

## Summer concentrations of NMHCs in ambient air of the Arctic and Antarctic

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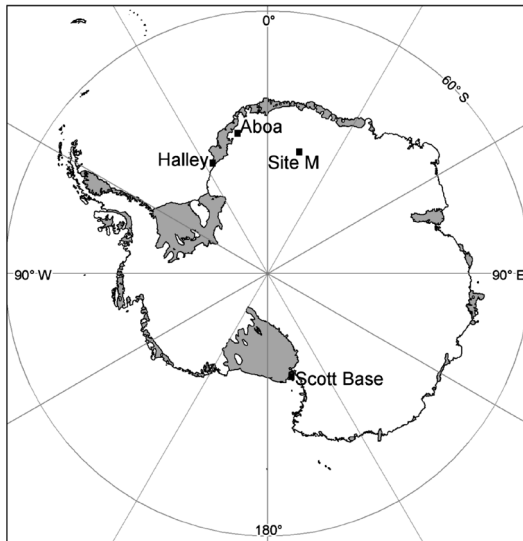
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Summer concentrations of C<sub>2</sub>–C<sub>6</sub> non-methane hydrocarbons (NMHCs) were measured in Antarctica and in the Arctic in 2008. The results show that NMHC concentrations are on average five times higher in the Arctic than in Antarctica. In Antarctica, there were few concentration peaks, but during most of the remaining time concentrations were below or close to the detection limits. Over the Arctic pack ice area north of 80°, concentrations of most of the measured NMHCs were always above the detection limits. No differences based on air-mass origin were detected in Antarctica, but samples collected over the central Arctic Ocean showed higher concentrations in air masses being advected from the Kara Sea and the western-central Arctic Ocean. The relatively higher NMHC-to-ethyne molar ratios calculated for samples collected over the central Arctic Ocean suggest additional alkane sources in the region.

### Introduction

Non-methane hydrocarbons (NMHCs) play a key role in the photochemistry of the remote atmosphere. They are oxidised by hydroxyl (OH) radicals and subsequently lead to a net formation of peroxy radicals, which have a crucial role in the budget of tropospheric ozone (Finlayson-Pitts and Pitts 2000). The highest concentrations of NMHCs are usually measured in urban areas, being most pronounced in so-called megacities, i.e. those with a population exceeding 10 million. In remote air, the NMHCs experience more oxidation and dispersion than air masses in the source regions. Background air concentrations of NMHCs in the northern hemisphere are higher

than those in the southern hemisphere because of much higher surface emissions (Boissard *et al.* 1996). The main anthropogenic sources for NMHCs are fossil fuels, biomass burning and industrial processes (Reimann and Lewis 2007), but a few of NMHCs are also known to have biogenic sources, including emissions from vegetation, soil and oceans (Broadgate *et al.* 1997, Hakola *et al.* 2006b, Hellén *et al.* 2006a). Globally, biogenic emissions of NMHCs exceed those of anthropogenic origin (Müller 1992). The NMHCs determined in this study had mainly anthropogenic origin. Moreover, the northern hemisphere has been found to be an important exporter of ethane to more southerly latitudes (Xiao *et al.* 2008).



**Fig. 1.** Location of the sampling site in Antarctica.

During the last 15 years, only a limited number of studies reported ambient air concentrations of NMHCs in Antarctica (Clarkson *et al.* 1997, Gros *et al.* 1998, Kaspers *et al.* 2004, Read *et al.* 2007). Kaspers *et al.* (2004) derived concentrations of ethane, propane and ethyne for the year 2000 from measurements in firn air. Clarkson *et al.* (1997) reported on levels of ethane and propane measured during 1991–1996, and Gros *et al.* (1998) conducted ship measurements of  $C_2$ – $C_5$  NMHCs in the summer of 1993. Data from the Arctic areas are also scarce, and often measurements were conducted only in spring, during ozone depletion events (Jobson *et al.* 1994, Ariya *et al.* 1999, Ramacher *et al.* 1999, Bottenheim *et al.* 2002, Blake *et al.* 2003). Only a few round-the-year measurements have been reported (Solberg *et al.* 1996, Swanson *et al.* 2003, Gautrois *et al.* 2003). In addition to measurements of NMHCs in ambient air, some investigations of snow pack production and emissions of alkenes in the Arctic areas were carried out (Swanson *et al.* 2002, Bottenheim *et al.* 2002).

In background air, concentrations of NMHCs are typically lower in summer than in winter (Hakola *et al.* 2006a). This is causally related to relatively faster photochemical activity occurring in summer. Therefore, much shorter atmospheric lifetimes of these compounds in summer will restrict the distances over which NMHCs

are transported. Indications of an NMHC seasonal cycle were observed in the Arctic region (Solberg *et al.* 1996, Gautrois *et al.* 2003). Even if the atmospheric lifetimes of the NMHC in summer were not affected by the photochemical activity, the Arctic air mass becomes more confined to the polar region, reducing the influence of mid-latitude air masses (Stohl 2006). The air flow in Eurasia changes from south-westerly in winter to north-westerly in summer (Barrie 1986) and transport is only half as fast as in winter (Law and Stohl 2007). In Antarctica, alkanes, ethyne and benzene have shown a summer minimum and a winter maximum, but alkenes have not shown any clear seasonal variation (Clarkson *et al.* 1997, Read *et al.* 2007).

