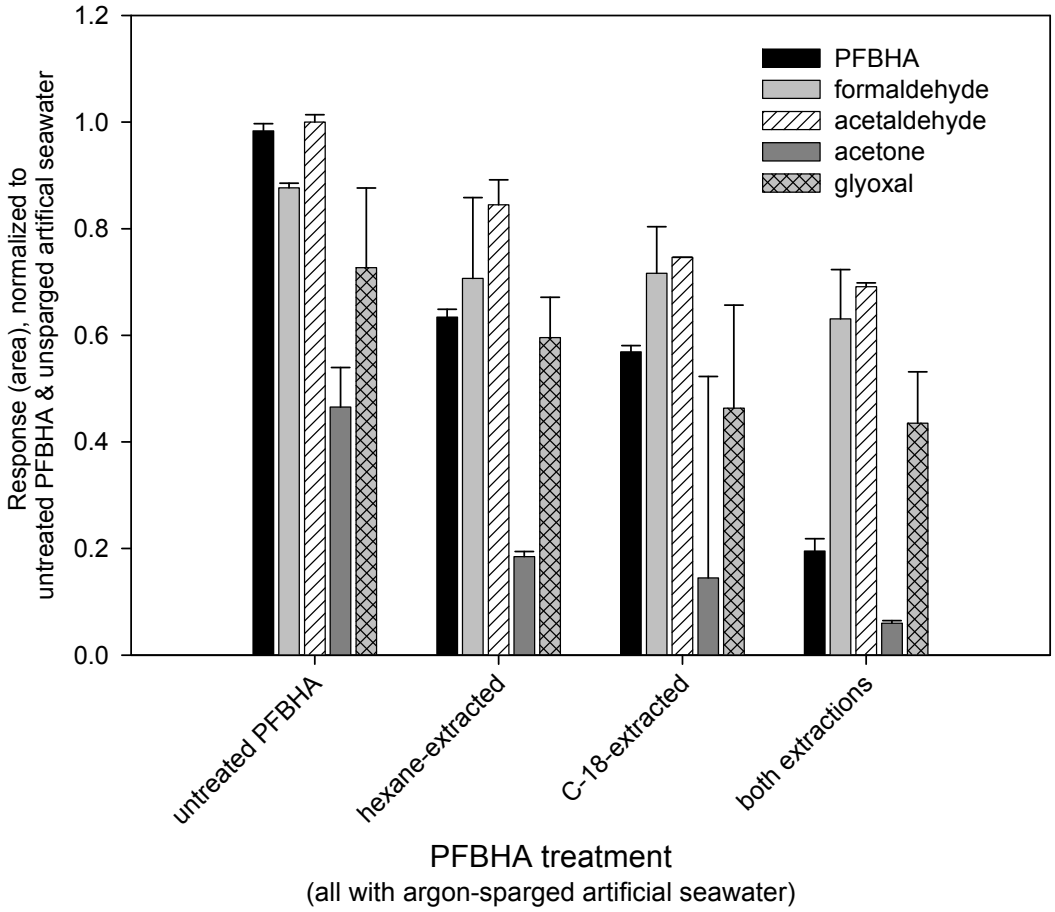


Figure 4-4. Effect of blank reduction measures, including argon sparging of the artificial seawater and PFBHA purification by solvent and solid phase extractions, on the concentration of PFBHA and selected PFB oximes in artificial seawater blanks. Concentrations are normalized to concentrations for untreated PFBHA and unsparged artificial seawater.

$$\log K^* = A + B/T \qquad (4\text{-}3)$$

where A and B are empirically fitted [5]. We used T = 21 °C, the typical temperature in our laboratories. For glyoxal and methylglyoxal no temperature-dependence coefficients have been reported, so K* at 25 °C was used. We assumed equilibrium was reached during gas-liquid contact, so that these results represent the greatest possible contamination, or analyte loss, for the concentrations used (see also the use of urban air mixing ratios, below). For the calculations, we used a range of carbonyl compound concentrations in seawater reported in the literature [1-2, 4, 7, 18]. Carbonyl compound mixing ratios used for air were those reported for the Los Angeles basin by Grosjean *et al*. [47]. Since these mixing ratios came from a relatively polluted urban environment, we took them to be among the highest in air to which a seawater sample might be exposed. Furthermore, their reported maximum formaldehyde mixing ratio of 10 ppbv [47] corresponds to the typical level measured in our laboratory air [48]. Further details of the calculations and source data are presented in the Supplementary Information available on-line, with full results in supplementary Tables 4-3 and 4-4.

The results indicate that for a 20-mL seawater sample exposed to urban air, the potential for contamination is substantial. Based on seawater concentrations reported by Zhou and Mopper [18] (among the lower values reported), formaldehyde concentrations may increase by 11% and 53% on equilibration with 20 mL and 100 mL of urban air, respectively (the latter might

occur for the last 20-mL aliquot taken from a 125-mL sample bottle). For these same volumes, acetaldehyde concentrations may increase by 23% and 117%, respectively, and acetone concentrations by 8.2% and 41%. For C_6-C_9 aliphatic aldehydes, reported at 0.05 - 0.1 nM in seawater [18], equilibration with 100 mL urban air may lead to a 1.4 to 4.7-fold overestimate of the carbonyl compound concentration. When higher reported seawater concentrations are considered (17.6 nM acetone [4], 15 nM formaldehyde [1]), the potential for contamination is less extreme (21% and 6 % overestimation, respectively, using 100 mL air) but nonetheless notable.

For the exposure of seawater samples to a carbonyl-free headspace or gas stream (such as UHP argon), the fraction of a carbonyl compound lost is independent of its original concentration in seawater. For such exposure, no loss (within the error in K^*) of the carbonyl compound from the seawater was predicted for the most water-soluble (largest K*) carbonyls- formaldehyde, glyoxal, and methylglyoxal, even for the largest headspaces modeled. For other very soluble carbonyl compounds (acetaldehyde, propanal, acetone, butanone, benzaldehyde), less than 0.5% loss was projected for a 20-mL seawater sample exposed to 20 mL gas, increasing to 1.0% for a 20 mL sample exposed to 100 mL gas. Nevertheless, the projected loss of carbonyl compounds increased with increasing carbon number (corresponding to lower solubility/ lower K* [5]), being particularly pronounced for nonanal, 8.0% of which would be lost on equilibration of 20 mL seawater with 20 mL gas, and 30.4% of which would be lost if 20 mL seawater equilibrated with 100 mL gas.

Since our calculations used the highest concentrations of carbonyl compounds in air likely to be encountered and assumed equilibrium was reached, they modelled the severest possible contamination. Nonetheless, they underscore that great care should be taken to limit exposure of the sample to ambient air. While much smaller inaccuracies result from exposure to clean gas, losses for the higher molecular weight carbonyl compounds can be significant, and measures are warranted to limit the size of headspaces and time of exposure to gas streams.

c) Purification of PFBHA. Workers using DNPH for carbonyl analysis in environmental samples have purified it by recrystallization [3] or solvent extraction [1, 49]. PFBHA is too expensive, and typically not available in large enough quantities, to recrystallize, and our prior attempts to purify it using solvent extraction resulted in further carbonyl contamination from trace carbonyls in the solvents.

Solid phase C8 and C18 extraction cartridges (100 and 200 mg) were used to extract 2 mL batches of aqueous PFBHA solution. Cartridges were first conditioned with 1 bed volume of HPLC-grade methanol and several bed volumes Milli-Q water before PFBHA was applied and eluted by positive pressure. The objective was to have oximes retained on the sorbent, while PFBHA passed through and was recovered in the aqueous eluent. Using 200 mg of either sorbent removed >95 % of the PFBHA itself and thus was not studied further, while 100 mg of C8 removed 89 % of PFBHA. C18 (100 mg) performed well for a range of oximes while still letting most PFBHA elute (Fig. 4-4). Interestingly, hexane

extraction appeared to perform similarly to C18 extraction when a freshly-opened bottle of HPLC hexane was used (Fig. 4-4), but it was deemed impractical to require freshly-opened hexane for all extractions conducted. Use of the two extraction methods in series removed 80 ± 1% of PFBHA. Treated PFBHA solutions were immediately stored under UHP argon. We conclude that precautions to minimizing sample contact with laboratory air are prudent, but appreciable reductions in blanks can also be achieved by sparging the artificial seawater for standard preparation, and by purifying the PFBHA used by solid-phase extraction and preventing its recontamination.

4.4.5 Calibration

Detection limits achieved were in the low-to-mid pM to low nM range (Table 4-1). Detection limits by GC-MS and GC-FID were generally comparable. R^2 of the calibration curves (regressions) was generally >0.99, except for methacrolein, pentanal, *trans*-2-hexenal and methylglyoxal by GC-FID (Table 4-1). Detection limits were comparable to those reported for fresh waters by Bao *et al*. [21], where available (Table 4-1), demonstrating that more universal detectors (FID, MS) can provide comparable performance to an electron capture detector specifically chosen [21] for its sensitivity to fluorinated derivatives. Weighted least squares linear regression was used in calibration calculations [50], since homoscedasticity could not be assumed across the concentration range used. Our detection limits for many compounds are also competitive with those obtained in

seawater by HPLC following DNPH derivatization, reported by Kieber and Mopper [1] as approximately 0.5 nM for most aldehydes and 5 nM for most ketones, although these authors noted that cartridge pre-concentration can reduce these detection limits by roughly an order of magnitude. The use of 4-fluorobenzaldehyde as an internal standard [21], as a control on derivatization and extraction efficiency, did not improve detection limits for all compounds and has several further disadvantages, including that it co-elutes with an analytically useful peak for benzaldehyde and that its addition, particularly to actual seawater samples, has the potential to introduce further contamination.

The higher detection limit for acetaldehyde is due to the acetaldehyde PFB oximes eluting on the tail of the PFBHA peak, leading to greater difficulties (variability) in peak integration. We attribute higher detection limits for formaldehyde and acetone to the ubiquity of these compounds in human environments (including laboratories), leading to some degree of contamination irrespective of precautions taken.

4.4.6 Cryopreservation on SPME fibres

Mean recoveries of PFB oximes from SPME fibres after 1 week of storage at –78 °C ranged from 46.2% (hexanal) to 82.6% (acetone) (Table 4-2), with considerable fibre to fibre variation for higher molecular weight oximes. These recoveries suggest that during storage, loss processes predominate over the formation of additional oximes which might occur between carbonyl compounds

Table 4-1. Detection limits (LoD) and calibration ranges (nM) for carbonyl compounds using PFBHA derivatization/SPME. Detection limits were calculated as 3× the standard deviation of the blank, divided by the slope of the calibration curve. R^2 values are based on means. Detection limits reported by Bao *et al*. [21] for fresh waters are included for comparison. ND = not determined.

	GC-MS			GC-FID			Bao *et al.* LoD (GC-ECD)
	LoD	**R^2**	**calibration range**	**LoD**	**R^2**	**calibration range**	
Saturated aldehydes							
Formaldehyde	7.90	>0.999	0.60 - 200	4.55	0.998	0.40 - 805	0.50
Acetaldehyde	23.5	>0.999	0.70 - 132	19.4	0.999	0.35 - 709	0.45
Propanal	0.16	>0.999	0.54 - 100	0.04	0.999	0.27 - 538	0.14
Butanal	0.06	0.999	0.33 - 109	0.02	0.998	0.22 - 439	0.20
Pentanal (valeraldehyde)	0.05	0.999	0.36 - 68	0.87	0.996	0.18 - 364	0.23
Hexanal	0.08	>0.999	0.24 - 81	0.18	0.994	0.16 - 326	0.25
Heptanal	0.19	0.997	0.20 - 67	0.16	0.997	0.14 - 271	0.35
Octanal	0.04	>0.999	0.34 - 45	0.14	0.999	0.12 - 241	0.23
Nonanal	0.06	>0.999	0.16 - 55	0.06	0.993	0.11 - 220	0.35

Table 4-1. (Continued)

Unsaturated aldehydes							
Acrolein	0.16	0.999	0.42 - 141	0.34	0.996	0.28 - 569	1.8
Methacrolein	0.08	0.999	0.34 - 112	0.18	0.985	0.90 - 202	ND
Crotonaldehyde	0.12	0.999	0.33 - 111	0.14	>0.999	0.89 - 200	0.42
trans-2-hexenal	0.02	0.998	0.31 - 57	0.25	0.988	0.61 - 137	0.15
Cyclic aldehydes							
Furfural (2-furaldehyde)	0.40	0.999	0.36 - 119	0.09	0.999	0.24 - 478	ND
Benzaldehyde	0.10	0.999	0.29 - 97	0.19	0.998	0.20 - 392	0.08
Ketones							
Acetone	3.62	0.999	0.54 - 100	4.41	0.993	0.27 - 538	1.4
Butanone	0.24	0.999	0.44 - 83	0.11	0.999	0.88 - 198	1.7
Methyl vinyl ketone	0.36	0.999	0.45 - 84	0.88	0.997	0.90 - 202	ND
3-methyl-2-butanone	0.12	0.997	0.36 - 68	0.90	0.999	0.73 - 165	ND
Dicarbonyls							
Glyoxal	0.15	0.998	0.52 - 98	1.89	0.998	1.04 - 234	0.17
Methylglyoxal	0.17	0.999	0.39 - 73	2.63	0.985	0.19 - 390	0.14
2,4-pentanedione (acetylacetone)	0.11	0.999	0.39 - 72	0.67	0.994	0.19 - 386	ND
Glutaraldehyde	0.01	0.998	0.42 - 78	0.11	0.999	0.83 - 187	ND

Table 4-2. Comparative recoveries (%) of PFB oximes after storage on two 100 µm PDMS SPME fibres on dry ice for 7 days. Concentrations range from 14.7 nM (nonanal) to 53.7 nM (formaldehyde)

	Fibre 1	Fibre 2	Mean of both fibres	% RSD
formaldehyde	77.8	77.7	77.8	0.1
acetaldehyde	65.9	80.5	73.2	14.1
glyoxal	53.8	45.9	49.9	11.3
acetone	77.0	88.3	82.6	9.6
propanal	73.5	78.6	76.1	4.7
acrolein	63.8	66.4	65.1	2.8
methylglyoxal	54.2	105.9	80.1	45.6
butanone	60.3	64.8	62.5	5.0
butanal	59.3	62.9	61.1	4.2
3-methyl-2-butanone	60.8	63.1	62.0	2.7
pentanal	57.3	66.3	61.8	10.4
2,4-pentanedione	44.8	57.9	51.4	18.0
furfural	51.1	57.1	54.1	7.8
hexanal	39.5	52.8	46.2	20.4
benzaldehyde	49.8	61.8	55.8	15.3
heptanal	41.2	67.9	54.5	34.7
octanal	42.0	69.5	55.7	34.9
nonanal	38.6	70.1	54.3	41.1

from the fibre's environment and PFBHA which was absorbed onto the fibre. This is consistent with slower oxime formation rates at the low temperatures. Sakamoto *et al*. [34] reported 97.4% mean recovery of dimethyl sulphide (DMS) from Carboxen-PDMS SPME fibres after up to 20 days storage in liquid nitrogen (–196 °C). We had expected that for PFB oximes, being of higher molecular weight, cooling to dry ice temperatures would be sufficient for storage, and thus not require as low a temperature to be maintained in the field. Wichard *et al*. [10] reported that PFB oximes of highly unsaturated aldehydes were stable in hexane solution for 11 days at –80 °C and relatively stable (80-90% recovery) in the same solution at room temperature. This suggests that the lower recoveries we observed may be due to sublimation or enhanced degradation on the greater exposed surface of the SPME fibre. Analysis by extraction and storage of analytes on an SPME fibre would also require calibration of each separate fibre used for storage [34, 51], and therefore add considerably to the overall analysis time in a particular study.

