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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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 h 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 16 S 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.

1. 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^{13} molecule cm^{-3}). They may impact the oxidative capacity of the lower troposphere (Donahue and Prinn, 1990, Donahue and Prinn, 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, Ariya et al., 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, Plass-Dülmer et al., 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, Ratte et al., 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, Ratte et al., 1998 determined that ethene, propene and 1-butene are photochemically

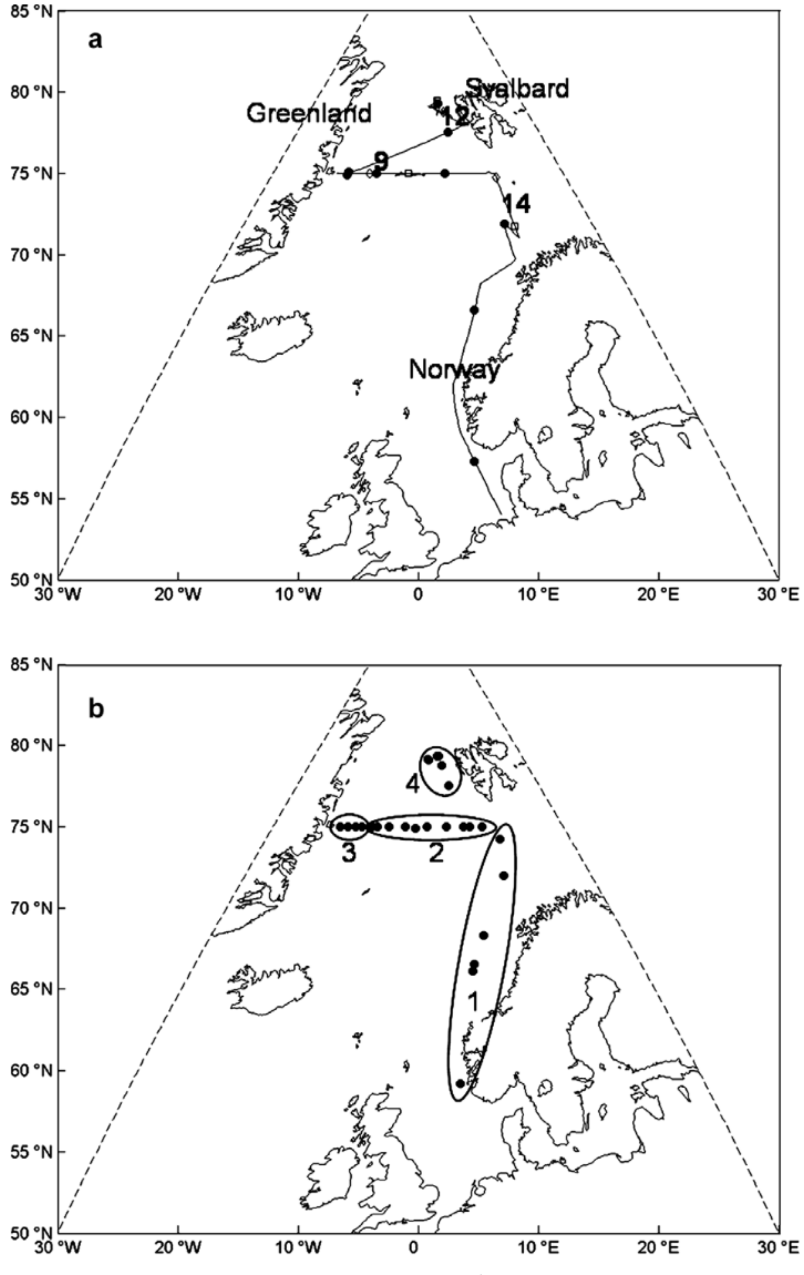

Fig. 1. Map of the study area, indicating (a) track of FS *Polarstern* cruise ARK-XX/1, and the location of air sampling sites (●) and aerosol sampling regions (start: □, end: ◊, number indicates length of sampling in hours) described in this paper, (b) locations for seawater sampling. (1) North Sea/Norwegian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

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 sunlight 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, Blanchard, 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, Matsumoto et al., 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. 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. Methods

2.1. 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), which aimed to cover a range of environments, from populated/coastal (North Sea) to remote marine and from temperate to high Arctic.