In earlier studies, relatively higher concentrations of NMHCs were found in the Arctic than in Antarctica (Hopkins *et al.* 2002, Read *et al.* 2007). However, because of limited data, it has been difficult to temporally compare concentrations measured at the two polar regions. In this study, we report summer concentrations of  $C_2$ – $C_6$  NMHCs measured both in Antarctica and in the Arctic during the same year, 2008, and using the same methods. This enabled their direct comparison.

## Methods

### Location and sampling

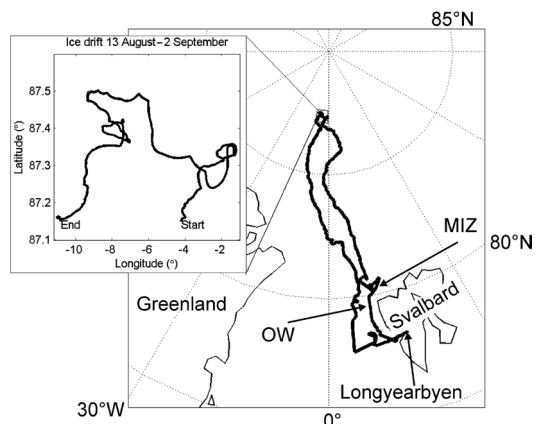
Measurements in Antarctica were conducted at the Finnish Antarctic research station of Aboa (73°03'S, 13°25'W, 470 m above sea level) in Queen Maud Land (Fig. 1). The setup of the station has been described in more detail in Virkkula *et al.* (2009). Samples were always collected within the clean sector, against the wind. The effects of any local emissions from the research station or people taking the samples on the observed concentrations were thus limited. No samples were collected if winds were below  $1 \text{ m s}^{-1}$  due to the fact that at stagnating conditions wind direction is very uncertain and air may get contaminated by exhaust gases from the diesel generator, snow mobile exhaust or other possible sources around the main building of Aboa. However, these stagnating condi-

tions were not frequent. In all 10-minute-average weather data collected during the campaign, the wind speed was  $< 1 \text{ m s}^{-1}$  only 3% of time and three hours was the longest continuous period with so low wind speed.

The air samples were collected into evacuated 0.85-l summa-polished stainless steel canisters (BRC, Rasmussen) using a Teflon membrane pump. Within 30 s canisters were pressurised to  $\sim 3$  bars. Prior to sampling, stainless steel inlet line (length  $\sim 50$  cm) was flushed with sampling air for at least one minute. Altogether 43 canister samples were taken at Aboa between 21 December 2007 and 1 February 2008 and 36 canisters during the ship cruise in the Arctic between 6 August 2008 and 8 September 2008.

The Arctic samples were collected during the Arctic Summer Cloud Ocean Study (ASCOS; [www.ascos.se](http://www.ascos.se)) on board the Swedish icebreaker *Oden* (see Fig. 2). The cruise started on 2 August 2008 in Longyearbyen. The NHMC measurements started on 6 August while sailing through the pack ice zone and recommenced during that phase of the expedition which the ship was moored to an ice floe, on 12 August near  $87.0^\circ\text{N}$ ,  $1.5^\circ\text{W}$ . After three weeks (referred to as the drift) of passive erratic drifting, during the biologically most active period between the late-summer melt season and into the transition to autumn freeze-up, the ship ended up on 2 September at  $87.1^\circ\text{N}$ ,  $11.0^\circ\text{W}$ . On the way back, stops were made at an additional marginal-ice zone (MIZ) station ( $80.7^\circ\text{N}$ ,  $8.9^\circ\text{E}$ ) on 6–7 September, and at an open water (OW) station ( $80.4^\circ\text{N}$ ,  $10.1^\circ\text{E}$ ) on 7 September, where the last samples were collected.

The sampling was conducted on the seventh (uppermost) deck, on the upwind side of the ship. More details can be found in Paatero *et al.* (2009). Post-expedition sorting of the NMHC data for possible ship pollution was based on the pollution sensor of the main sampling manifold for gases and aerosol particles. The manifold consisted of an ultrafine condensation particle counter (TSI 3025, TSI Inc.) connected to an intelligent controller (Ogren and Heintzenberg 1990). In addition, toluene was used as a tracer. The setup showed that air samples were uncontaminated by ship-originated emissions provided that the wind was within a  $\pm 70^\circ$  sector of the



**Fig. 2.** The route and stations of the Arctic Ocean Expedition ASCOS in 2008 (MIZ = marginal-ice-zone station, OW = open-water station). In the left-hand-side panel, the drift route with an ice floe is shown

bow and greater than  $2 \text{ m s}^{-1}$ . More details are given in Leck *et al.* (2001).