4.4.7 Analysis of Lower St. Lawrence Estuary waters

Carbonyl compound concentrations in surface waters from the Lower St. Lawrence Estuary, taken at 2-3 m depth, are shown in Figure 4-5. These waters exhibited salinities from 30.77 (station 20) to 23.79 (station SAG), temperatures in the range 4.0-9.3 °C, and dissolved oxygen concentrations of 293-312 μM (corresponding to O_2 saturation states of 88.4-114 %) at the times sampled. DOC

concentrations decreased seaward along the estuary from 1.46 mg/L at station SAG and 1.13 mg/L at station 24 to 0.877 mg/L at station 20, consistent with the trend observed in previous years. Total concentrations of carbonyl compounds detected ranged from 0.85 nM (station 24) to 15.5 nM (station 23), and were significantly correlated ($P<0.05$) with surface water pH ($R^2=0.71$) and O_2 saturation state ($R^2=0.73$). Nine C_2-C_6 compounds were detected in the samples; other aldehydes and ketones were below detection limits. Hexanal and methyl vinyl ketone were detected at the most sites. 2,4-Pentanedione was present at 3 sites, at concentrations up to 5.2 nM, and has not previously been reported in surface ocean waters, although Noziere and Riemer [52] used this compound as a model for carbonyl-rich organic matter in the atmosphere. No concentration trends along the estuary were evident for any compound. Hexanal, the substance most commonly detected, has been reported to be one of the principal products of the photodegradation of linoleic acid, a biologically derived fatty acid, in oxic seawater [53], which would explain its near-universal presence in these oxic waters. However, propanal and nonanal, which might be expected from the photo-oxidation of ω-3 and ω-9 fatty acids, respectively, were not detected or could not be quantified; the relative abundance of ω-3, -6 and -9 and fatty acids in organic matter in these waters is also not known. Methyl vinyl ketone is produced in the atmosphere from the oxidation of biogenic hydrocarbons such as isoprene [54], and it is possible that it may be similarly produced from isoprene oxidation in surface waters.

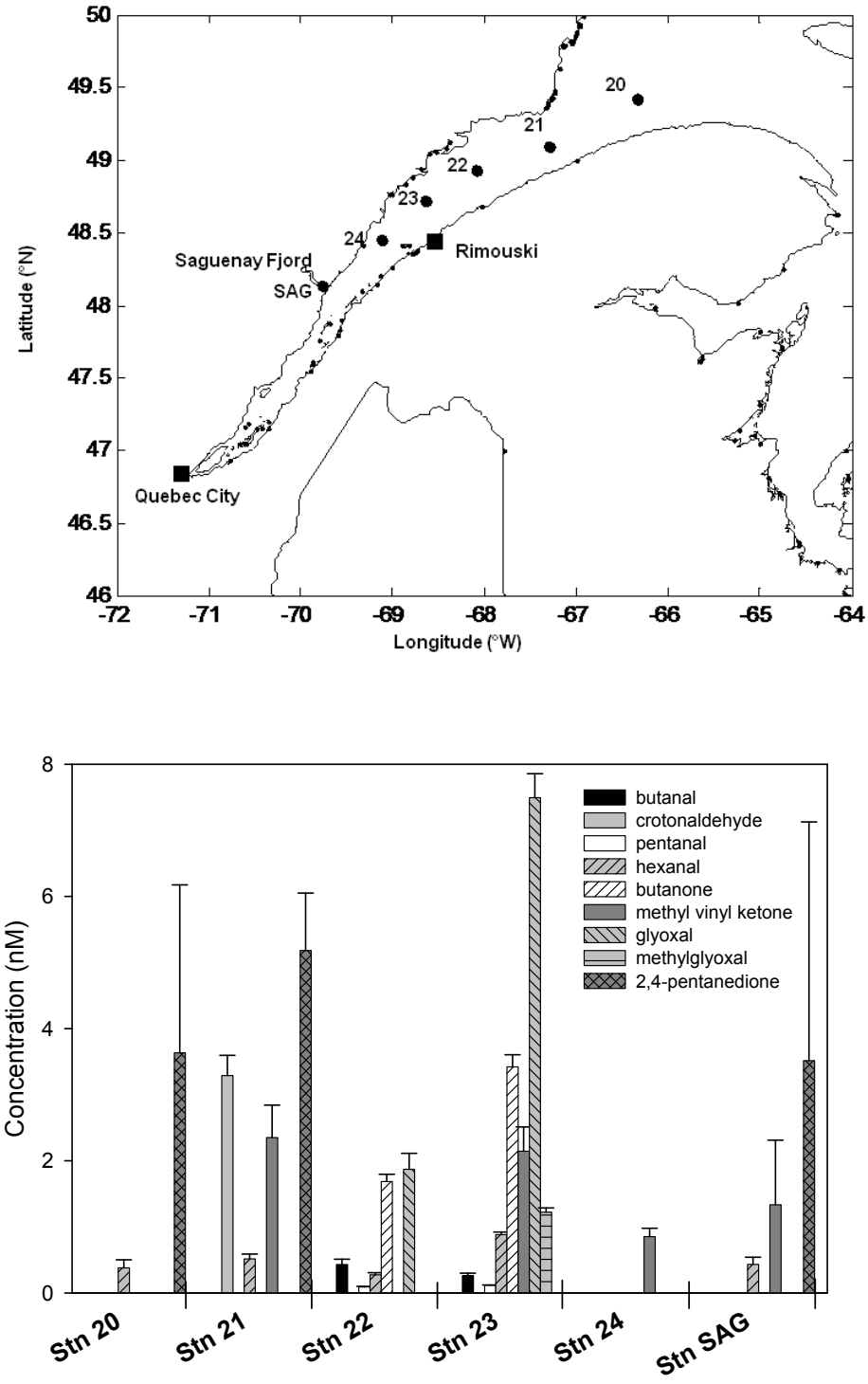


Figure 4-5. **a.** Surface seawater sampling locations in the Lower St. Lawrence Estuary; **b.** Carbonyl compound concentrations in surface waters from the stations indicated (mean ± SD, n = 2).

Concentrations of individual compounds were not correlated with DOC concentrations, suggesting that their formation and degradation is neither limited by overall DOC concentration nor restricted to DOC from a terrestrial/freshwater or marine source. If these carbonyl compounds are indeed produced by photochemistry, solar irradiance (which was not measured during sampling) would introduce an additional variable which may mask a potential relationship between DOC and carbonyl concentrations. When station 23 (the station with the highest total carbonyl compound concentration and the station closest to an urban area- Rimouski) (Fig. 4-5) is not considered, total carbonyls at the remaining 5 stations are significantly correlated ($P<0.05$) with concentrations of particulate organic carbon (POC) ($R^2 = 0.86$) and particulate nitrogen ($R^2 = 0.92$); these can be regarded as indicators of phytoplankton production, suggesting phytoplanktonic sources for these substances. At station 23, the higher total carbonyl concentration suggests an additional source of carbonyl compounds, especially glyoxal, 7.5 nM of which was measured for this site. We caution that any biogeochemical interpretations of the data at this stage are speculative due to the small sample set, and further investigation with a greater range of sampling locations and times is required.

C_1-C_3 carbonyls expected to be prevalent in surface waters based on previous studies [1, 17-18] (in particular formaldehyde, acetaldehyde, and acetone) could not be quantified due to concern about contamination of the blanks, which highlights the care needed in future shipboard sampling and/or laboratory work. Mopper and co-workers also highlighted the potential for ship-

derived and laboratory contamination when determining carbonyls in seawater [17-18], and indeed conducted their sampling from a zodiac upwind of the main research vessel.

4.5 Outlook

Given the need for comprehensive spatial studies of carbonyl concentrations in surface seawaters, we aim to take advantage of the method's portability for eventual shipboard use, thus avoiding both transport and storage effects for seawater itself and the need for cryogenic preservation of analytes/derivatives on an SPME fibre. Future studies may also continue to focus on reduction of method blanks, on method automation to improve sample throughput and reproducibility, and on development of suitable preservation protocols for seawater if samples need to be analyzed on shore.

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4.8 Supplementary information to accompany Edward D. Hudson, Parisa A. Ariya and Yves Gélinas, *A method for the Simultaneous quantification of 23 C_1-C_9 trace aldehydes and ketones in seawater.*

4.8.1 Calculation of potential contamination or loss of carbonyl compounds

We modeled exchange between a seawater sample and any gas to which it was exposed (a headspace of laboratory or ambient air or ultra-high purity (UHP) argon) as follows:

a constant volume of water, V_W, is in contact with a constant volume of gas, V_G. Initially (time 0), the water contains a certain molar concentration C_0 of a dissolved carbonyl compound, and the gas contains a certain partial pressure P_0 of the same compound. The concentration and partial pressure change by ΔC and ΔP, respectively, coming to an equilibrium concentration C_{eq} and equilibrium partial pressure P_{eq}, which are related as described by Zhou and Mopper [1] by

$$K^* = C_{eq} / P_{eq} \qquad (4\text{-}4)$$

For a closed system, any number of moles *n* of compound lost from the seawater is gained by the gas (or *vice versa*), thus

$$\Delta n_W = - \Delta n_G \qquad (4\text{-}6)$$

Furthermore,

$$\Delta n_W = \Delta C V_W \qquad (4\text{-}6)$$

$$\Delta P V_G = \Delta n_G RT \qquad (4\text{-}7)$$

Rearrangement and substitution gives

$$\Delta C = \frac{K^* P_0 - C_0}{\left(\frac{K^* RT V_W}{V_G} + 1\right)} \qquad (4\text{-}8)$$

from which $C_{eq} = \Delta C + C_0$ is readily calculated.

For a headspace of UHP argon, P_0 was assumed to be zero, and thus the percentage change (loss) in carbonyl compound concentration C in seawater depends only on the ratio of V_W to V_G. Therefore, results for any value of C_0 are shown; the percentage of each carbonyl compound lost to the headspace is independent of this (Table 4-3). The percentage change in C in seawater when air, containing carbonyl compounds at various mixing ratios, is introduced into the headspace is shown in Table 4-4.

Table 4-3. Expected reduction in concentrations of carbonyl compounds in seawater on equilibration with a carbonyl-free headspace (UHP argon).

Compound	Volume (mL)		% change in seawater concentration
	Seawater	Headspace	
Formaldehyde	20	20	0.00
Acetaldehyde	20	20	-0.24
Propanal	20	20	-0.31
Butanal	20	20	-0.44
Pentanal	20	20	-0.65
Hexanal	20	20	-0.94
Heptanal	20	20	-1.44
Octanal	20	20	-2.84
Nonanal	20	20	-8.03
Benzaldehyde	20	20	-0.10
Acetone	20	20	-0.11
Butanone	20	20	-0.21
Glyoxal	20	20	0.00
Methylglyoxal	20	20	0.00
Formaldehyde	20	100	0.00
Acetaldehyde	20	100	-1.21
Propanal	20	100	-1.52
Butanal	20	100	-2.16
Pentanal	20	100	-3.17
Hexanal	20	100	-4.51
Heptanal	20	100	-6.80
Octanal	20	100	-12.7
Nonanal	20	100	-30.4
Benzaldehyde	20	100	-0.51
Acetone	20	100	-0.57
Butanone	20	100	-1.03
Glyoxal	20	100	0.00
Methylglyoxal	20	100	0.00

Table 4-4. Expected equilibrium concentrations of carbonyl compounds in seawater for various starting concentrations of these compounds in seawater and in air to which it is exposed. Assumptions for initial seawater and air carbonyl concentrations are based on the references listed. *maximum mixing ratio reported by Grosjean *et al.* [2]; other listed mixing ratios reported by these authors are averages. ** estimate

Compound	Initial concentration in seawater (nM)	Initial mixing ratio in air (ppbv) [2]	Volume (mL)		Equilibrium concentration in seawater (nM)	% change in seawater concentration
			Seawater	Air (headspace)		
Formaldehyde	3.88 [3]	10*	20	20	4.3	11
	3.88 [3]	10	20	100	6.0	53
	15 [4]	10	20	20	10.4	4.1
	15 [4]	10	20	100	12.1	21
Acetaldehyde	1.38 [3]	8.0*	20	20	1.7	24
	1.38 [3]	8.0	20	100	3.0	117
	7.0 [5]	8.0	20	20	7.3	4.5
	7.0 [5]	8.0	20	100	8.6	22
Acetone	3.0 [3]	6.0*	20	20	3.2	8.1
	3.0 [3]	6.0	20	100	4.2	41
	17.6 [6]	6.0	20	20	17.8	1.3
	17.6 [6]	6.0	20	100	18.7	6.5
Glyoxal	0.28 [3]	3.8*	20	20	0.44	56
	0.28 [3]	3.8	20	100	1.1	280
	5.0 [4]	3.8	20	20	5.1	3.5
	5.0 [4]	3.8	20	100	5.8	16

Table 4-4. Continued.

Compound	Initial concentration in seawater (nM)	Initial mixing ratio in air (ppbv)	Volume (mL)		Equilibrium concentration in seawater (nM)	% change in seawater concentration
			Seawater	Air (headspace)		
Propanal	0.4 [3]	0.79	20	20	0.43	7.9
	0.4 [3]	0.79	20	100	0.55	39
	2.0 [5]	0.79	20	20	2.0	1.3
	2.0 [5]	0.79	20	100	2.1	6.5
Methylglyoxal	0.2 [3]	2.3*	20	20	0.30	48
	0.2 [3]	2.3	20	100	0.68	240
Butanal	0.2 [3]	0.71	20	20	0.23	14
	0.2 [3]	0.71	20	100	0.34	70
Butanone	0.5**	8.0*	20	20	0.83	66
	0.5	8.0	20	100	2.1	330
Pentanal	0.11 [3]	0.41	20	20	0.13	15
	0.11 [3]	0.41	20	100	0.19	72
Hexanal	0.05 [3]	1.2*	20	20	0.10	98
	0.05 [3]	1.2	20	100	0.28	470

Table 4-4. Continued.

Compound	Initial concentration in seawater (nM)	Initial mixing ratio in air (ppbv)	Volume (mL)		Equilibrium concentration in seawater (nM)	% change in seawater concentration
			Seawater	Air (headspace)		
Heptanal	0.05 [3]	0.64	20	20	0.08	51
	0.05 [3]	0.64	20	100	0.17	240
Octanal	0.05 [3]	0.53	20	20	0.07	40
	0.05 [3]	0.53	20	100	0.14	180
Nonanal	0.09 [3]	1.09	20	20	0.12	38
	0.09 [3]	1.09	20	100	0.22	140
Benzaldehyde	0.5**	0.6	20	20	0.52	4.9
	0.5	0.6	20	100	0.62	24

4.8.2 Fractional factorial experiment to consider factor interactions

A 2^{4-1} half-factorial experiment [7] was conducted on derivatization and SPME conditions to evaluate the influence of four parameters simultaneously- SPME fibre type (sorbent), pH, SPME sorption time, and sample volume. The experiment was undertaken to consider the possibility that key factors may interact to influence optimum conditions. Maximum (+) and minimum (–) values for each parameter were:

- Fibre type (A): 65 µm polydimethylsiloxane/divinylbenzene (PDMS/DVB) (+) vs. 100 µm polydimethylsiloxane (PDMS) (–)
- pH (B): pH 4.7 (+) vs. pH 2.2 (–)
- sorption time (C): 30 min (+) vs. 15 min (–)
- sample volume (D): 20 mL (+) vs. 10 mL (–)

Each set of conditions was run in duplicate to provide an intrinsic error estimate over the entire experimental domain. The factor table (Table 4-5) shows that the design allowed for the evaluation of main factor effects and two-factor interactions, but not higher-level factor interactions. Furthermore, two-factor interactions involving sample volume were aliased with other two-factor interactions; this was on the expectation that sample volume would interact negligibly with the other three factors screened, since previous experiments had suggested a minimal effect of sample volume. Results were plotted using Statgraphics Centurion XVI software (StatPoint Technologies, Warrenton, VA).

The experimental space was restricted by certain considerations such as the impracticality of long extraction times and the difficulty of maintaining basic pHs

reproducibly. Figure 4-6 illustrates the effect of the four simultaneously tested factors (coded (+) and (–) ; see Table 4-5), and their interactions, on the peak area response for selected carbonyl PFB oximes (Fig. 4-6a-e) as well as for the total PFB oxime peak area (Fig. 4-6f). The effect of factors on peak areas was calculated as the mean difference between the response when the factor was coded (+) versus when it was coded (–)[7], and is normalized to the standard error due to all factors, calculated from all duplicate measurements (8 degrees of freedom). Sorption time (C) was always a significant factor, with the 30 minute sorption always giving a greater response. For most PFB oximes as well as for the total oxime peak area, the fibre (sorbent) choice (A) and sorption time had the greatest effect on response, with the 65 μm PDMS/DVB fibre giving the greater response, as found previously. Nevertheless, for C_5-C_9 aliphatic aldehydes (Fig. 4-6c), the effect of fibre choice did not show up as significant in this experiment. This suggests that for these oximes, the effect of sorbent choice only becomes important at optimal pH (compare Fig. 4-1, for which a pH of 3.7 was used). No general trend was evident between the two pH's used, although pH 4.6 gave a greater response than pH 2.2 for a greater number of oximes. As noted previously (Fig. 4-3), the overall optimal pH lies between these two pHs and the effect of pH appears to be non-linear, and is therefore not well studied through a 2-level factorial experiment. The interaction between fibre choice (A) and pH (B) was rarely significant at pHs of 2.2 or 4.6, except for acetaldehyde, methylglyoxal and 2,4-pentanedione.