2.2. 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 h) at 100–120 °C, flushing them with ultra-high purity (UHP) helium three times, and subsequently re-evacuating them. Twenty-six whole air samples were taken at sites over a variety of latitudes, of which nine (Fig. 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 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}–80 °C, 22 °C min^{-1}–130 °C, and 15 °C min^{-1}–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. Seawater

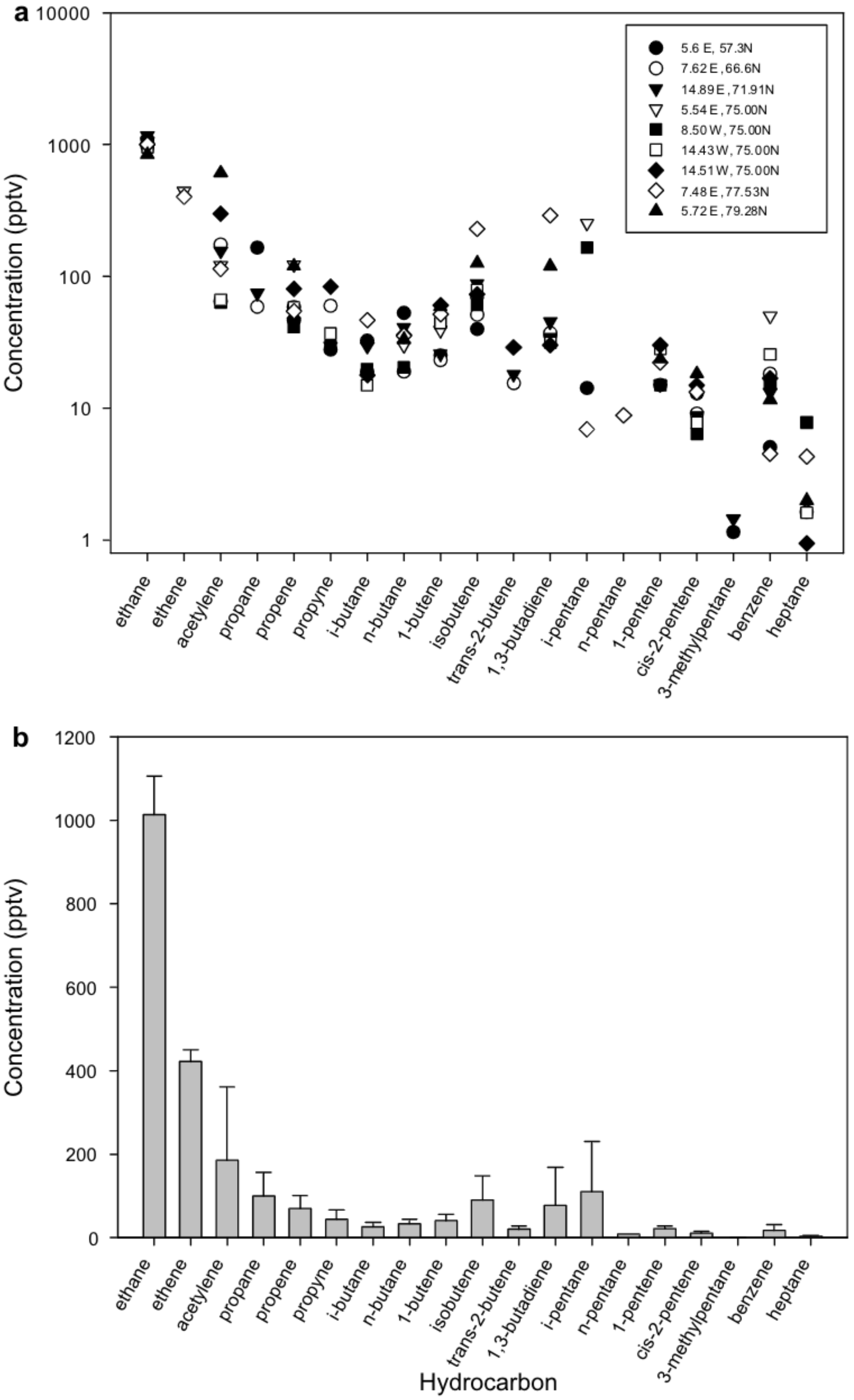

Fig. 2. (a) Individual non-methane hydrocarbon concentrations at sites representing a range of latitudes. (b) Non-methane hydrocarbon concentrations averaged over the sites above (mean ± SD, *n* = 9).

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 10m 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 h in a box with a reflective interior and containing eight 15 W black light bulbs ($350 \leqslant \lambda \leqslant 400$ 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. Ten millilitre aliquots of seawater in pre-combusted glass vials were extracted by immersing SPME fibres, with stirring, for 30 min 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 (30 m × 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}–80 °C, then 15 °C min^{-1}–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.

2.4. 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, MN), 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 h), but were typically ca. 12 h (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 h 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.

2.5. 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 h sample; July 1, 2004, 9.4 h sample; July 14, 2004, 12 h 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).

2.6. 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.

3. Results and discussion

3.1. Meteorology

108 h 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.

3.2. Air samples – non-methane hydrocarbons

Concentrations of NMHCs in air from nine sites, spanning the full range of latitudes, are shown in (Fig. 2). We were cautious in our use of the canister samples, and excluded from the reported data set any which, despite precautions 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, 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 $[OH] = 8 \times 10^5$ 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), may reflect that the ship was operating in that area over an extended period (Fig. 2a), 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, Ariya et al., 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.

3.3. Surface waters – dissolved organic carbon

To examine concentrations of dissolved organic carbon, surface water samples were grouped into four different cruise sections (Table 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 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.

Table 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

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)

The quantities marked* differ significantly from each other at $P = 0.05$ (Student's *t*-test).

[DOC] appeared to decrease 5–8% after 24 h of UV irradiation, although for only one site (75.00° N, 5.94° W) was the decrease (6%) statistically significant (Table 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.

3.4. Aerosols

For characterization by SEM-EDX, aerosol samples were chosen representing the early, mid and latter parts of the cruise (June 23, 2004, 14 h sample; July 1, 2004, 9.4 h sample; July 14, 2004, 12 h sample) (Fig. 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. Fig. 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, Posfai et al., 1995). Particles in our samples include sea salt