## Chemical analyses

The samples were analyzed later in the laboratory of the Finnish Meteorological Institute (FMI) using a gas chromatograph (Agilent 6890) equipped with a flame ionization detector and an  $\text{Al}_2\text{O}_3/\text{KCl}$  PLOT column (50 m, inner diameter 0.32 mm). The sample volume was 760–1010 ml (the exact sample volume being determined by measuring the pressure in the canister prior to and after the analysis) and the samples were pre-concentrated in two liquid nitrogen traps, in a stainless steel loop (125 cm, 1/8") with glass beads and in a capillary trap. The sample was passed through a 10-cm-long stainless steel tube filled with  $\text{K}_2\text{CO}_3$  and NaOH in order to dry it and to remove  $\text{CO}_2$ . The calibration was performed using a gaseous standard from the UK National Physical Laboratory containing 27 hydrocarbons and analyzed as regular samples. It was not possible to measure light alkenes, since they were found to be formed in the canisters during storage.

The detection limits for a selection of the determined NMHCs are listed in Table 1. The measures of precision of sampling and analysis have earlier been evaluated for background air

conditions (Hakola *et al.* 2006a). The overall uncertainty of the NHMC method in use was defined from uncertainties of sampling and analyses, calibration level and gaseous standard. The overall uncertainty was determined to be less than 20% for most of the compounds and highest (33%) for *i*-hexane. For values very close to the detection limit, uncertainty increases. The laboratory at the Finnish Meteorological Institute has participated in several intercalibrations (e.g. Slemr *et al.* 2002, Rappenglück *et al.* 2006) that showed the statistical measures of the overall quality of the sampling and analysis to be within the overall uncertainty of each intercalibration.

During ASCOS, supporting surface ozone data was determined with Environnement S.A. ozone analysers based on UV absorption. To be used as a tracer for air that had been in contact with land within the last three days  $^{222}\text{Rn}$  progeny was measured every hour also located on the seventh deck of the *Oden*. The sample air was pumped through a HEPA filter which removed all the radionuclides, including short-lived  $^{222}\text{Rn}$

progeny attached to ambient aerosol particles (Paatero *et al.* 2009).

### Air mass backtrajectories

Seven-day three-dimensional (3D) air mass trajectories, which arrived at 470 m above sea level i.e. at the height of the measurement site, were used in interpreting the Antarctic data. As the air sampled during the course of ASCOS was generally confined to a well-mixed surface based layer (~200 m deep), five-day 3D trajectories were calculated with an arrival height of 100 m at the position of the icebreaker. The 3D trajectories were calculated from the re-analysis data library using the HY-brid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT4) model (<http://ready.arl.noaa.gov/HYSPLIT.php>). The data originated from the National Weather Service's National Centers for Environmental Prediction's (NCEP) Global Data Assimilation System (GDAS).

**Table 1.** Detection limits for this study together with mean summer concentrations and the range of the concentrations (pptv) at Antarctic found in this and earlier studies. DL = detection limit.

Area Reference	Antarctic This study	Antarctic Read <i>et al.</i> 2007	Antarctic Kaspers <i>et al.</i> 2004	Antarctic Gros <i>et al.</i> 1998	Antarctic Clarkson <i>et al.</i> 1997	
Month(s)	Dec–Jan	Dec–Feb	Dec–Feb	Dec–Feb	Jan	
Year(s)	2008	2004–2005	2000	1993	1991–1996	
Location	Aboa 73°03' S, 13°25' W	Halley Base 75°35' S, 26°19' W	Site M* 75°00' S, 15°00' W	Ship 43°–77° S	Scott Base 77°51' S, 166°45' E	
	DL (pptv)					
Ethane	5	101 (79–197)	126	100–140**	291	200
Propane	4	10 (4–356)	16	0–30**	61	25
2-methylpropane	3	3 (< DL–24)	1		26	
Ethyne	7	16 (< DL–30)	1	0–12**	48	
Butane	3	3 (< DL–109)	1		51	
2-methylbutane	3	9 (4–40)				
Pentane	3	3 (< DL–27)			37	
Propyne	3	< DL				
2-methylpentane	4	< DL (< DL–10)				
3-methylpentane	4	< DL (< DL–9)				
Hexane	4	< DL (< DL–18)				
Heptane	2	2 (< DL–25)				
Benzene	2	8 (< DL–35)	2			

\* For location of site M see Fig. 1. \*\* Calculated from firn air measurements.

## Potential Source Contribution Function (PSCF)

To identify the spatial distributions and potential source areas of the NMHCs observed at the location of the icebreaker *Oden*, a potential source contribution function (PSCF) was used (Ashbaugh *et al.* 1985). Previously PSCF has usually been used when investigating the potential sources of pollutants (e.g. Yli-Tuomi *et al.* 2003).