Whereas preliminary experiments suggested that sample volume (D) had little effect, the current experiment found a greater peak area response for a 20-mL sample volume than a 10-mL sample volume for higher molecular-weight (>C_5) aliphatic

aldehydes (e.g, Fig 4-6c). This indicated that a greater sample volume is preferable, which is also commensurate with minimizing the vial headspace. The greater peak area when a 20-mL sample volume was used could be due to the loss of higher molecular weight aldehydes to the headspace (Table 4-3) present with 10 mL of sample.

The experiment aliased two-factor effects which included sample volume with other two-factor effects (e.g., Fig 4-6a: AC + BD). Nevertheless, for any oximes for which sample volume significantly affected peak area response, no two-factor effect including sample volume was found to be significant. Overall, no two-factor interactions were detected which were antagonistic to the main effects, suggesting that our individual optimization experiments were not missing any optima arising from two-factor interactions.

4.8.3 References

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Table 4-5. Factor table for half-factorial evaluation of SPME conditions.

Sample	Factor or factor combination						
	Fibre Type (A)	pH (B)	Sorption time (C)	Fibre·pH AB	Fibre·time AC	pH·time BC	Sample Volume (D = ABC)
1	PDMS/DVB (+)	4.6 (+)	30 min (+)	+	+	+	+
2	PDMS/DVB (+)	4.6 (+)	15 min (–)	+	–	–	–
3	PDMS/DVB (+)	2.0 (–)	30 min (+)	–	+	–	–
4	PDMS/DVB (+)	2.0 (–)	15 min (–)	–	–	+	+
5	PDMS (–)	4.6 (+)	30 min (+)	–	–	+	–
6	PDMS (–)	4.6 (+)	15 min (–)	–	+	–	+
7	PDMS (–)	2.0 (–)	30 min (+)	+	+	–	+
8	PDMS (–)	2.0 (–)	15 min (–)	+	–	+	–

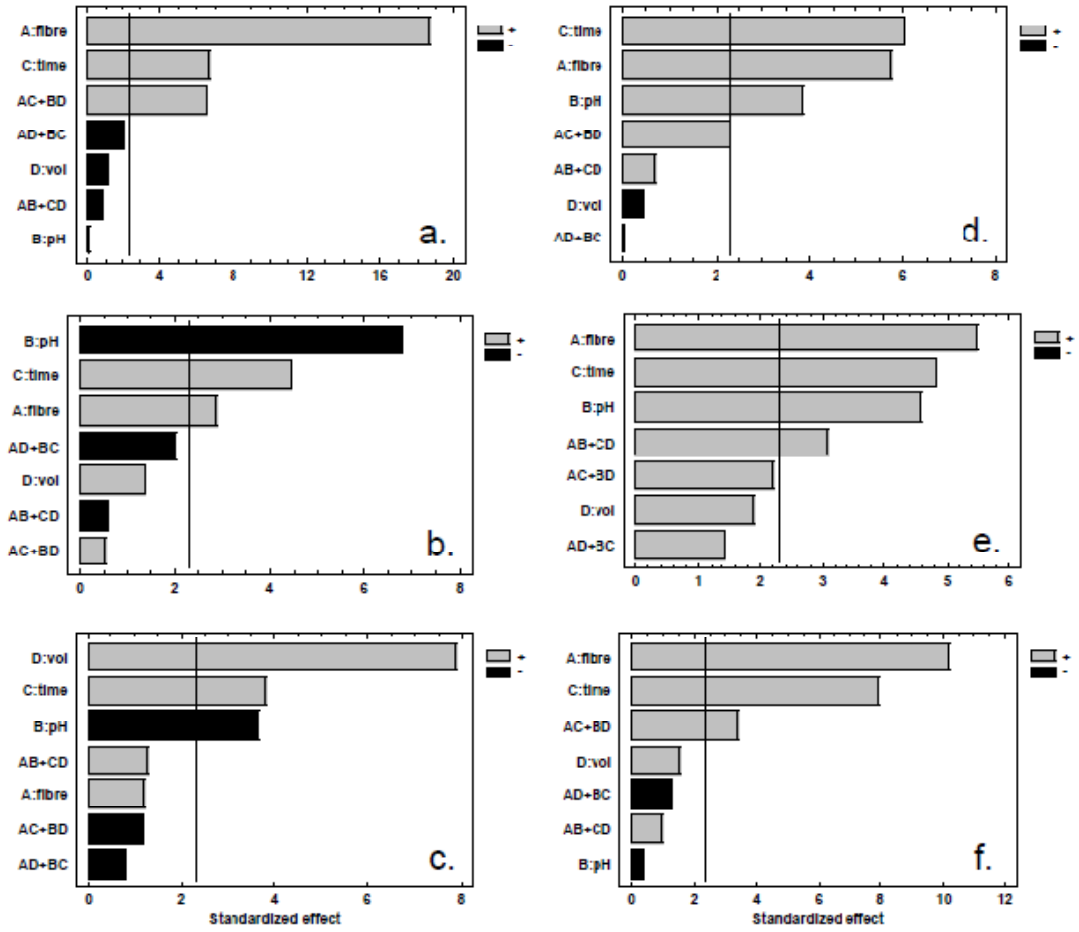

Figure 4-6. Pareto plots for four simultaneously tested factors, at 2 levels, affecting peak area response for selected carbonyl PFB oximes. a. formaldehyde, b. propanal, c. hexanal, d. acetone, e. methylglyoxal, f. total of all PFB oximes. Effect on peak areas is calculated as the mean difference between the response when the factor is coded (+) vs. (-) (see also Table 4-5) and is normalized to the standard error across effects. Vertical lines represent a significant effect at $P<0.05$.

Chapter 5

Aldehydes and Ketones in Surface Waters of the North-western Atlantic

As described in chapter 4, the SPME method developed for carbonyl compounds in seawater was tested on a limited number of samples from an estuarine environment. Because of the low number of samples, any biogeochemical interpretation of those data was at best speculative. We thus undertook to apply the method to a wider ranging sampling campaign, by profiling seawaters from the Labrador Sea and the Scotian Shelf, two open ocean areas of the northwestern Atlantic which are separated by over 1500 km , have different climatic regimes, and have waters which might exhibit differing carbonyl compound profiles. This work yielded the first concentrations of many carbonyl compound for waters of the Northwestern Atlantic. We were further able to estimate ocean/atmosphere fluxes for a number of aldehydes in both these ocean environments.

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Aldehydes and Ketones in Surface Waters of the North-western Atlantic

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5.1 Environmental context

Low-molecular weight aldehydes and ketones formed in the oceans may be transferred to or from the troposphere, impacting its oxidant chemistry and capacity, and thus the lifetimes of other trace gases, as well as leading to secondary organic aerosol formation. Both these effects have climatic implications. Few measurements of these compounds in temperate and polar waters have been reported, hindering the estimation of global fluxes from, or to, the oceans.

5.2 Abstract

Volatile carbonyl compounds (aldehydes and ketones) in seawater are of interest because they can be both a product of and a substrate for biology, because they represent a sink for a portion of marine dissolved organic matter (DOM), and because, after transfer across the sea-air interface, they may affect oxidative processes in the troposphere. We present the first survey of temperate and sub-arctic surface seawaters from the Labrador Sea and from the Scotian Shelf and Slope, in the northwestern Atlantic. Eleven C_1 - C_9 carbonyl compounds were quantified using a low-cost, environmentally-friendly solid phase microextraction method optimized in our laboratory. A substantial disequilibrium between measured concentrations of glyoxal and formaldehyde in seawater, and published concentrations in the marine atmosphere, suggests that in these regions the ocean is a sink for these compounds. Estimated fluxes

of nonanal, octanal, pentanal, and butanal from the ocean to the atmosphere are 0.11 – 14, -0.26 – 2.34, -6.9 –

-1.8, and -13 – -3.7 μmol/m^2/day, respectively. 1.45 nM nonanal also occurred at depths of up to 3460 m in the central Labrador Sea, with no marked decrease in its concentration with depth down the water column, suggesting either a source at depth or rapid entrainment and no sink at depth for this compound.

Keywords: volatile organic compounds, Gas Chromatography/Mass Spectrometry, dissolved organic carbon, SPME, subarctic marginal seas, sea-air exchange

5.3 Introduction

Low molecular weight aldehydes and ketones in surface seawaters may originate from dissolved organic matter (DOM) photochemistry[1], direct algal[2] or bacterial production[3-4] or by uptake from the atmosphere[5-6] if mixing ratios in the marine boundary layer exceed equilibrium concentrations with respect to surface waters. Thus, these substances are of interest in conjunction with the cycling of marine DOM, and as a carbon source for marine heterotrophs[1, 7]. Furthermore, the high mixing ratios of acetone, acetaldehyde, formaldehyde and other carbonyl compounds which occur over parts of the remote oceans[8-9] may affect the oxidative capacity of the remote troposphere and may contribute a significant fraction of tropospheric odd hydrogen (HO_x) production[8, 10] at higher, drier altitudes. (For example, at 10-12 km altitude, HO_x production from acetone may exceed that from the $O(^1D) + H_2O$ reaction by a factor of 5[8, 11]). It is not known whether, globally, the oceans are a source or a sink of many carbonyl compounds with respect to the atmosphere. For example, the tropical and subtropical Pacific appears to be a net acetone source[5], while the tropical Atlantic appears to be a sink[12]. To date, there have been few studies reporting concentrations of carbonyl compounds in seawater (Table 5-1), and most of the reported measurements are for the tropical and subtropical oceans[1-2, 5, 12-15]. Furthermore, acetone is the only carbonyl compound for which extensive spatial surveys have been undertaken[5, 12]. Due in part to the paucity of seawater concentration data, appreciable gaps remain in our understanding of the global budget and biogeochemistry of these compounds. We report measurements of a C_1-C_9 aldehydes and ketones in waters from the North Atlantic (Fig. 5-1), using a solid phase microextraction method recently optimized in our laboratory[16].

Table 5-1. Aldehyde and ketone concentrations previously reported in surface seawaters. [a]coastal, sampled from shore, [b]upper limit (may represent acetone + propanal). [1]range, [2]mean (range), [3]mean ± SD

Compound	Concentrations (nM)	Region	Method
Formaldehyde	10-50	Caribbean Sea[17]	DNPH- HPLC
	3.88 ± 0.26[3]	Sargasso Sea[15]	DNPH- HPLC
	473 (219-802)[2]	Terra Nova Bay, Antarctica[18]	fluorescence-FIA
Acetaldehyde	1.38 ± 0.08[3]	Sargasso Sea[6]	DNPH- HPLC
	2-140[1]	Caribbean Sea[17]	DNPH- HPLC
Glycolaldehyde	48-60[1]	Aegean Sea[14]	DNPH- HPLC
Propanal	0-20[1]	Caribbean Sea[17]	DNPH- HPLC
C_4-C_{10} aldehydes	0.2-5[1]	Sargasso Sea[6]	DNPH- HPLC
C_6-C_{15} aldehydes[a]	0-0.58[1]	Buzzards Bay, MA[19]	Purge & trap/GC
Acetone	17.6 ± 8.1[b,3]	Equatorial Atlantic[12]	PTR-MS
	13.9 ± 11.7[b,3]	Tropical Pacific[5]	APCI-MS
	13.6 ± 3.0[b,3]	Mid-latitude Pacific[5]	APCI-MS
	3.00 ± 0.23[3]	Sargasso Sea[15]	DNPH- HPLC
	3-50[1]	Caribbean Sea[6]	DNPH- HPLC
	5.5-6.9[1]	Nordic Seas[20]	SPME-GC/MS
Glyoxal	5-15[1]	Caribbean Sea[13, 17]	DNPH- HPLC
Methylglyoxal	0.1-1.5[1]	Sargasso Sea[6]	DNPH- HPLC

Methods: DNPH-HPLC = 2,4-dinitrophenylhydrazone derivatization-high performance liquid chromatography, FIA = flow injection analysis, GC = gas chromatography, PTR-MS = proton transfer reaction mass spectrometry, APCI-MS = atmospheric pressure chemical ionization mass spectrometry, SPME-GC/MS = solid phase microextraction-gas chromatography/mass spectrometry.

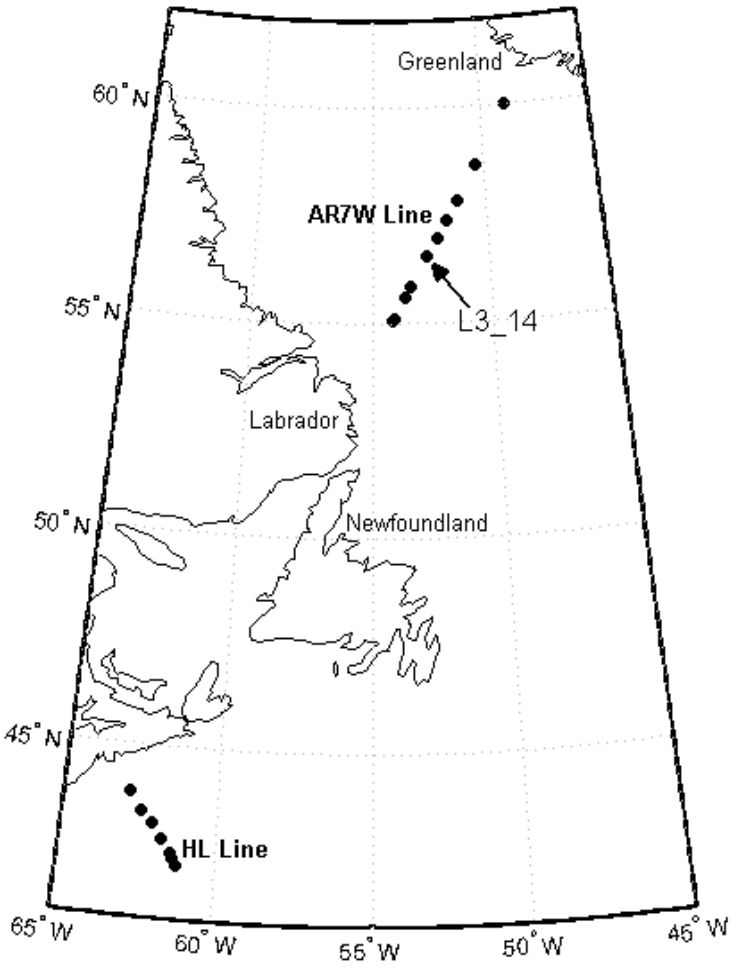

Figure 5-1. Sampling sites in the Northwestern Atlantic during June 2009, showing Labrador Sea sites (AR7W line) and Scotian Shelf/Scotian Slope sites (HL line) and the location of the depth profile (station L3_14).

We compare and contrast carbonyl compound concentrations from surface waters of the Labrador Sea, a remote Subarctic environment characterized by two cold boundary currents (the West Greenland current and the Labrador Current) and a winter deep convection regime which annually entrains surface waters[21-22], and the Scotian Shelf and Slope, an open ocean environment bounded by warmer surface waters from the south (the North Atlantic Current). Furthermore, we have profiled carbonyl compounds at a site in the central Labrador Sea to a depth of 3500 m. This is the first systematic survey, to our knowledge, of a variety of carbonyl compounds over a wide marine area, and the first for the North Atlantic.

5.4 Results and discussion

5.4.1 SPME method performance

Samples from the Labrador Sea and Scotian Shelf/Slope were analyzed for aldehydes and ketones using derivatization and solid phase microextraction (SPME) [16] (see Experimental Methods, section 5.6). Detection limits for these determinations were in the sub-nanomolar to low nanomolar range (Table 5-2), depending on the compound, and also varied somewhat with the SPME fibre used, since each SPME fibre must be calibrated individually. Two fibres were used to make the measurements reported here, hence the two detection limits for each compound in Table 5-2.

One of the principal remaining challenges of the method is identifying and suppressing contamination in method blanks, since C_1-C_3 aldehydes and ketones are ubiquitous in shipboard, urban and laboratory environments. We attribute the high

detection limits for acetaldehyde, acetone and formaldehyde to variability in these method blanks. Purification of the derivatization reagent (PFBHA) and transfer of samples and standards under UHP argon addressed PFBHA and laboratory air, respectively, as contamination sources. However, any aldehydes and ketones remaining in the ultrapure (Milli-Q) water used in the preparation of standards would be present in standards but not samples, thus being inappropriately subtracted from the latter. Therefore, our reported concentrations should be considered lower limits.

