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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)

Edward D. Hudson [a], Parisa A. Ariya [a,b,*]

[a] *Department of Chemistry, McGill University, 801 Sherbrooke Street W., Montreal, QC H3A 2K6, Canada*
[b] *Department of Atmospheric and Oceanic Sciences, McGill University, 805 Sherbrooke Street W., Montreal, QC H3A 2K6, Canada*

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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.


*Keywords:* Volatile organic compounds; Marine aerosols; Bioaerosols; Dissolved organic matter; Marine boundary layer

## 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 $= 2.45 \times 10^{13}$ 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

* Corresponding author. Address: Department of Chemistry, McGill University, 805 Sherbrooke Street W., Montreal, QC H3A 2K6, Canada. Tel.: +1 514 398 3797; fax: +1 514 398 3797.
*E-mail addresses:* edward.hudson@mail.mcgill.ca (E.D. Hudson), parisa.ariya@mcgill.ca (P.A. Ariya).

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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, 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,

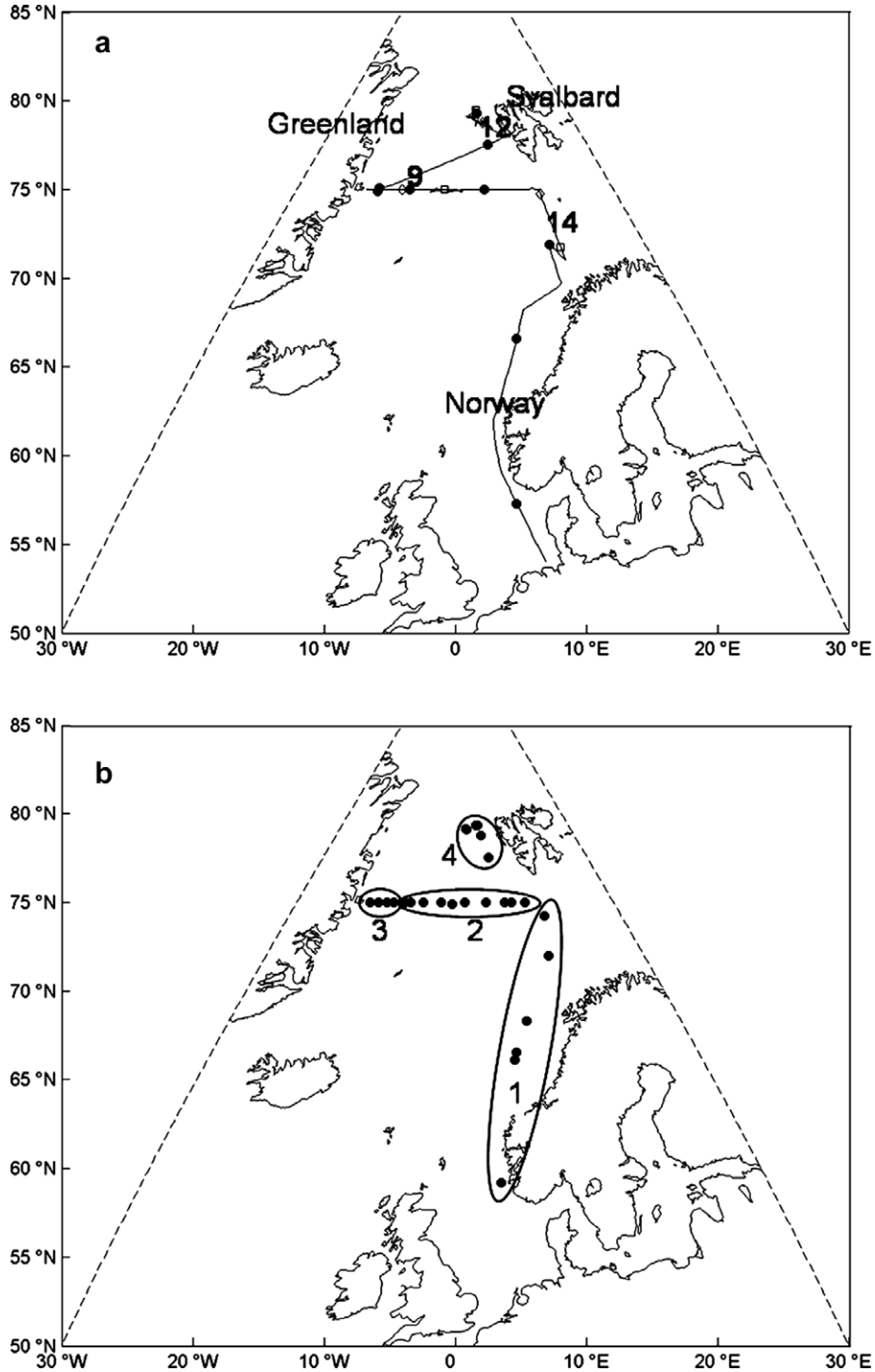


Fig. 1. Map of the study area, indicating (a) track of FS *Polarstern* cruise ARK-XX/1, and the location of air sampling sites (●) and aerosol sampling regions (start: □, end: ◊, number indicates length of sampling in hours) described in this paper, (b) locations for seawater sampling. (1) North Sea/Norwegian 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.