The PSCF can be viewed as a receptor model that combines meteorological information in the form of trajectories with the observed concentrations of the NMHCs, in an attempt to produce probability fields for the observed data. In this study, the five-day back trajectories arriving at 100 m above the *Oden*'s position were recalculated hourly. To perform the PSCF analyses, each trajectory and its associated endpoints were then associated with the measured NMHC concentration representative for the time resolution of the calculated trajectory.

The northern hemisphere was divided into  $1.8^\circ \times 2.5^\circ$  grid cells. When a trajectory enters a  $ij$  cell, it is assumed to collect the concentration field from that cell and transport it along the trajectory. The PSCF analysis is then performed in the following way: The probability,  $P_{ij}(A)$ , that air has been transported from a specific grid cell to the receptor point is calculated as follows:

$$P_{ij}(A) = \frac{n_{ij}}{N} \quad (1)$$

Here  $N$  is the total number of trajectories used in the sampling and  $n_{ij}$  is the number of trajectories passing through this grid cell. If a certain criterion is met at the receptor site (i.e., a threshold value of any observed variable, here the 50th and 25th percentiles of the measured NMHC concentration is used), the entire trajectory with its end points associated with this time is assumed to have the set threshold value. The probability,  $P_{ij}(B)$ , that a grid cell has met the criteria,  $m_{ij}$ , is given by:

$$P_{ij}(B) = \frac{m_{ij}}{N} \quad (2)$$

The conditional probability that a trajectory passing through a grid cell also having the specific criteria met, is then given by:

$$\text{PSCF}_{ij} = P_{ij}[B|A] = \frac{P_{ij}[B]}{P_{ij}[A]} = \frac{m_{ij}}{n_{ij}} \quad (3)$$

In order to avoid high probability values when the total number of trajectories in a grid cell is low (non representative), only cells with at least five or more trajectory entries ( $n_{ij}$ ) are used, and these PSCF values are also multiplied by a weighting function:

$$W(n_{ij}) = \begin{cases} 1.0 & \text{when } 50 \leq n_{ij} \\ 0.8 & \text{when } 10 \leq n_{ij} < 50 \\ 0.0 & \text{when } 5 \leq n_{ij} < 10 \end{cases}$$

The PSCF provides an effective tool when investigating patterns and larger source areas, though it is obviously affected by the uncertainties inherent in the back-trajectories, and is sensitive to sources located close to the receptor point; in some cases this effect could yield false patterns producing distant sources not present in reality. This problem should not, however, arise in this study as no combustion sources are present at  $87^\circ\text{N}$ . Due to limited data set, reliability of the available PSCF plots in identifying the spatial distributions and potential source areas of the NMHCs observed at the location of the icebreaker *Oden* is reduced. In spite of this, the PSCF results should be able to give information of main transport paths and directions of source areas. Longer trajectories (7-day or 10-day trajectories) were not used due to increased uncertainty with time of transport and to the relatively short lifetimes of the NMHCs studied.

## Results and discussion

### Measurements in Antarctica in summer

In our NMHCs measurements performed during December–January (summer in the southern hemisphere), the lightest alkanes were the only ones of the analysed NMHCs showing persistent concentration levels above the detection limit (Table 1). The average ethane concentration was 101 pptv. This is in good agreement with the earlier studies by Read *et al.* (2007), where the average ethane concentration during December–February was reported to be 126 pptv. Also