5.4.2 Aldehydes and ketones identified in seawater

An overview of aldehydes and ketones detected in surface waters of the two regions sampled is presented in Table 5-2. Mean surface water temperatures for the Labrador Sea and Halifax Line transects were 2.4 °C and 9.6 °C, respectively. Formaldehyde was not detected at all sites; where detected, it was present at 9.4 -18.5 nM. Mean formaldehyde concentrations did not differ significantly between the Labrador Sea and Scotian Shelf regions. No other formaldehyde concentrations for temperate Atlantic waters have appeared in the literature for comparison. The concentrations detected are similar to those reported for the Caribbean Sea by Mopper and Stahovec[17] (Table 5-1), but an order of magnitude lower than values reported in coastal Antarctica, where Largiuni *et al.*[18] attributed high surface water formaldehyde concentrations to dense phytoplankton blooms.

Table 5-2. Mean concentrations of aldehydes and ketones (nM) detected in surface waters of the Labrador Sea and Scotian Shelf/ Slope during May 2009. Means are of those concentrations (n) above the detection limits. BDL = below detection limit. Compounds not detected at any sites, or at only a single site, are not reported.

	Labrador Sea Mean ± SD (range) *(n)*	**Scotian Shelf/Slope** Mean ± SD (range) *(n)*	**Detection limits** (nM)
formaldehyde	12 ± 4 (BDL – 15.9) *(3)*	13 ± 6 (BDL – 18.4) *(5)*	9.3, 9.3
butanal	0.2 ± 1.6 (BDL – 0.17) *(2)*	0.10 ± 0.07 (BDL – 0.14) *(6)*	0.06, 0.22
methacrolein	-	0.4 ± 0.2 (BDL – 0.52) *(5)*	0.15, 2.1
pentanal	-	0.08 ± 0.31 (BDL – 0.15) *(5)*	0.04, 0.52
hexanal	-	0.17 ± 0.01 (BDL – 0.17) *(2)*	0.13, 0.40
heptanal	-	0.11 ± 0.02 (BDL – 0.13) *(2)*	0.10, 0.45
octanal	0.6 ± 0.7 (BDL – 0.7) *(3)*	0.4 ± 0.2 (BDL – 0.78) *(6)*	0.18, 0.60
nonanal	1.8 ± 1.9 (BDL – 4.0) *(4)*	1.1 ± 0.4 (0.80 – 1.7) *(7)*	0.30, 0.54
methyl vinyl ketone	1.6 ± 1.1 (BDL – 2.0) *(4)*	1.9 ± 0.7 (0.64 – 2.7) *(7)*	0.42, 1.24
glyoxal	1.9 ± 0.4 (BDL – 2.4) *(7)*	3.0 ± 0.9 (2.0 – 4.6) *(7)*	1.50, 0.94
methylglyoxal	-	0.11 ± 0.02 (BDL – 0.13) *(2)*	0.27, 0.26

Glyoxal was the compound detected in the largest number of our samples, at mean concentrations of 1.9 and 3.0 nM along the Labrador Sea and Halifax Line transects, respectively. These concentrations are lower than those measured in the Caribbean Sea (Table 5-1), where it is formed by photochemical processes and shows a pronounced diurnal cycle[17]; thus, the lower concentrations we measured are not unexpected given the less intense solar insolation at higher latitudes.

C_5-C_7 aliphatic aldehydes were detected at many more sites along the Halifax Line than in the Labrador Sea; this would be consistent with their *in situ* formation in seawater by photochemical processes, given the stronger insolation and warmer water temperatures on the Scotian Shelf. The region also receives some surface waters from the Gulf of St.-Lawrence outflow[23], which may carry a higher burden of dissolved organic matter. Nonanal and octanal are particularly abundant; the mean concentrations of nonanal in both regions (Table 5-2) is towards the higher end of the range reported for tropical waters[6, 15]. Nonanal might be expected to be formed from the photo-oxidation of algal ω-9 fatty acids, in an analogous process to the production hexanal from the photodegradation of linoleic acid in oxic seawater[24].

A number of C_2-C_4 aldehydes and ketones thought to be important to the chemistry of the troposphere, notably acetone, acetaldehyde and propanal, were not detected in any samples, although this is most likely due to the high detection limits for these substances (5.5 nM, 21 nM and 0.58 nM, respectively).

5.4.3 Spatial variation of surface water carbonyl compounds

Aldehydes and ketones in these surface waters exhibited high spatial heterogeneity, with no identifiable trends along either transect (Figs. 5-2 and 5-3). To our knowledge, the only carbonyl compound for which systematic spatial surveys in surface seawaters have been conducted is acetone[5, 12], which we do not report in this study. In both the equatorial Atlantic[12] and in the Pacific[5], site-to-site variability in acetone concentrations over long distances was high (>10-70 nM in the equatorial Atlantic), suggesting variations in the balances of photochemical production, biological production and consumption, and/or atmosphere ocean exchange. These processes may also all contribute to the concentrations of the carbonyl compounds presented here.

A notable pattern along the Halifax Line concerns the lowest concentrations, or complete non-detection, for several substances at stations HL_05 and HL_06 (Fig. 5-3, at 100 km and 147 km, respectively, from station HL_03, the northernmost end of the transect). For example, formaldehyde (Fig. 5-3a) and methacrolein (Fig. 5-3b) were detected at all sites except these two. These two sites were the only ones on the Halifax Line sampled at night, and this may indicate the prominent role of sunlight in the formation of these compounds, either in seawater itself or in the atmosphere prior to their transfer across the sea surface.

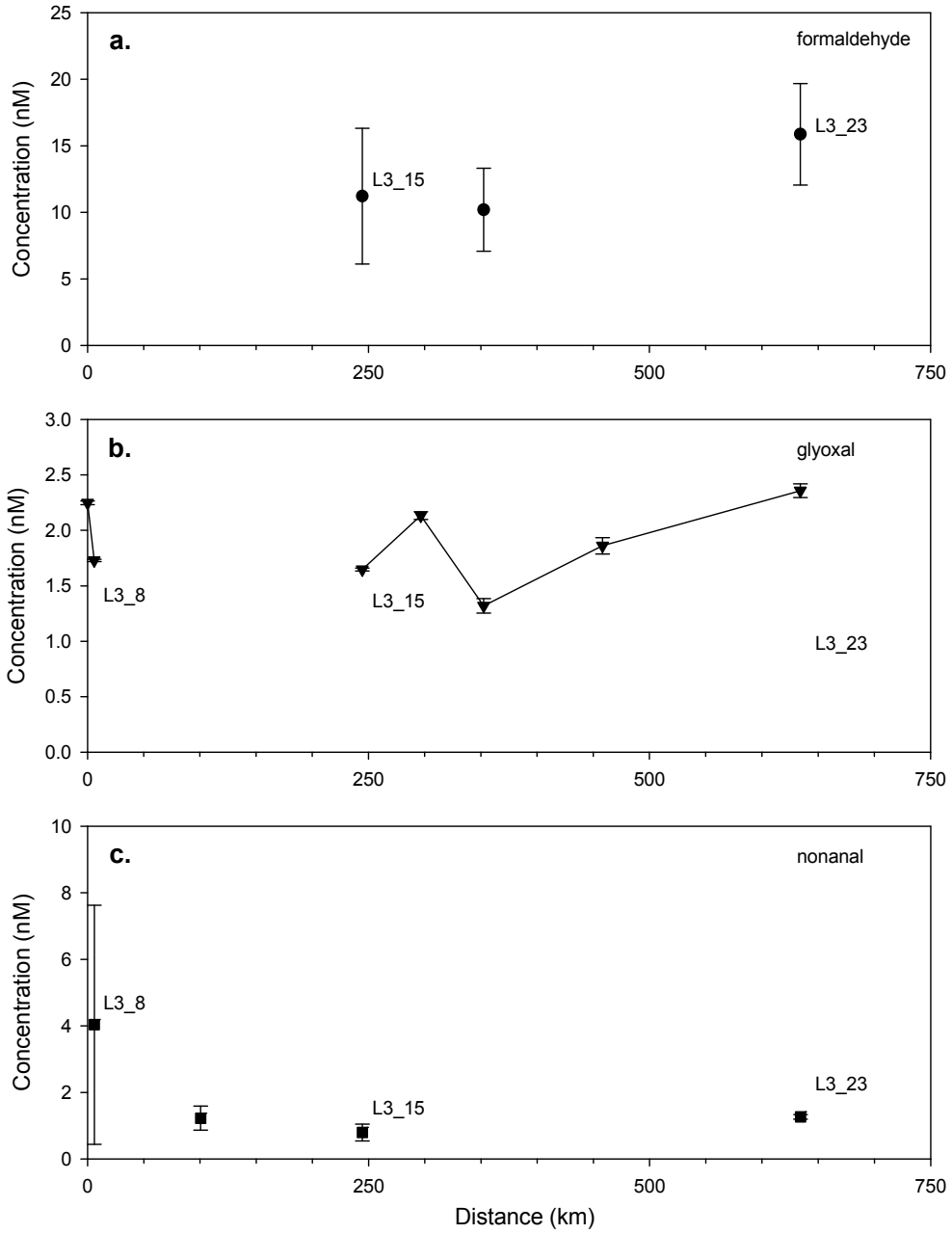

Figure 5-2. Surface water concentrations of selected aldehydes and ketones along AR7W line (Labrador Sea). Transect is displayed from southwest (station L3_7.5, left) to northeast (station L3_23, right). Points are mean ± SD, n = 2. Concentrations not shown are below detection limits.

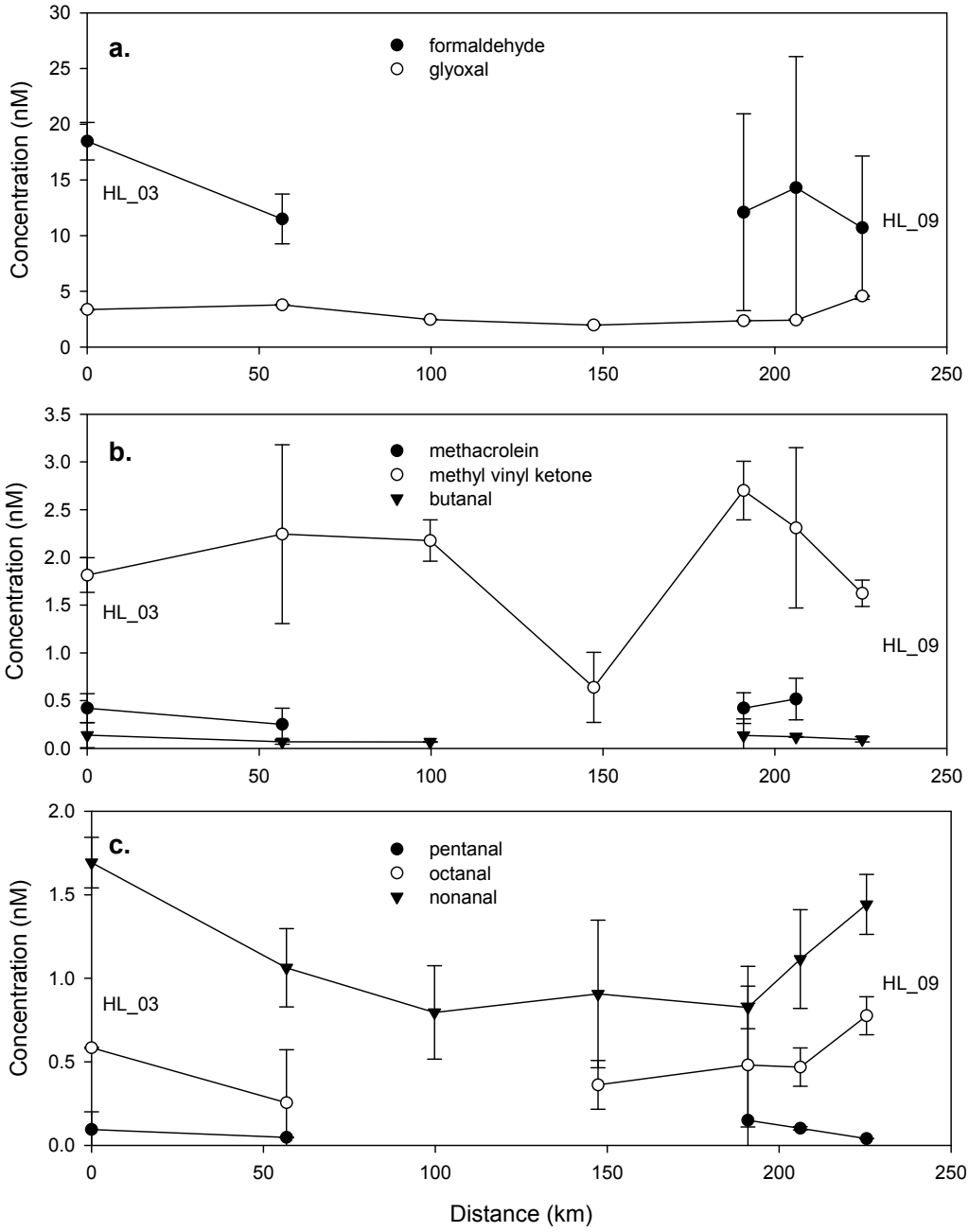

Figure 5-3. Surface water concentrations of selected aldehydes and ketones along the Halifax line (Scotian Shelf and Slope). Transect is displayed from northwest (station HL_03, left) to southeast (station HL_09, right). Points are mean ± SD, n = 2. Concentrations not shown are below detection limits.

5.4.4 Estimated ocean-atmosphere exchange fluxes

We were unable to measure actual concentrations of aldehydes and ketones in the atmosphere at the sites sampled. Nevertheless, we have attempted to estimate fluxes of selected compounds between the ocean and the atmosphere based on atmospheric concentrations reported in the literature (Table 5-3). For C_4-C_9 aldehydes, no concentrations in marine air for temperate or subarctic regions have been reported, and we therefore use the range of concentrations for the Sargasso Sea reported by Zhou and Mopper[6]. We selected these aldehydes because we could readily assume no liquid phase enhancement to gas transfer[15, 25]. For formaldehyde and glyoxal, we can report appreciable air-sea disequilibria. We assumed 200-500 pptv formaldehyde (8.9 -22 pmol L^{-1} at standard temperature and pressure) in the clean atmospheric boundary layer over the northwestern Atlantic (as reported by Frost, Tanner and co-workers [26-27]), and 5-80 pptv glyoxal[6, 28], and use the temperature-dependent apparent partition coefficients (K*, M atm^{-1}) for these substances reported by Zhou and Mopper[6] for formaldehyde and the Henry's Law constant from Ip *et al.*[29] for glyoxal. This leads to predicted seawater concentrations in the ranges 2.7 - 12.9 μM for formaldehyde and 24 -810 μM for glyoxal. These greatly exceed the measured concentrations, suggesting a flux of formaldehyde and glyoxal into the ocean in these regions, and rapid, possibly microbial[30-32] sinks of these substances in seawater. Such an atmosphere to ocean formaldehyde flux would also be consistent with a night-time decrease in seawater formaldehyde concentrations,

consistent with the diurnal cycling (afternoon maximum due to photochemistry) of formaldehyde in the remote marine troposphere[33-34].

We calculated fluxes for C_4-C_9 aldehydes in the manner of Williams *et al.*[12]. The flux, F, of a compound is determined by its air and seawater concentrations (C_a and C_w, respectively), as per equation 5-1,

$$F = k\,(C_w - HC_a) \qquad (5\text{-}1)$$

where k is the gas transfer velocity and H is the Henry's Law constant, C_w / C_a (as defined by Williams *et al.*[12]). As used here, H is equivalent to K* [6].

The transfer velocity is dependent on the mean wind speed, *u*; we used the Wanninkhof relation[35] in the form recommended for use with short-term wind speed measurements (equation 5-2) to describe this dependence.

$$k = 0.31\,u^2\,(660/Sc)^{0.5} \qquad (5\text{-}2)$$

The Schmidt number, *Sc*, is defined as *v/D*, the kinematic viscosity of seawater (*v*) divided by the compound's diffusion coefficient (*D*). Temperature-adjusted kinematic viscosities were taken from Jumars *et al.*[36] Diffusion coefficients

were calculated by the method of Hayduk and Laudy[37], using molar volumes reported by Panidi *et al.*[38] and dynamic viscosities from Jumars *et al.*[36].