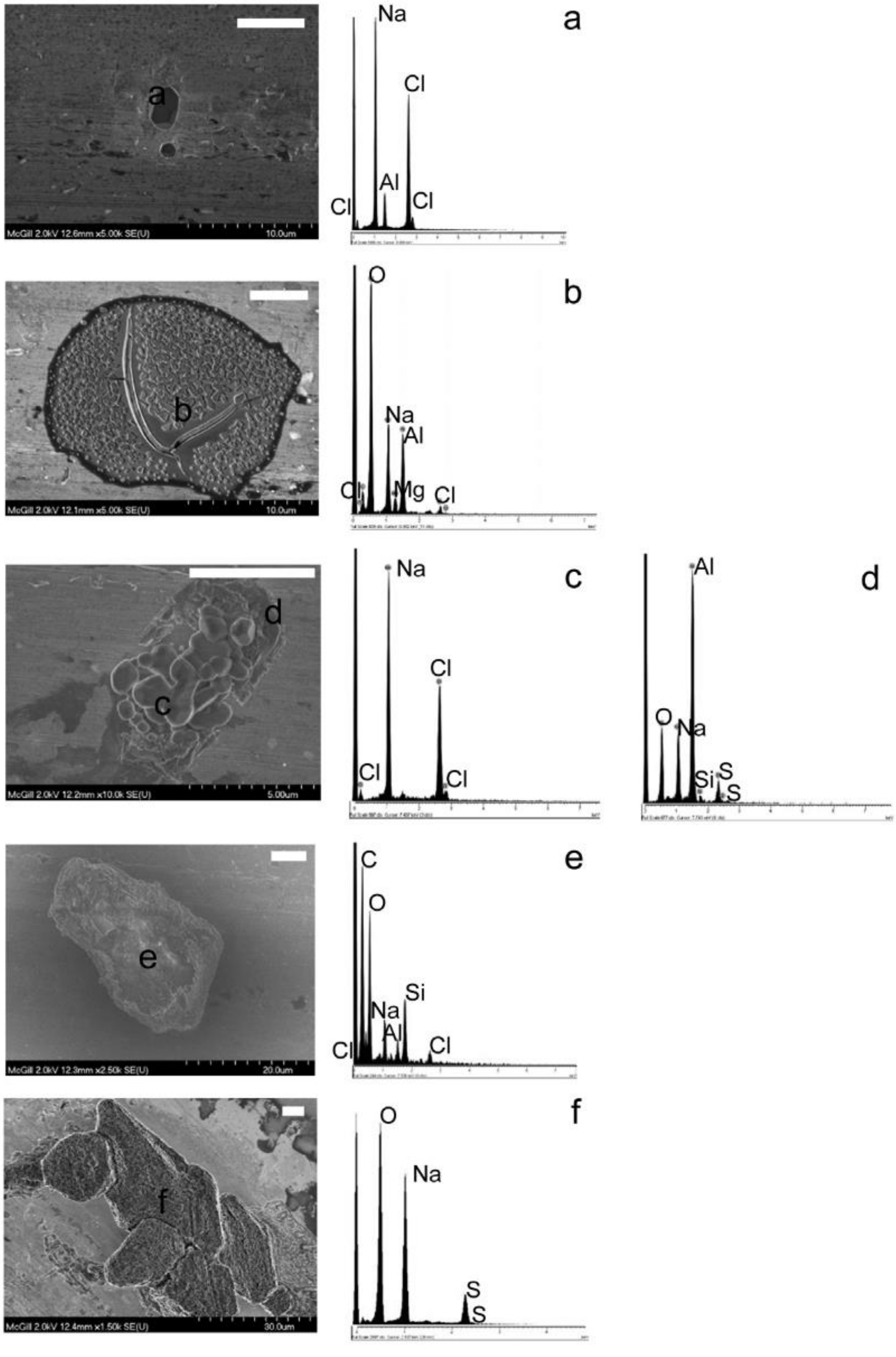

Fig. 3. Overview of typical aerosol forms (with energy dispersive X-ray spectra) observed in Nordic sea samples. (a–e) Particles from the largest (9.9–18 μm) fraction; (f–h) particles from 1.8–3.1 μm fraction; (i, j) particles from the 0.18–0.31 μm fraction. The horizontal white bar in each image represents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

(Fig. 3a), sulfate (Fig. 3f) and mixtures of these phases (Fig. 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 Fig. 3b were commonplace, and are interpreted as resulting from the evaporation of droplets or highly deliquescent aerosols that impacted the substrates. Calcium sulfate (Fig. 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. 3i). Besides carbonates, little carbonaceous matter was detected in any size fraction, although one particle observed (Fig. 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. 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, Wittmaack et al., 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. 3a).

3.5. 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, Posfai et al., 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 sampled, 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.

4. 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 h 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.

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Appendix A.

Supplementary dataSupplementary 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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