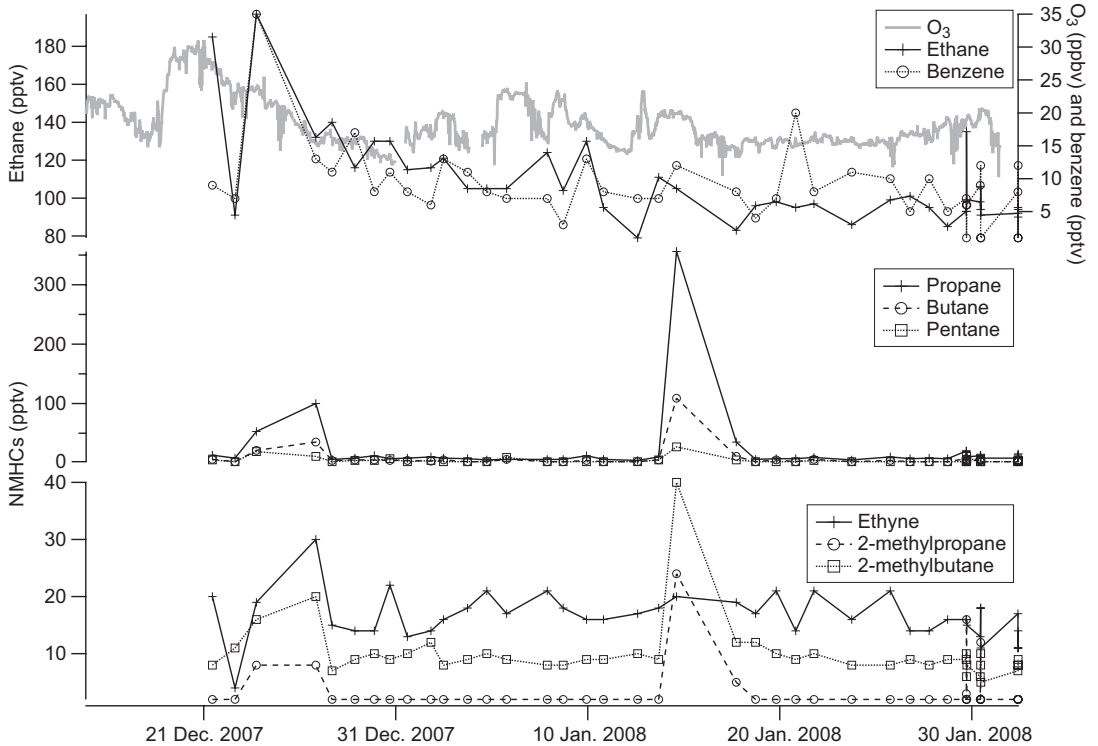


Fig. 3. Concentrations of NMHCs (pptv) and  $O_3$  (ppbv) in Antarctica.

concentrations of the other alkanes determined were in good agreement with Read *et al.* (2007). Measurements conducted during the early 1990s (Clarkson *et al.* 1997, Gros *et al.* 1998) showed in general higher summer concentrations than those measured in this study and by Read *et al.* (2007) in 2004–2005 (Table 1).

All the alkanes except ethane show concentration peaks on 23 and 26 December and 14 January (Fig. 3). At other times, concentrations were generally below or very close to the detection limits. This indicates that the observed levels are in general not influenced by recent anthropogenic emissions and thus represent remote unperturbed background air. The main feature of the measured concentrations of ethyne and benzene is that they did not show a similar temporal development to that of the alkanes, in that they did not exhibit, for example, the peak concentrations on 14 January. Our average benzene and ethyne concentrations (8 and 16 pptv, respectively) are slightly higher than those reported by Read *et al.* (2007). During the last three days, four samples were taken on each day. Standard deviations of the daily means

( $n = 4$ ) were between 1 and 7 pptv except for ethane (20 pptv on 29 January).

NMHC-to-ethyne molar ratios were studied to get indications of the origin of the sources. In Antarctica, the ratios remained close to 10 except on 23 December and 14 January, when they were 21 and 38, respectively. On 22 December, ethyne concentration was below the detection limit and the ratio could not be calculated. On 23 December, the ratios for all alkanes and benzene were higher than average, but that for ethyne remained at the average level. This gives an indication of a local or regional source of e.g. evaporative emissions of gasoline or diesel whose emissions contain lots of alkanes and benzene, but no ethyne (Hellén *et al.* 2006b, Watson *et al.* 2001, Fujita 2001). On 14 January, concentrations of ethane, ethyne and benzene did not increase, but concentrations of other alkanes were clearly higher. These relatively high concentrations of propane and butane could, thus, indicate the influence of close source of liquefied petroleum gas, which is known to have high content of propane and also some butane (Fujita 2001).

When the trajectories were subjectively divided into three potential source clusters (oceanic coming directly from the sea, coastal coming along the coastline and continental), similar average concentrations were found for each of the clusters (150–170 pptv for alkanes). Air mass trajectories were thus not able to explain the differences in concentrations in Antarctica during this study. This finding is consistent with Read *et al.* (2007). Air masses during the concentration peaks on 23 December and 14 January came along the coastline from the east, but on 26 December the air was coming from the sea. In addition, According to Pearson's correlation analysis, no relation of NMHCs with temperature, incoming radiation or O<sub>3</sub> was found. This was to be expected, since in Antarctica there are no temperature-dependent biogenic or other emission sources and the lifetimes of the NMHCs (Table 2) are so long that local incoming radiation does not play a significant role.

### Measurements of NMHCs in the high Arctic in summer

NMHCs concentrations measured between 80°N and 87°N were in general slightly lower (5%–40%) than the levels typically registered at the Finnish GAW station at Pallas (67°58'N, 24°07'E) in summer (Hakola *et al.* 2006a). Pallas is closer to main source areas in Europe and results from there describe background air in northern Europe on the way when European emissions are transported to the Arctic. The NMHC levels in August measured during this study seem to be in good agreement with those reported in earlier studies (*see* Table 2). The NMHC levels measured at the beginning of the 1990s seem to have been slightly higher as compared with those reported here, which is also confirmed by modelling studied representing that period (Xiao *et al.* 2011). These results meet the expectations, since at least in Europe emissions of NMHCs decreased by 20%–50% during the 1990s (Solberg *et al.* 2002).