Using our seawater carbonyl compound concentrations for both areas studied, we estimate that the sea surface in these regions is a source of certain C_4-C_9 aldehydes to the atmosphere but a sink for others (Table 5-3). For for Scotian Shelf sites, median estimated fluxes for butanal and pentanal were 6.0 and 4.7 μmol/m^2/day into the ocean, respectively. This suggests the area is a sink for these two compounds, but a source of atmospheric octanal and nonanal (fluxes of 0.28 and 1.7 μmol/m^2/day out of the ocean, respectively). For Labrador Sea

Table 5-3. Estimated sea-air fluxes for selected aldehydes in the Labrador Sea and Scotian Shelf. Air mixing ratios used are those from the Sargasso Sea[6]. Positive sea-air fluxes indicate emission from the ocean to the atmosphere. ND = not determined

Compound	**Mixing ratio in air (pptv)**	**Estimated sea-air flux (μmol/m^2/day) range (median)**	
		Scotian Shelf	**Labrador Sea**
butanal	80	-13 - -3.7 (-6.0)	ND
pentanal	100	-4.7 - -1.8 (-4.7)	ND
octanal	100	-0.26 - 2.34 (0.28)	-1.3 - 0.20 (-0.06)
nonanal	150	0.48 - 6.1 (1.7)	0.11 - 14 (5.5)

sites, median estimated fluxes of octanal and nonanal to the atmosphere were -0.06 and 5.5 μmol/m^2/day, respectively. These values seem reasonable as they are in the same range as the ocean-atmosphere acetone flux (median 8.5 μmol/m^2/day) from the equatorial Atlantic reported by Williams *et al.*[12]. Our results are also in accord with the suggestion of Zhou and Mopper[6] that for the lowest solubility aldehydes (C_8 – C_{10}, in their study), fluxes out of the ocean would be expected, but for lower molecular weight aldehydes ($\leq C_7$), the flux direction will be very dependent on local environmental conditions (e.g., wind, temperature). We caution, however, that flux estimates are particularly sensitive to many assumptions. For example, when we performed the calculations using monthly climatological mean winds based on the COADS data sets[39] rather than measured velocities, with the associated recommended change from 0.31 to 0.39 in the first term of the Wanninkhof relation (equation 5-2)[35], the ocean at the Labrador Sea sites appeared to be a modest source of octanal with respect to the atmosphere. Furthermore, calculations based on bulk surface waters, even from a depth of 2 m, do not account for any enrichment of organic compounds which may occur in the sea surface microlayer[15].

5.4.5 Carbonyl concentrations in the Labrador Sea water column

For seawater samples taken at a variety of depths in the central Labrador Sea (station L3_14), most carbonyl compounds measured were below their detection limits at most or all depths; all were below detections limits at the

surface (2 m depth). A depth profile for nonanal, detected at a number of depths, is shown in Figure 5-4 (concentrations below the detection limit of 0.54 nM are shown as zero). Maximum nonanal concentration occurred in the deepest water (1.45 nM, at 3460 m) and close to the surface (1.16 nM, at 50 m), still within the euphotic zone. This supports the notion of nonanal production associated with organic matter from algal primary production, but also that this compound may degrade slowly in deeper waters. Away from solar irradiation and without a means of venting through contact with the atmosphere, the two most likely sinks of nonanal would no longer be acting on it at depth. These deeper waters (the so-called Denmark Straight Overflow Water, DSOW) originate in the Greenland Sea[22] and will typically have last had atmospheric contact approximately 3-5 years earlier, in contrast to the overlying North-Western Atlantic Deep Water (NWADW), with an age of 10-15 years. Zhou and Mopper[6] note that solubility of aliphatic aldehydes decreases with carbon number, decreasing the water-air apparent partition coefficient and presumably promoting transfer to the atmosphere. This would explain the non-detection of nonanal in surface waters at the same site.

Several other aldehydes were detected in a very few deep water samples only (9.30 and 9.44 nM formaldehyde at 1070 m and 1730 m, respectively, 1.00 and 1.44 nM methyl vinyl ketone at 50 m and 3460 m, respectively, 1.20 nM glyoxal). Few aldehyde or ketone concentrations for subsurface waters have been previously reported, and only one for temperate or polar waters (formaldehyde at depths to 50 m in Terra Nova Bay, Antarctica[18]); our measurements represent the

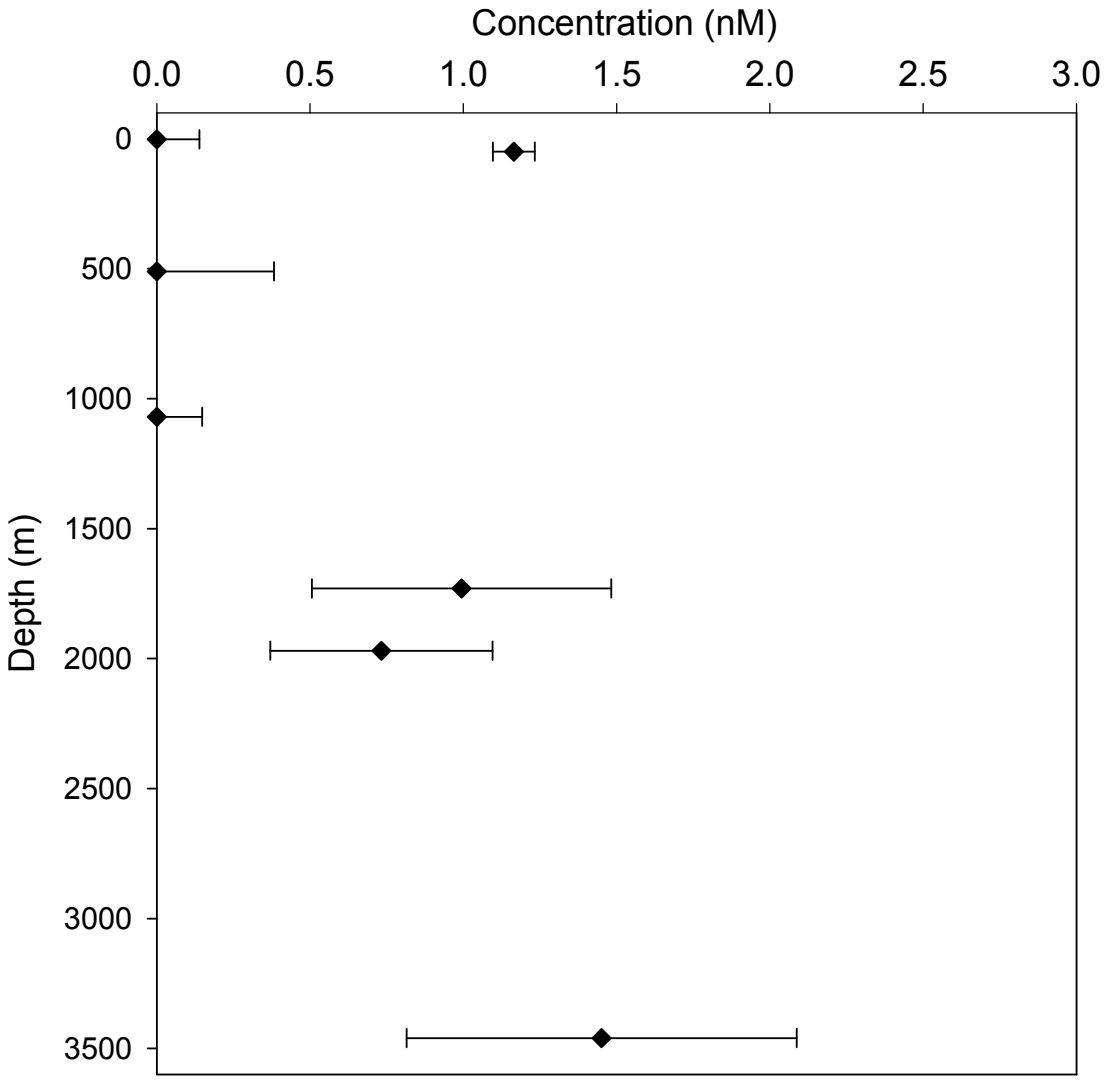

Figure 5-4. Depth profile of nonanal in the central Labrador Sea (Station L3_14: 56.57 °N, 52.67 °W, water depth 3517 m). Points are mean ± SD, n = 2. Concentrations below the detection limit are shown as zero.

first for the North Atlantic, and for temperate and Arctic waters, and the first for aldehydes or ketones larger than C_4. Kieber and Mopper[13] reported glyoxal (2-5 nM) and formaldehyde (9-17 nM) concentrations down to 150 m depth at an oligotrophic site in the Caribbean Sea. Glyoxal concentration was highest at the surface (5 nM) and invariantly 2-3 nM below 10 m, while formaldehyde displayed several subsurface maxima, attributed to "atmospheric. . . photochemical and biological processes" (p. 1481). Obernosterer *et al.* reported 30-70 nM glycolaldehyde (which they attributed to algal production) in the top 0-100 m of the Aegean Sea, with no discernable consistent pattern with depth. At 3 equatorial mid-Atlantic sites[12], 1-10 nM acetone was measured in the top 200 m of the water column, with highest concentrations at the sea surface. Production of formaldehyde, acetaldehyde and glyoxal was highest from irradiation of DOC from deepest waters (2500-4000 m) from the Sargasso Sea[1], suggesting the potential for carbonyl compound production in deeper waters, inhibited solely because this material is well below the euphotic zone. Lastly, Largiuni *et al.*[18] reported 0.15-1.39 μM formaldehyde in Terra Nova Bay, with a maximum at 20-30 m corresponding to the chlorophyll fluorescence maximum, but cautioned against strong biogeochemical conclusions due to their small number of samples. Similarly, our limited data preclude any firm conclusion regarding the water column depth distribution of carbonyl compounds. Further improvements in our detection limits and more complete sampling of the water column at different locations and seasons would allow the water column biogeochemistry of these compounds to be better elucidated. It would be of particular interest to determine

if nonanal is found at depth throughout the Labrador Sea basin, and if its concentration and distribution is correlated with the age of various deep water masses (e.g, DSOW) in different locations.

5.5 Conclusions

We have reported the first seawater concentrations of a range of aldehydes and ketones for the northwestern Atlantic. We estimated fluxes ranging from -13 to 14 μmol/m^2/day from the ocean to the atmosphere for selected C_4-C_9 aldehydes, and noted a substantial disequilibrium between seawater concentrations and reported air mixing ratios (several orders of magnitude depletion in seawater) for formaldehyde and glyoxal. The estimated air-sea fluxes contain appreciable uncertainties, in part due to the lack of measured air concentrations at these sites. Work in our laboratory is currently aimed at optimizing a derivatization-SPME method with detection limits low enough for shipboard application to carbonyl compounds in marine air. This would allow measurements of carbonyl compounds in air and seawater samples matched in time and space, and thus a more certain estimation of sea-air fluxes for these compounds. Lastly, broader spatial and seasonal coverage is required to reveal patterns in carbonyl compound distribution and to better understand the cycling and biogeochemistry of these compounds.

5.6 Experimental methods

5.6.1 Seawater sampling

All glassware for the transport and analysis of samples was cleaned by rinsing with ultrapure water (MilliQ QPAK-1 system and Simplicity Plus 185 system, Millipore, Billerica, MA), and subsequently combusted overnight in a muffle furnace at 450 °C to remove any organic contaminants. Glassware for which this was not possible (e.g., volumetric flasks) was rinsed multiple times with ultrapure water and ethanol and dried overnight at 125 °C.

Seawater sampling was conducted in May 2009. Samples in the Labrador Sea and the Scotian Shelf (Fig. 5-1) were taken during Bedford Institute of Oceanography cruise HUD2009015 on the CCGS *Hudson.* Surface seawater was sampled using standard 10-L Niskin bottles at 17 locations (Fig. 5-1) on both the Labrador Sea AR7W line and the Halifax (HL) line. The nominal sampling depth was 2 m except at station HL_09, where water from 10 m depth was used. Ice conditions on the Labrador Shelf prevented sampling at any sites along the western portion of the AR7W line (ice not shown in Figure 5-1), on the continental shelf itself. At station L3_14 (56.57 °N, 52.67 °W), in the deepest portion of the Labrador Sea (Fig. 5-1), samples were also taken at depths of 50, 510, 1070, 1730, 1970 and 3460 m, in addition to the surface sample. Seawater temperature and salinity were measured using a Seabird CTD sensor attached to the water sampling rosette. Wind speeds used in flux calculations were 5-minute vector averages, measured by a Young Wind Monitor (Marine Model 05103-L) mounted on the ship's forward antenna mast.

Seawater samples were drawn from Niskin bottles into pre-combusted 125-mL amber glass bottles with Teflon-lined caps. The bottle and cap were rinsed three times with sample water, and the bottle was filled to overflowing with minimal bubble entrainment and capped leaving no headspace. Nitrile gloves were used throughout, since latex gloves may contribute carbonyl compounds[40]. Samples were stored unfiltered in the bottles at 4 °C until analysis, and were spiked with 0.5 mM sodium azide (NaN_3) as a preservative [41-42]. Samples were not filtered due to concerns about increasing carbonyl compound concentrations by bursting algal cells[13, 17].

5.6.2 Analysis for carbonyl compounds

Seawater samples were analyzed by the method described in detail in Hudson *et al.*[16]. Briefly: 0.0476 *M* solutions of O-(2,3,4,5,6-pentafluorobenzyl)-hydroxylamine (PFBHA) hydrochloride (Fluka, St. Louis, MO), prepared daily, were purified by passage through a C18-functionalized silica solid phase extraction cartridge (100 mg/1 mL Strata C18, Phenomenex, Torrance, CA). Seawater aliquots (20 mL) were adjusted to pH 3.6 using 0.2 M hydrochloric acid (approximately 31 μL), 100 μL of purified PFBHA solution added, and the samples stirred (550 rpm) for two hours to convert aldehydes and ketones to their pentafluorobenzyl (PFB) oximes. The oximes were then immediately sorbed by solid phase microextraction (SPME) for 30 minutes using a 100 μm polydimethylsiloxane SPME fibre (Supelco, Bellefonte, PA) and then analyzed by

Gas Chromatography-Mass Spectrometry (GC-MS) (HP 6890 GC with 5973 MSD, Agilent, Palo Alto, CA) on a HP 5-MS (5%-Phenyl-methylpolysiloxane) column (30 m × 0.25 mm i.d. × 0.25 μm film thickness)[16].

Quantification was conducted by external calibration with standard carbonyl solutions made in an artificial seawater, as previously described[16, 20]. For matrix-matching purposes, standards were spiked with the same NaN_3 concentration as the seawater samples. Weighted linear regression[43-44] was used to determine standard curves, since homoscedasticity could not be assumed across the concentration range used.

5.7 Acknowledgements

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5.8 References

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Chapter 6.

Conclusions

6.1 Summary

Nineteen non-methane hydrocarbons were measured in surface air over the Nordic seas. The heterogeneity of the data, particularly for short-lived (C_4 and C_5) hydrocarbons, suggests localized marine origins for these compounds. Their formation from dissolved organic carbon (DOC) photochemistry in the underlying surface seawaters was supported by an observed decrease of 6-8 % in DOC concentrations on 24-hour ultraviolet (UV-A) irradiation in selected samples. The isolation of a culturable bacterium (*M. Luteus*) for the largest aerosol fraction suggests that microorganisms may be contributing organic material to the boundary layer through aerosols in this region.

Following the detection of several volatile organic compounds in Nordic surface seawater by solid phase microextraction, an SPME method was developed and optimized to allow the economical determination of low molecular weight aldehydes and ketones in seawater. These compounds were derivatized using O-(2,3,4,5,6-pentafluorobenzyl)-hydroxylamine (PFBHA) and pre-concentrated by SPME for gas chromatography with mass spectrometric (GC/MS) or flame ionization (GC-FID) detection. The method was optimized for 23 C_1 – C_9 carbonyl compounds, giving detection limits in the range 0.01 nM to 23.5 nM. The method functioned optimally at a pH of 3.7, and proved to be sensitive to carbonyl compounds present in the laboratory environment, requiring close

attention to the contribution of blanks. Sparging of artificial seawater (for standards) with UHP argon, and C-18 solid phase extraction of the PFBHA, were found to be the most effective methods for reducing high process blanks.

Acetone concentrations of 5.5 –9.6 nM were measured in surface waters from the Greenland and Norwegian Seas and the Fram Strait. In the St.-Lawrence Estuary, nine C_2 – C_6 carbonyl compounds were detected (including glyoxal, methylglyoxal and 2,4-pentanedione), at individual concentrations up to 7.5 nM and total concentrations up to 15.5 nM. The concentrations of 11 C_1 - C_9 carbonyl compounds in surface seawaters from the Labrador Sea and from the Scotian Shelf were reported, representing the first survey of these compounds in seawaters outside of the tropics. These last measurements allowed estimated fluxes of nonanal, octanal, pentanal, and butanal from the ocean to the atmosphere to be calculated, giving 0.11 – 14, -0.26 – 2.34, -6.9 – -1.8, and -13 – -3.7 μmol/m^2/day, respectively. They also suggest that the North Atlantic is a sink for glyoxal and formaldehyde.

6.2 Original Contributions to Knowledge

The work documented in this thesis makes the following original contributions:

- The first bacterium sampled from the marine atmosphere, using an aerosol impactor, which was cultured and identified. This suggests that marine

aerosols may be a means for the transfer organic matter from the surface oceans to the atmosphere.

- The development and optimization of PFBHA derivatization and solid phase microextraction as a method for the analysis of carbonyl compound in seawater (a new matrix which is of global relevance).
- A thorough characterization of the contribution of various factors to blank signals which affect the use of PFBHA for carbonyl compound analysis, and of methods for ameliorating these blanks.
- The first measurements of carbonyl compounds in seawaters from the coastal and open temperate Atlantic or Arctic, and the first broad survey of a range of aldehydes/ketones from seawaters with a wide spatial distribution, as well as a depth profile at a subarctic site.
- The first flux estimates for C_4-C_9 aldehydes between the surface oceans and the atmosphere.

6.3 Recommendations for future studies

Future studies which might stem from this work fall into three broad categories: further improvements to the methods developed here, their application to fundamental chemical studies, and their application and further evaluation for marine field studies.

6.3.1. Further method developments

In order to increase sample throughput and to reduce variability due to the operator, it may be possible to automate some or all of the operations of the pre-concentration system used for nonmethane hydrocarbons. Similarly, acquisition and optimization of an SPME-capable autosampler would increase throughput and possibly reduce variability of the PFBHA derivatization-SPME method for aldehydes and ketones in seawater.

Rigorous calculation of carbonyl compound fluxes between the oceans and the atmosphere requires atmospheric carbonyl compound measurements matched with those in seawater, and thus, ideally, a facile, readily accessible method applicable to both matrices. Application of a PFBHA derivatization-SPME method to air would require pre-loading the PFBHA onto an SPME fibre [1-2], allowing it to react with carbonyl compounds *in situ*. Work on this method, to achieve the detection limits needed for air in remote environments, is already in progress in our laboratory.

The method as currently formulated does not detect all carbonyl compounds of potential biogeochemical interest; specifically, it does not detect oxoacids [3-4] such as pyruvic and glyoxalic acids. It would be of interest to further expand the scope of the SPME method to include these, either using additional SPME fibres with other coatings (for example, polyacrylate) to allow sorption of more polar compounds, or separate derivatization of the carbonyl group using PFBHA and the carboxyl group using, for example, BF_3/methanol [4-5].

A longer-term goal would be a shipboard comparison of multiple methods for analysing carbonyl compounds. These would a number of chromatographic methods able to detect a wide range of carbonyl compounds (including the PFBHA derivatization followed by SPME and GC as described in this thesis, and 2,4-dinitrophenylhydrazine derivatization followed by HPLC) and proton transfer reaction-mass spectrometry (PTR-MS) [6], characterized by high time resolution and low detection limits for a number of specific compounds (acetone, acetaldehyde). The SPME method could thus be used to validate higher time resolution methods such as PTR-MS or to separate the contributions to PTR-MS signals from isobaric masses (e.g. propanal vs. acetone)[6]. Such method comparisons in the field have been conducted for marine NMHCs [7] and for atmospheric formaldehyde [8]. Similarly, storage and preservation methods for seawater samples could be compared with respect to suitability for carbonyl compounds, and compared to shipboard measurements. A project of this scope would be resource-intensive, requiring significant commitments of instrumentation and labour. It may best be conducted collaboratively by a number of laboratories and could help delineate recommended 'best practices' for future measurements of carbonyl compounds in seawater and marine air.

6.3.2 Application to fundamental chemical studies with environmental implications

It was apparent, during estimation of carbonyl compound fluxes for the north-western Atlantic, that Henry's Law constants (H or K_H) or apparent

partition coefficients (K*) are currently not available for a number of carbonyl compounds in seawater, including methyl vinyl ketone and methacrolein. For other compounds, including glyoxal and methylglyoxal, the temperature or salinity dependence of these constants has not been determined. These parameters are needed to determine the direction of any disequilibrium between the ocean and atmosphere and to calculate the flux of these compounds at the sea surface. These constants could be evaluated, in an analogous manner to that used by Zhou and Mopper [9], using PFBHA derivatization and SPME as developed here.

6.3.3 Applications to marine field studies

Very little is known about seasonal or spatial variation of carbonyl compound concentrations in the surface oceans, and knowledge of diurnal variation comes from a few restricted environments. It is hoped that an accessible method for determining these compounds would allow more routine surveys of their concentrations, in a variety of ocean regions, allowing higher resolution flux calculations which would then better constrain the role of carbonyl compounds in atmospheric photochemical models.

Having demonstrated the culturing of a bacterium sampled with marine aerosols, a survey of culturable microorganisms sampled in marine aerosols should be undertaken, using more environmentally matched culture conditions (e.g., lower culture temperatures) and less mechanically harsh sampling

techniques. It is not yet known to what extent microorganism diversity in marine aerosols reflects the rich microbial diversity [10] in the oceans themselves.

As noted in chapter 1, aldehydes may be produced by atmospheric NMHC oxidation. NMHCs with short atmospheric lifetimes have postulated marine sources (Chapter 2), and carbonyl compounds produced from their oxidation may be transferred back to surface waters. Thus, concomitant measurement at sea of carbonyl compounds and non-methane hydrocarbons, in both surface waters and the atmosphere, would be of interest, since each compound class can serve as a pre-cursor for the other.

6.4 References

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Appendix A

Operation and performance of the pre-concentration system/GC-FID for non-methane hydrocarbons (NMHCs)

A-1 Description and operation of the pre-concentration unit

This description and schematic of the pre-concentration system for NMHCs in ambient air is additional to that in Chapter 2 and its supplementary material. The system was designed and built in-house, originally by Mr. Alexios Gidas, and re-built and further added to by the author. The system is built around a 4-port valve and a 6-port valve (vA and vB, respectively, in Figures A-1 to A-5). All tubing in the flow path is 1/8" chromatographic-grade stainless steel tubing (Supelco, Bellefonte, PA). Air from the sample (SUMMA) canister was routed into a pre-evacuated reference volume (2.016L) (Fig A-1); an Active Strain Gauge (ASG, BOC-Edwards) upstream of the reference volume determined the pressure of the air sample admitted to 0.1 Torr precision, and also allowed flow rate to be monitored. Sample flow rate was controlled by a needle valve on the line between the CO_2 trap and the water trap. Steps in pre-concentrating NMHCs and introducing them into the GC were as follows:

1. Evacuation (Figs A-1 and A-2)
    - The pump (DirecTorr, Sargent-Welch Inc.) is connected to the reference volume via 3-port valve v2 and via valve vB (Fig A-1), evacuating the reference volume (approximately 20 min.)
    - Changing the positions of valves v2 and v3 evacuates the cold trap itself (Fig A-2)

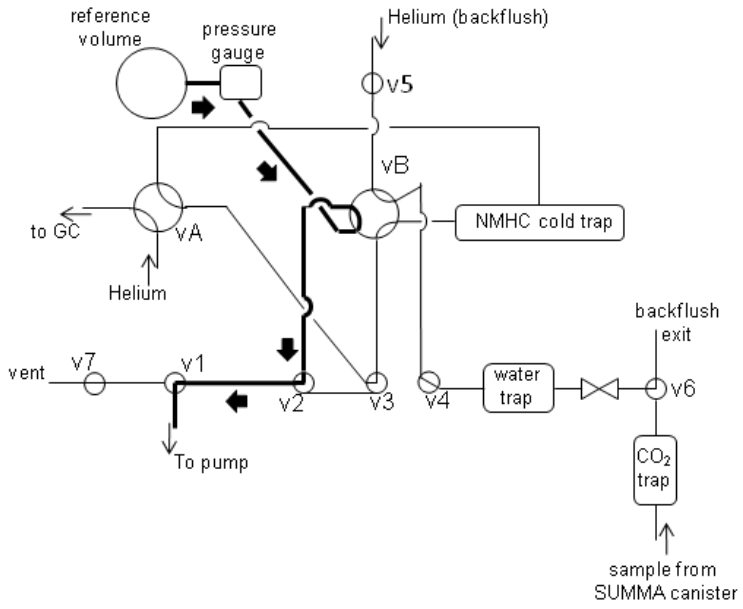

Figure A-1. Pre-concentration system with valves in evacuation (1) position-evacuating the reference volume. Flow path is shown in bold and indicated by heavy arrows.

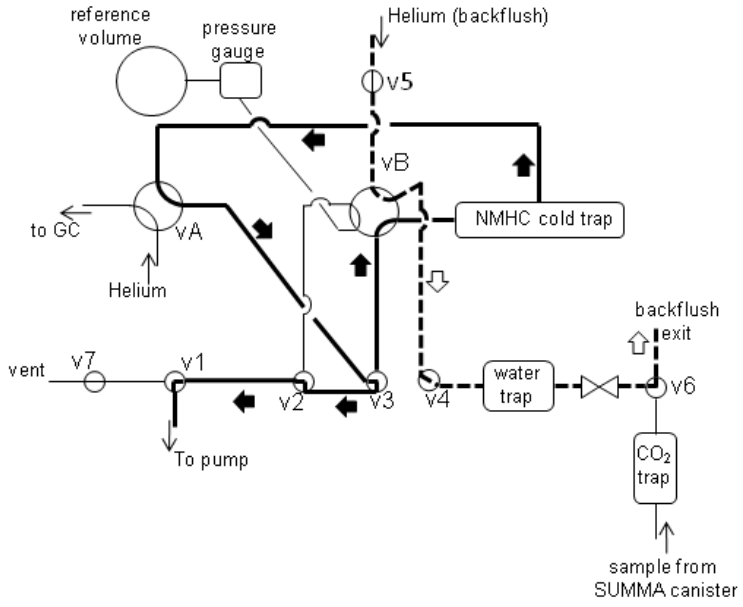

Figure A-2. Pre-concentration system with valves in evacuation (2) position-evacuating the cold trap. Water trap is also back-flushed (dotted flow path).

- During this stage, any water vapour from the previous sample can be back-flushed from the water trap using helium and heating of the trap to 100 °C using a heat gun.

- GC carrier gas (Helium) bypasses the system through valve vA, going directly to the GC.

2. Sample preconcentration (loading) (Figs A-3 and A-4)

   - Changing the positions of valves v3, vB and v6 (Fig A-3) connects the canister to the cold trap and reference volume. Before the valve on the SUMMA canister is opened, the cold trap is immersed in a Dewar flask of liquid nitrogen and the water trap placed in a box over dry ice (achieving -50 - -60 °C). The air sample follows the path indicated to the reference volume, with NMHCs condensing in the cold trap.

   - Once the desired volume (pressure) of air has passed into the reference volume, the position of valve vB only is changed. This isolates the cold-trapped NMHCs in the loop denoted by dotted lines (Fig A-4).

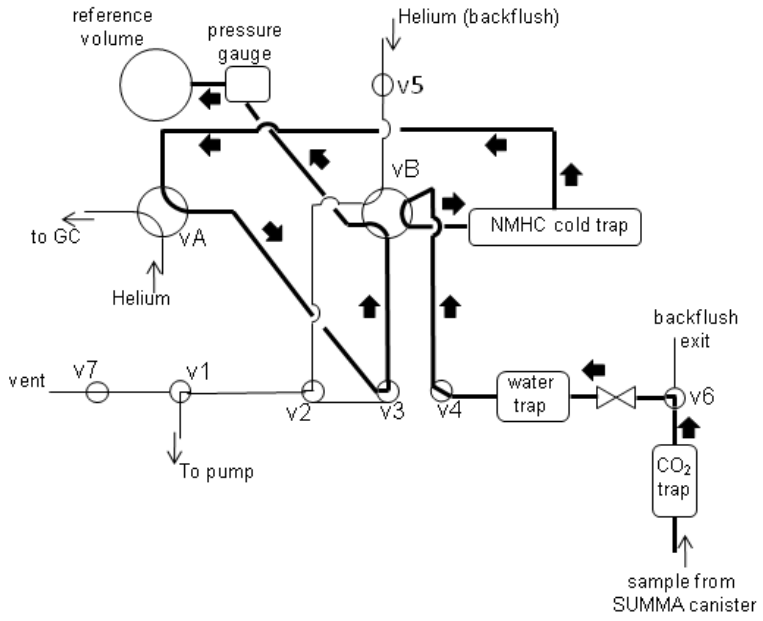

Figure A-3. Pre-concentration system with valves in sample pre-concentration position. Flow path of sample indicated in bold.

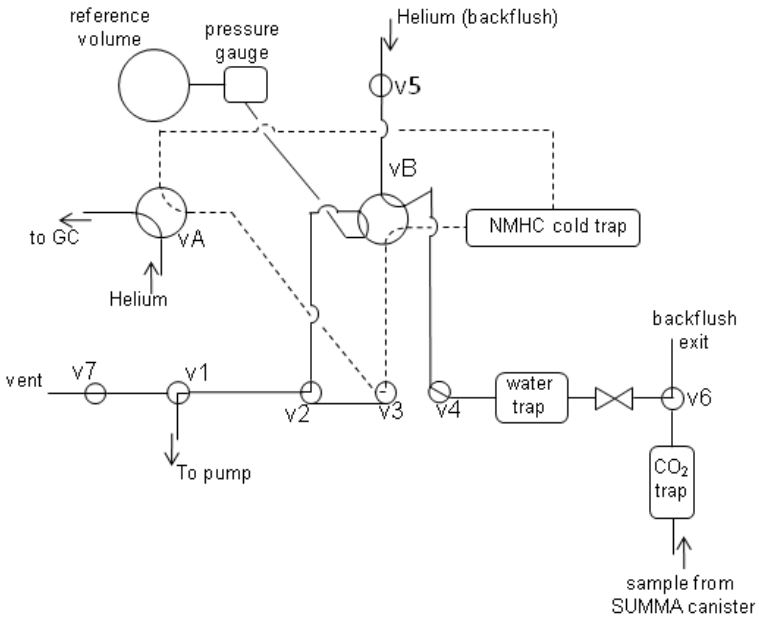

Figure A-4. Pre-concentration system with valves set to confine pre-concentrated sample (on cold trap) to loop indicated by dotted line.

3. Sample injection (Fig A-5)

   - In fast sequence, valve vA is rotated, allowing GC carrier gas to pass through the system, the liquid nitrogen dewar on the cold trap is removed, and the trap is resistively heated to 120 °C using windings of NiChrome wire powered via a variable resistor. The NMHCs are swept from the cold trap to the GC.

   - A cryofocuser in the GC oven (Chapter 2) re-focuses the NHMC sample on the head of the GC column, alleviating any band broadening resulting from these steps.

   - This positioning of the valves allows evacuation of the reference volume for the next sample to begin during chromatography of the current sample, increasing sample throughput.

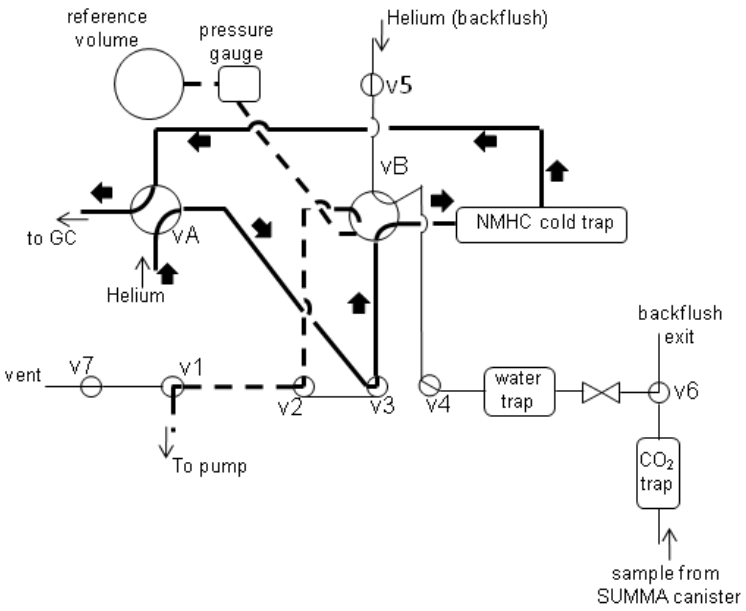

Figure A-5. Pre-concentration system with valves in sample injection position (bold flow path). Evacuation of the reference volume can also begin (dotted flow path).

A-2 Sample chromatogram and retention times of NMHCs

Figure A-2 shows the separation of NMHCs achieved on a 50-m Al_2O_3/ Na_2SO_4 PLOT column (HP AL/S 50 m × 0.32 mm i.d. × 8 μm porous layer thickness; Agilent, Palo Alto, CA). Mixing ratios in the SUMMA canister ranged from 0.41 ppbv (heptane) to 0.98 ppbv (n-butane), corresponding to 25 to 61 pmol introduced to the column.