The average ethane concentration (616 pptv) was only 5% lower than that measured at the GAW station (Table 2). Concentrations of propane and ethyne were also clearly above the

detection limits in all the samples collected during ASCOS. However, their concentrations were more than 30% lower than those measured at Pallas. The three to four times longer average lifetime of ethane enables it to be transported in air over longer distances than propane and ethyne. The observations revealed the lowest NMHC levels during the drift at the 87th latitude (Fig. 4 and Table 2). Higher concentrations were measured for most compounds on the way back to Longyearbyen. Only ethyne remained at the same level as registered during the drift. Butane, pentane, benzene, 2-methylpropane and 2-methylpentane concentrations followed a generally similar temporal development, but ethane concentrations were more variable. According to Pearson's correlation analysis, no relations between afore-mentioned compounds and ozone concentrations exist.

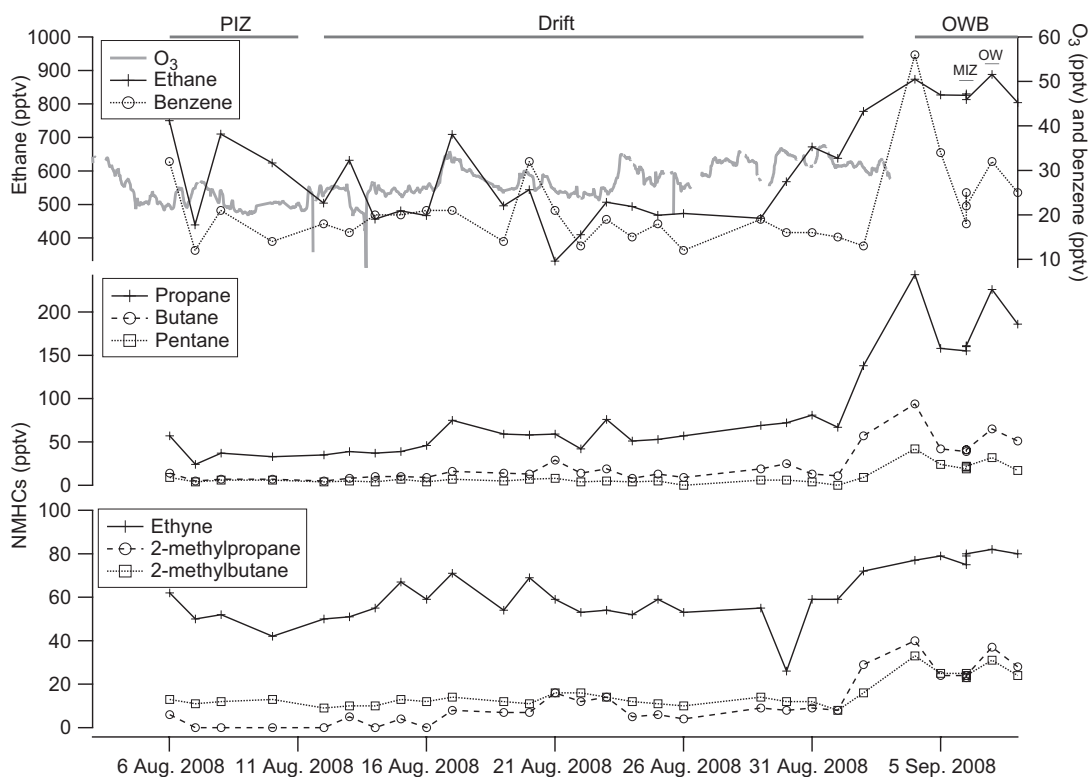
The Arctic molar ratio of NMHC-to-ethyne was close to 15 except on 30 August when it was 30. It was only during that day when the ethyne concentration was relatively low, whereas the other compounds remained at the average level. To explain the concentration, air mass coming to the site should be cleaner, but more influenced by e.g. evaporative emissions of gasoline or diesel than average days.

The Kara Sea and, to some extent, also the Barents Sea and the adjacent land are the potential source regions for the group of NMHCs measured in the high-Arctic pack-ice area (Fig. 5). In addition to this, the Greenland Sea makes some contribution in the case of all the other compounds except ethane and propane. Exploitation of petroleum and natural gas in the Kara Sea area (Ulmishek 2003) and could be a source of alkanes. In addition to this, the air masses from that direction may have been influenced by the West Siberian oil basin, which is the largest petroleum basin in the world. Crude oil production and natural gas venting are known to produce considerable emissions of light alkanes, but not of ethyne or benzene (Friedrich and Obermeier 1999). In natural gas, there is especially a high content of ethane and propane compared to the other NMHCs. This would explain why our results indicate that the Kara Sea and the adjacent land is the most important source/transport area for ethane and propane, but for the other com-

**Table 2.** Mean summer concentrations and concentration range of NMHCs (pptv) reported in this and earlier studies for high northern latitudes and for Pallas (northern Europe). The average atmospheric life times ( $\tau$ , days) for the listed NMHCs in reaction with OH radicals is given in units of days. Concentrations for OH radicals ( $6.4 \times 10^5$  molecule  $\text{cm}^{-3}$ ) are daytime averages for summer (Jun–Aug) in northern Europe (Hakola et al. 2003). Reaction rates at 298 K are from Atkinson (1994). DL = detection limit.