Table A-1. Retention times of NMHCs separated on a 50-m Al_2O_3/Na_2SO_4 PLOT column

Peak number (Figure A-2)	*Compound*	*Retention time (min)*
1	ethane	2.64
2	ethene (ethylene)	3.53
3	propane	4.60
4	propene	7.32
5	*i*-butane	7.82
6	n-butane	8.10
7	ethyne (acetylene)	8.78
8	*trans*-2-butene	9.93
9	1-butene	10.17
10	*i*-butene	10.54
11	*cis*-2-butene	10.75
12	*i*-pentane	11.10
13	n-pentane	11.42
14	1,3-butadiene	12.25
15	propyne	12.43
16	1-pentene	13.19
17	2-methylpentane	14.04
18	3-methylpentane	14.08
19	n-hexane	14.68
20	butyne	14.79
21	isoprene	14.79
22	heptane	16.75
23	benzene	17.83
24	toluene	22.09

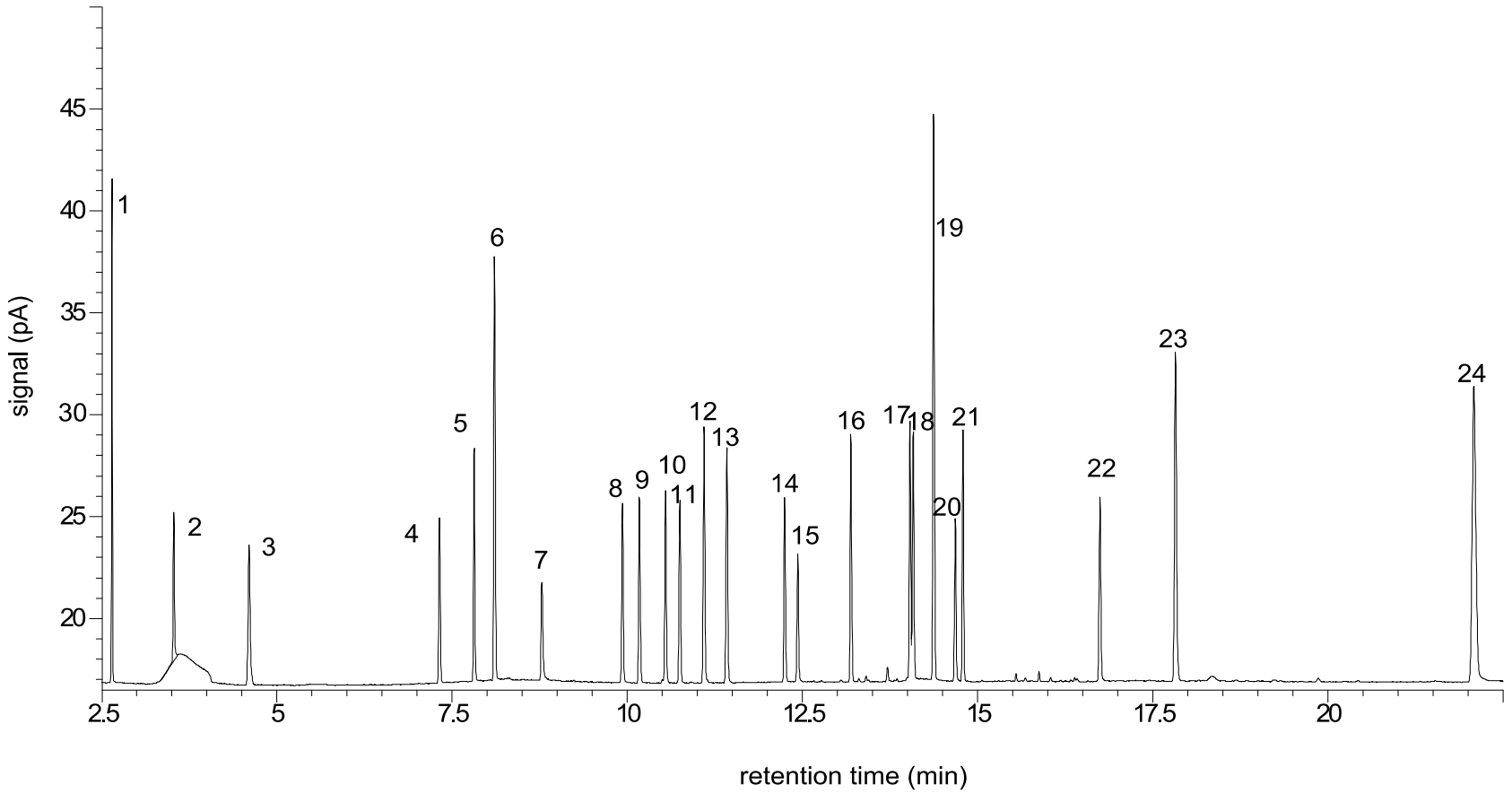

Figure A-6. GC-FID chromatogram of a non-methane hydrocarbon standard preconcentrated from a 6-L SUMMA canister and separated on a 50-m Al_2O_3/Na_2SO_4 PLOT column. For peak identities see Table A-1.

A-3 Calibration data for NMHCs analyzed by cryogenic trapping/GIC-FID

Table A-2 shows calibration data for selected NMHCs pre-concentrated from a humidified SUMMA canister. The mixing ratio detection limits were calculated based on the typical 400 Torr (53.3 kPa) of sample being admitted into the reference volume.

Table A-2. Calibration curves and detection limits for hydrocarbons cryogenically pre-concentrated, separated on a 50-m Al_2O_3/Na_2SO_4 PLOT column and detected by FID.

Compound	*Regression equation (± SE)* *(y: signal, pA·s; x: nL of hydrocarbon)*	R^2	*Detection limit (pptv)*
ethane	$y = (10.4 \pm 0.6)x + (0.09 \pm 0.39)$	0.99	133
ethene	$y = (9.9 \pm 2.2)x + (1.0 \pm 1.3)$	0.87	288
propane	$y = (17.8 \pm 0.7)x + (0.3 \pm 0.4)$	>0.99	55
propene	$y = (16.7 \pm 0.6)x + (-0.3 \pm 0.4)$	>0.99	0.6
i-butane	$y = (23.0 \pm 0.8)x + (-0.2 \pm 0.5)$	>0.99	12
n-butane	$y = (22.5 \pm 0.7)x + (-0.1 \pm 0.8)$	>0.99	25
i-butene	$y = (23.3 \pm 0.7)x + (-0.2 \pm 0.4)$	>0.99	5.0
i-pentane	$y = (27.7 \pm 0.4)x + (0.1 \pm 0.2)$	>0.99	9.6
n-pentane	$y = (24.7 \pm 0.5)x + (0.1 \pm 0.2)$	>0.99	49
1-pentene	$y = (22.4 \pm 0.3)x + (-0.1 \pm 0.2)$	>0.99	6.1
2-methylpentane	$y = (29.9 \pm 0.2)x + (0.1 \pm 0.1)$	>0.99	10.5
3-methylpentane	$y = (28.7 \pm 0.1)x + (0.02 \pm 0.03)$	>0.99	6.5
heptane	$y = (26.3 \pm 0.2)x + (0.1 \pm 0.1)$	>0.99	2.2
benzene	$y = (28.7 \pm 0.3)x + (0.02 \pm 0.2)$	>0.99	48

Appendix B

Further notes on the development of derivatization-SPME methodology for carbonyl compounds in seawater.

B-1 Introduction

During the development of the derivatization/solid phase microextraction method for carbonyl compounds in seawater (Chapter 4) and its subsequent application (Chapters 4 and 5), a number of experiments were conducted which may be of interest to those wishing to build on this work, but which were not included in manuscripts for publication- primarily due to space or focus constraints- or were alluded to only briefly. They are included in this appendix. Retention time and mass spectral data for the pentafluorobenzyl (PFB) oximes analyzed are also included. The exact values of these will vary somewhat from system to system, depending on the instruments (GC, GC-MS) and column used, but are expected to be a useful guide to those using the same or similar apparatus.

B-2 Chromatography and mass spectra of carbonyl PFB oximes

The extracted ion chromatogram in Figure B-1 shows SMPE-extracted carbonyl PFB oximes derived from a carbonyl compound standard in artificial seawater. Concentrations of individual carbonyl compounds range from 8 nM nonanal to 30 nM formaldehyde. The relative ion abundances indicated for each PFB oxime's mass spectrum are those typically observed at tens of nanomolar concentrations. At lower (low nM – sub-nM) concentrations, less abundant

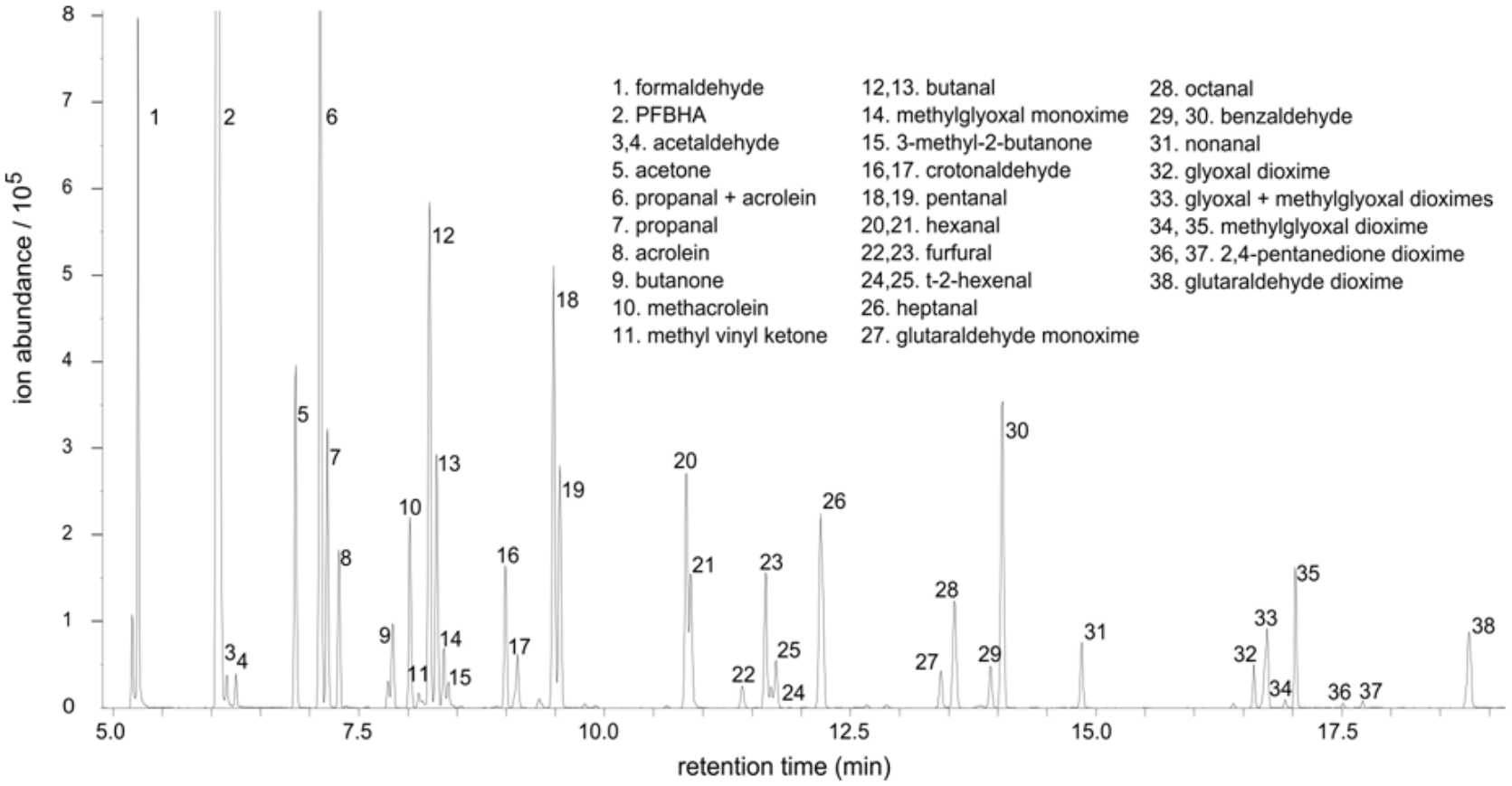

Figure B-1. Extracted ion chromatogram (m/z 181) showing the retention times of carbonyl compound PFB oximes. See also Table B-1.

Table B-1. Retention times and characteristic ions for carbonyl compound PFB oximes as analyzed by GC-MS. * = as PFB dioxime. Retention times in brackets are coelutions or minor isomers, not used for calibration.

Compound	*Retention time(s) (min)*	*Characteristic mass spectral ions (relative abundance) (M^+ = molecular ion)*
formaldehyde	5.26	181 (100), 195 (12)
acetaldehyde	6.16, 6.25	181 (100), 195 (5), 209 (6), 239 (2)(M^+)
acetone	6.86	181 (100), 195 (4), 206 (5), 223 (5), 236 (5), 253 (5)(M^+)
propanal	(7.11), 7.18	181 (100), 195 (4), 223 (2), 236 (14), 253 (0.6)(M^+)
acrolein	(7.11), 7.30	181 (100), 195 (4), 221 (3), 234 (1), 250 (8), 251 (7)
butanone	7.80,7.84	181 (100), 195 (8), 234 (0.9), 250 (22), 267 (3)(M^+)
methacrolein	8.02	181 (100), 195 (4), 235 (2), 248 (4), 265 (7)(M^+)
methyl vinyl ketone	8.11, 8.15	181 (100), 195 (6), 235 (2), 264 (12), 265 (10)(M^+)
butanal	8.22, 8.29	181 (100), 195 (6), 222 (0.8), 239 (16), 250 (2), 267(0.4)(M^+)
3-methyl-2-butanone	8.41	181 (100), 195 (8), 236 (2), 253(14), 264(11), 281 (5)(M^+)
crotonaldehyde	8.99, 9.11	181 (100), 195 (4), 250 (25), 265 (4)(M^+)
pentanal	9.48, 9.54	181 (100), 195 (5), 222 (3), 239 (16), 252 (1), 264 (1), 281(0.2)(M^+)
hexanal	10.83, 10.88	181 (100), 195 (3), 222 (3), 239 (15), 252 (2), 278 (0.7), 295 (0.2)(M^+)
furfural	11.41, 11.64	181 (100), 195 (4), 201 (2), 248 (10), 261 (4), 291 (30)(M^+)
t-2-hexenal	11.68, 11.74	181 (100), 195 (), 293 ()(M^+)

Table B-1. (Continued)

Compound	*Retention time(s) (min)*	*Characteristic mass spectral ions (relative abundance) (M^+ = molecular ion)*
heptanal	12.20	181 (100), 195 (3), 222 (3), 239 (22), 252 (1)
octanal	13.56	181 (100), 195 (3), 222 (4), 239 (25), 252 (2)
benzaldehyde	13.93, 14.04	181 (100), 195 (3), 258 (2), 271 (10), 284 (2), 301 (20)(M^+)
nonanal	14.85	181 (100), 195 (4), 207 (6), 221 (4), 252(2), 239 (26)
glyoxal*	16.61, (16.74)	181 (100), 195 (6), 418 (0.6), 448 (2)(M^+)
methylglyoxal*	(16.74, 16.92), 17.03	181 (100), 195 (4), 265 (5), 432 (0.7), 462 (1)(M^+)
2,4-pentanedione*	17.51, 17.71	181 (100), 195 (5), 236 (3), 293 (32), 470 (0.6)
glutaraldehyde*	18.79	181 (100), 195 (5), 278 (5), 293 (4)

abundant ions often fall below the mass spectrometer's ion count threshold (150 counts). The consistent base peak at m/z 181 in all the oxime mass spectra nonetheless allows quantification using this ion.

B-3 Protocol for PFBHA purification

Effective use of C-18 solid phase extraction (SPE) cartridges to purify PFBHA required a consistent loading and elution procedure to ensure that the fraction of PFBHA recovered was consistent. The following protocol was adopted.