Area	Arctic	Northern Europe	Arctic	Arctic	Arctic	Arctic	Arctic	Arctic
Reference	This study	This study	This study	Swanson et al. 2003	Hopkins et al. 2002	Gaustrois et al. 2003	Solberg et al. 1996	
Month(s)	Aug–Sep	Aug–Sep	Aug–Sep	August	August	Jun–Aug	August	
Year(s)	2008	2008	2008	1997–1998	1999	1989–1996	1992–1995	
Location	Ship all 78–87°N	Ship drift > 87°N	Pallas 68°N, 24°W	Greenland Summit 72.57°N, 38.48°W	Ship 53–81°N	Alert, Canada 82°N, 62°W	Zeppelin 78°55'N, 11°54'E	
$\tau$ (d)								
Ethane	70	517	651	603	442	1008	771	
Propane	16	56	134	77	56	158	82	
2-methylpropane	7.8	7	20		4	23	14	
Ethyne	22	56	91		29	67	96	
Butane	7.2	14	38	17	10	50	25	
2-methylbutane	4.6	12	22		6		8	
Pentane	4.6	5	16		12	16	9	
Propyne	3.1	< DL	< DL					
2-methylpentane	3.2	< DL (< DL–95)	5		2			
3-methylpentane	3.2	< DL (< DL–67)	< DL		1			
Hexane	3.2	4 (< DL–95)	6		6	8		
Heptane	2.6	13 (< DL–91)	4		2			
Benzene	14	21 (< DL–141)	26		50	34		





**Fig. 4.** Concentrations of NMHCs (pptv) and  $O_3$  (ppbv) and phases of the cruise during ASCOS (PIZ = sailing through the pack ice zone, Drift = drifting with an ice floe ( $> 87^\circ N$ ), OWB = on the way back to Longyearbyen, MIZ = stopped in the marginal ice zone and OW = stopped in open water).

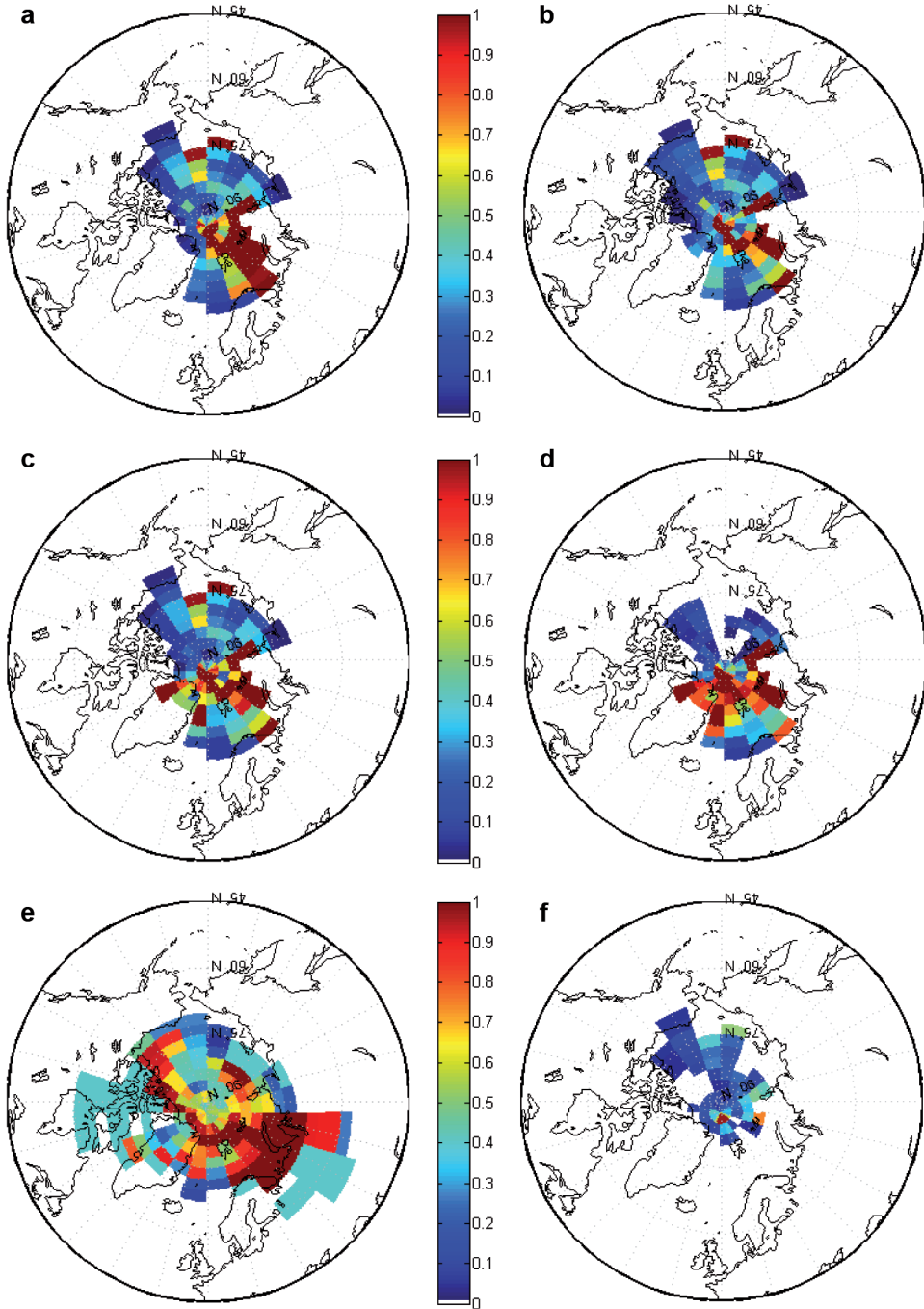
pounds also other areas could be important contributors. The air from Greenland was subsiding and moving northwards along its eastern coast, which probably meant that we were sampling free-tropospheric air involving possible pollution sources from lower latitudes. There are no sources of the studied NMHCs over the pack-ice area (see Fig. 5f). In their study of  $^{222}Rn$ , Paatero *et al.* (2009) showed that air masses coming from the Kara Sea and the eastern-central Arctic Ocean had the most contact with land areas (see Fig. 5e). However, the  $^{222}Rn$  distribution shown is not necessarily related to those anthropogenic activities that are expected to be main sources of alkanes.