1. 2-5 mL of PFBHA solution was prepared, using 12.2 mg PFBHA hydrochloride per mL Milli-Q water.
2. A 100 mg/1 mL C-18 silica SPE cartridge (C18-E, Phenomenex, Torrance, CA) was conditioned by applying and forcing through 2 successive tube volumes (2 × approximately 1 mL) of HPLC-grade acetonitrile, stopping the flow when the top of the solvent reached the top of the sorbent bed. Liquids were forced though the sorbent bed with a 3 mL polypropylene syringe pressed to the top of the cartridge.
3. The cartridge was flushed with 4 successive tube volumes of Milli-Q water, again stopping the flow of water when the top of the water column reaches the top of the sorbent bed.
4. Approximately 0.2 mL PFBHA solution was applied to the cartridge. The solution was forced solution into/through the sorbent at 1 drop every 3-4 seconds; the first six drops were discarded.
5. Further PFBHA solution (top up to 1 tube volume) was added and forced through the sorbent, again at 1 drop per 3-4 seconds; PFBHA was collected in pre-combusted 2-mL amber glass and any remaining headspace filled with UHP argon. Two tube volumes of PFBHA solution could be collected per cartridge. Any further PFBHA needed was purified through (an) additional cartridge(s).

Using this protocol, batch to batch consistency in PFBHA recovery, judged by the PFBHA peak area in subsequent SPME chromatograms, did not differ significantly among 4 purifications ($P<0.05$).

B-4 Effect of extended SPME extraction

As optimized in chapters 3 and 4, the PFBHA derivatization/SPME method uses a constant 30 minute sorption time. Lower oxime signals when 15-minute extractions were used (chapter 4) suggested that this was indeed in the pre-equilibrium regime [1]; we undertook longer sorption times to confirm this. Standard solutions of carbonyl compounds in artificial seawater were subjected to SPME for various times, starting 2 hours after PFBHA addition. Higher signals were still being reached after 60, 90 or 120 minutes for some oximes (Fig. B-2). This includes those for which maximum yield from the derivatization itself is achieved within 30 minutes, such as formaldehyde (Fig. 4-2). For some such aldehydes, such as formaldehyde and pentanal, the decrease in signal for a 120 min sorption over a 90 minute sorption may reflect degradation of the oxime in solution. For ketones such as acetone and butanone, for which derivatization has not reached its maximum yield even after 4 hours (Fig. 4-2), the increase in signal on longer adsorption may also be due to continuing oximation in solution.

Other authors have acidified the solution after a pre-set derivatization time, for example by adding 2 drops of 2M sulphuric acid [2], presumably preventing further oxime formation by lowering the pH. However, manufacturers literature cautions against using most SPME sorbents below pH 2, and it was demonstrated (Chapter 4) that even at pH 2.2, oxime yield is still appreciable. It is therefore not possible at this stage to separate the effects of SPME sorption and of PFB oxime formation in solution as to the relative contribution of each to the amount of the oximes detected on a SPME fibre. To separate these effects would

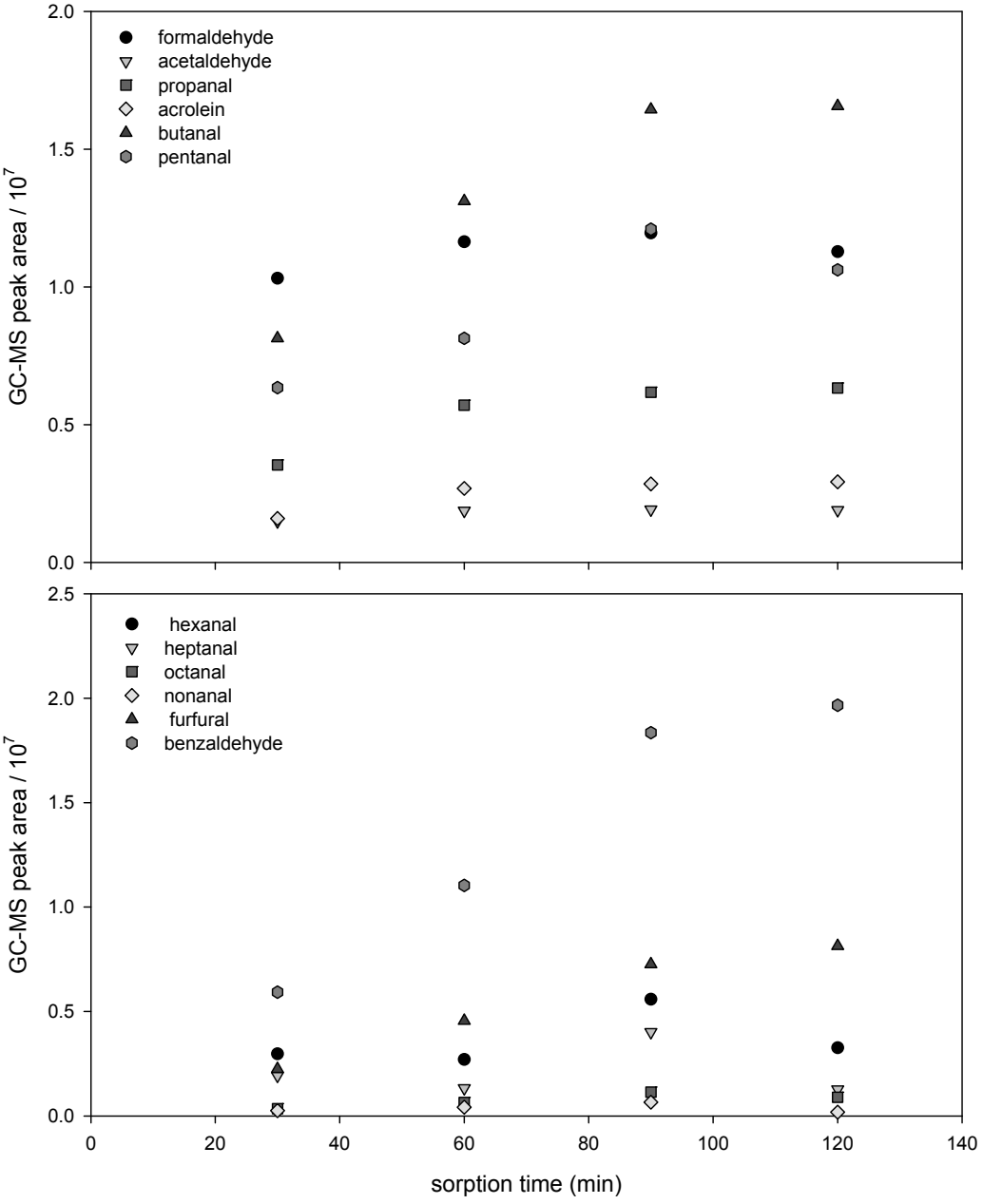

Figure B-2. Effect of extended SPME extraction time for carbonyl PFB oximes in artificial seawater using a 100 μm PDMS SPME fibre.

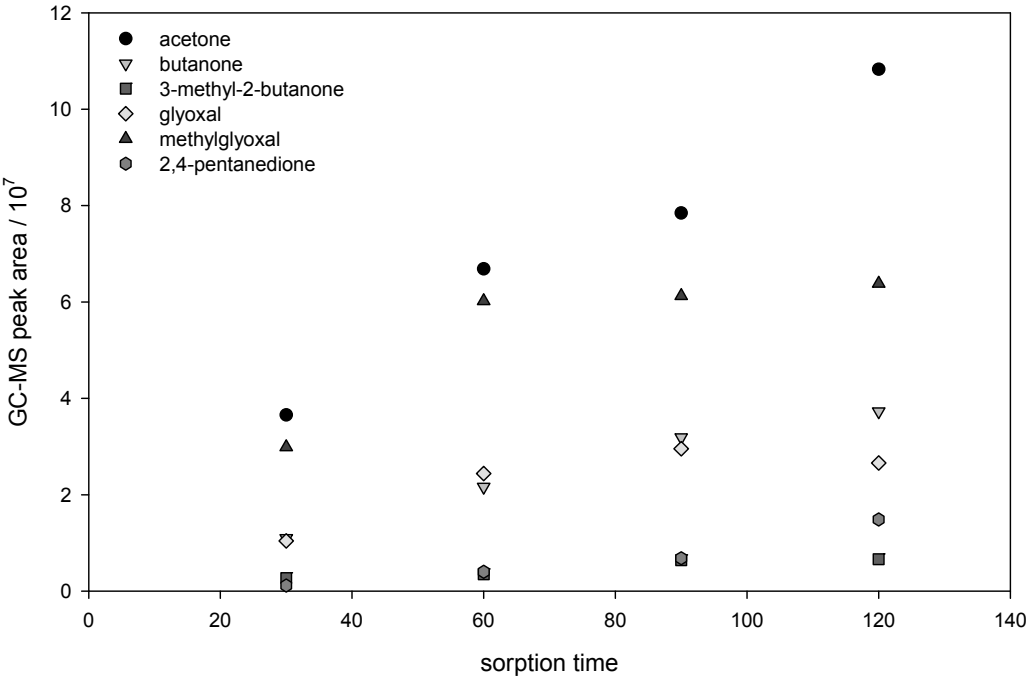

Figure B-2. (continued)

necessitate derivatization in the original aqueous solution, suppression of further oximation (e.g., by acidifying), separation of the oximes from remaining PFBHA, re-dissolution of the oximes in aqueous solution, and SPME. It is anticipated that, at environmentally realistic concentrations, the risk of contamination with other carbonyl compounds (e.g., during solvent extraction) would be substantial, and for analysis of seawater samples, the contamination risk, and environmental implications of solvent use, would negate some of the principal advantages of the method.

B-5 Timing of acidification

As indicated in chapter 4, we tested whether acidifying prior to derivatization or only prior to extraction led to significantly different quantities of oxime extracted. Acidification prior to derivatization led to significantly greater ($P < 0.05$) oxime signals only for furfural, benzaldehyde, acetone and butanone (Fig. B-2), while acidification only prior to extraction was not optimal for any of the compounds investigated.

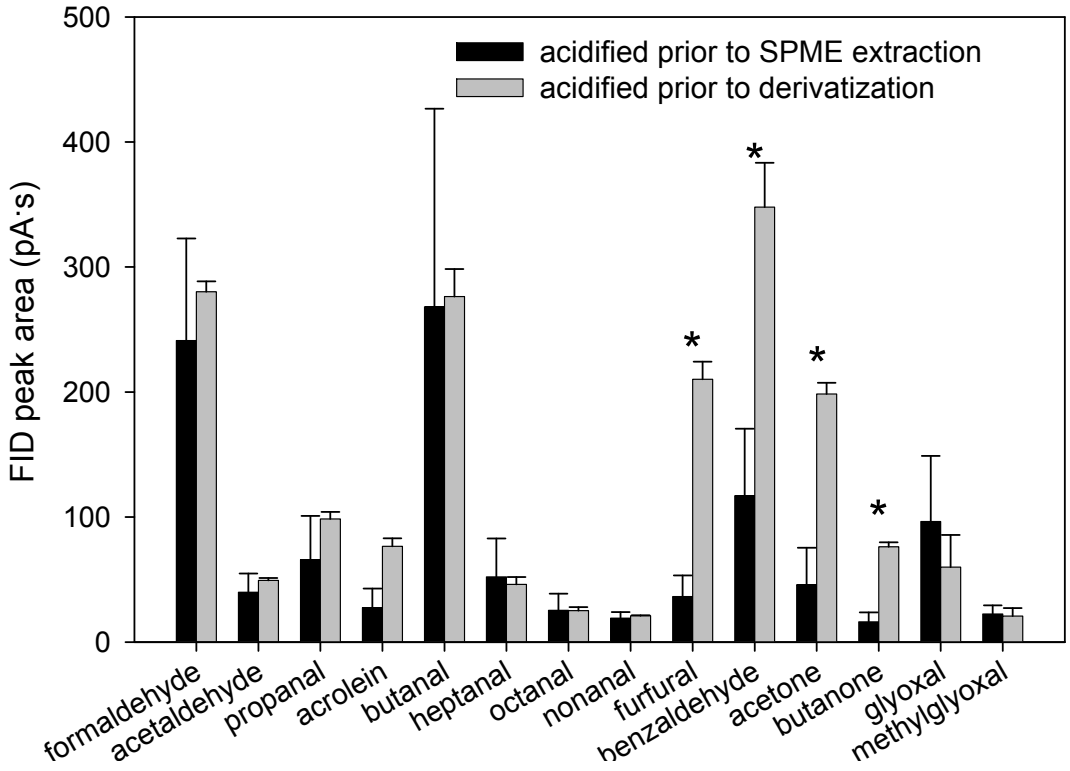

Figure B-3. Effect on PFB oxime yield/extraction efficiency of acidification prior to derivatization vs. acidification immediately prior to extraction. Points are mean ± SD; n= 3. * = differ significantly at $P < 0.05$

B-6 References

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2. Bao, M. L.; Pantani, F.; Griffini, O.; Burrini, D.; Santianni, D.; Barbieri, K., Determination of carbonyl compounds in water by derivatization - solid-phase microextraction and gas chromatographic analysis. *J. Chromatogr. A* **1998,** *809*, (1-2), 75-87.

Appendix C

Operation of the MOUDI.

This appendix briefly describes the operating principles of the Micro-orifice Uniform Deposit Impactor (MOUDI), used to sample aerosols as part of the work reported in Chapter 2.

Aerosol impactors function by directing the flow of air being sampled around an obstacle (the impaction plate) [1]. When the direction of the air flow changes sharply, the inertia of particles within it will cause them to continue travelling in a straight line (Fig. C-1). They will therefore collide with the impaction plate, may stick and thus be collected. One way to describe he impaction (collection) efficiency, η, is by equation C-1 [1]

$$\eta = \frac{D^2 V \rho}{18 \mu D_b} \qquad (C\text{-}1)$$

where D is the particle diameter, V is the flow velocity of the air, ρ is the particle density, μ is the gas viscosity, and D_b is a function of the impactor's form and dimensions (such as the diameter of the inlet nozzle) which determine the curvature of the air flow.

Cascade impactors collect and fractionate aerosol particles by size (aerodynamic diameter) by applying this process in series (Fig. C-1). Air is

directed through progressively smaller nozzles or holes above each impaction plate, causing the air to move progressively faster at each successive stage [1]. This leads to the collection of smaller particles at each stage (increasing η with increasing V, equation C-1).

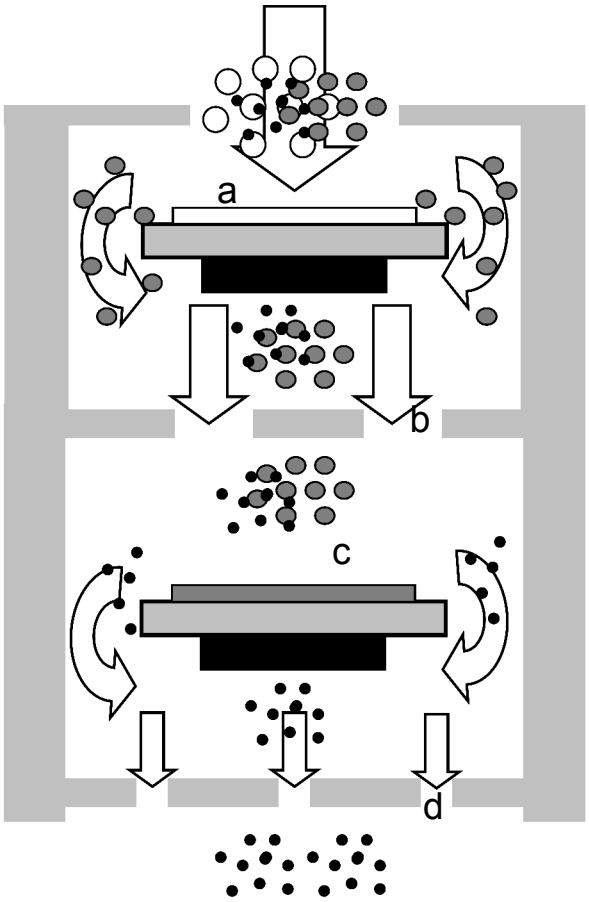

Figure C-1. Schematic of a cascade impactor, showing top two stages. Air flows are shown by arrows. Largest particles (white) are sampled by impaction on the top plate (a); smaller particles (grey) continue in the airflow, through smaller nozzles (b), and are sampled on the next plate (c); smallest particles (black) continue to next set of (smaller still) nozzles (d).

The MOUDI (MSP Corporation, St. Paul, MN) [2] is a form of cascade impactor. It allows the impaction plates (stages) to be rotated during collection to produce a more uniform deposition of sampled aerosols on the plates. Substrates made of aluminum foil or quartz fibres are attached to the top of the impaction plates themselves, and can then be easily removed for analysis of the aerosols. The 8-stage version used in our laboratory collects aerosols in the following nominal size classes: > 18 μm, 9.9 – 18 μm, 6.2 – 9.9 μm, 3.1 – 6.2 μm, 1.8 – 3.1 μm, 1.0 – 1.8 μm, 0.55 – 1.0 μm, 0.31 – 0.55 μm, and 0.19 – 0.31 μm.

References

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