### Comparison of the Arctic and Antarctic

On average, NMHC concentrations were five times higher in the Arctic than in Antarctica. The greatest difference was found for propane whose

concentrations was nine times higher and butane whose concentrations was eight times higher over the central Arctic Ocean and the Arctic pack-ice area. The lowest difference was for 2-methylbutane whose concentration was only twice as high. The relatively higher concentrations found in the Arctic indicate that the air in that region is more affected due to combustion sources located in close proximity. This is in agreement with earlier studies (Boissard *et al.* 1996, Hopkins *et al.* 2002, Read *et al.* 2007). It is well-known that the emissions are clearly higher in the northern than in the southern hemisphere (Wang *et al.* 1998, Xiao *et al.* 2008).

In Antarctica, a few peak events were registered for the measured NMHCs; outside these peaks, the concentrations were relatively stable and close to the detection limits. This also indicates that air masses in Antarctica are transported over longer distances which is supported by the trajectory analysis. Based on the trajectories and



**Fig. 5.** PSCF plots of (a) 50% ethane, (b) 50% propane, (c) 50% ethyne, (d) 50% benzene, (e) 50% radon, and (f) 25% pentane in the Arctic.

the PSCF analysis, within the Arctic region the air masses advected from the western-central Arctic Ocean and the Kara Sea showed the highest NMHC concentrations, but no corresponding

difference based on air-mass origin was detected in Antarctica.

It would be expected that the NMHC-to-ethyne molar ratio is higher in more remote air

than closer to the source areas, since ethane is dominating in total NMHC concentrations in background air and its lifetime is three times higher than for ethyne (Table 2). However, in the Arctic, where general concentrations are higher, the molar ratio is also higher than in Antarctica. This indicates some additional alkane source in the north as compared with the south and gives support to the PSCF analyses which indicated that the west-Siberian oil basin and the Kara Sea with the adjacent land, where petroleum and natural-gas are exploited, are important source areas for Arctic NMHCs.

## Conclusions

Summer concentrations of NMHCs were measured in Antarctica and over the central Arctic Ocean. In Antarctica, the concentrations were very close to the detection limit most of the time. During the sampling period, only ethane, propane and 2-methylbutane were always above the levels of detection. Over the high Arctic pack-ice region and along the marginal-ice zone, the lowest concentrations were measured during the drift period north of the 87th latitude. However even then, concentrations of most of the studied compounds were clearly above their detection limits. Our results show that the summer concentrations of NMHCs in the Arctic were on average five times higher than those in Antarctica. The highest Arctic-to-Antarctic ratio was observed for propane. In both polar regions, the concentrations of the NMHC's measured by us were in agreement with those of earlier studies. No differences based on air-mass origin were detected at in Antarctica, but samples collected over the central Arctic Ocean showed higher concentrations in air masses being advected from the Kara Sea and the western-central Arctic Ocean. In addition to this, subsiding air from Greenland seems to have made some contribution for all compounds other than ethane and propane. The relatively higher NMHC-to-ethyne molar ratios calculated for samples collected over the central Arctic Ocean suggest additional alkane sources in the region. The high Arctic pack-ice area was not considered a source area for the NMHC determined in this study.

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