

C₂-C₇ Hydrocarbon Concentrations in Arctic Snowpack Interstitial Air: Potential Presence of Active Br within the Snowpack

PARISA A. ARIYA^{1*}, JOHN F. HOPPER², and GEOFFREY W. HARRIS³

Abstract. Samples of interstitial air from within the snow pack on an ice floe on the Arctic Ocean were collected during the April 1994 Polar Sunrise Experiment. The concentrations of C₂-C₇ hydrocarbons are reported for the first time in the snow pack interstitial air. Alkane concentrations tended to be higher than concentrations in free air samples above the snow but very similar to winter measurements at various locations in the Arctic archipelago. However, ethyne concentrations in both interstitial and free air were highly correlated with ozone mixing ratios, consistent with previous demonstrations of the effects of Br atom chemistry. The analysis of total bromine within the snow pack indicate an enrichment in total Br at the interface layer between snow and free troposphere. The mixing ratios of some brominated compounds, such as CHBr₃ and CHBr₂Cl, are found to be higher in this top layer of snow relative to the boundary layer. Results were inconclusive due to the limited number of samples, but suggest the possible presence of active bromine in the snow pack and also that some differences exist between chemical reactions occurring in interstitial air compared to air in the boundary layer.

Key words: hydrocarbon measurements, interstitial air, snow pack, Arctic, active bromine.

1. Introduction

Since the first observations of tropospheric ozone depletion in the high Arctic around polar sunrise (Barrie *et al.*, 1988), there have been many measurements of trace constituents thought to be involved in the process, as well as of related compounds and atmospheric properties (eg., Barrie *et al.*, 1994; Solberg *et al.*, 1994). Kinetic interpretations of observed C₂-C₇ concentrations and chemical modeling (Jobson *et al.*, 1994; Sander *et al.*, 1997; Ariya *et al.*, 1998) have demonstrated the occurrence of photochemical reactions involving HO, Cl, and Br radicals occur. Jobson *et al.* (1994) showed that each radical had different effects on hydrocarbon concentration patterns. Reactions with HO are responsible for seasonal cycles in concentration, but are too slow to account for

the rapid depletion of hydrocarbon associated with polar sunrise ozone depletion which occurs within 1-2 days (Hopper *et al.*, 1997a; 1997b). Oxidation by Cl atoms significantly affects alkane concentrations on time scales of days, but the Cl atom concentration deduced from the alkane behaviour was insufficient to explain the complete loss of ozone. Jobson *et al.* (1994) observed drastic changes in ethyne mixing ratios during the ozone depletion events over and above that expected from Cl atom attack and concluded that Br atom chemistry is most likely responsible for the drastic destruction of ethyne and ozone. More recently, Ariya *et al.* [1997] showed that in addition to ethyne the changes in trichlorethene and tetrachloroethene, also indicate the significance of Br chemistry.

It had been initially conjectured that Br is produced from photolysis of marine CHBr_3 accumulated in the snow during the dark polar winter (Barrie *et al.*, 1988), but later laboratory measurements of the production rate of Br from CHBr_3 showed this source to be inadequate to account for the observed rates of destruction (Moortgat *et al.*, 1993). Although there have been several suggested sources of Br atoms (e.g., Schroeder and Urone, 1974; Finlayson-Pitts *et al.*, 1983; Barrie *et al.*, 1988; Finlayson-Pitts *et al.*, 1989; McConnell *et al.*, 1992; Fan and Jacob, 1992; Zetzch and Behnke, 1993; Mozurkewich, 1995; Vogt *et al.*, 1996) the actual source of Br atoms remains unclear (Ariya *et al.*, 1998).

The situation is complicated by uncertainties about the role of atmospheric aerosols and/or the underlying snow and ice surfaces in these processes. The Arctic snow pack, for instance, could be characterized as being either completely inert and having no role in ozone depletion, or as being chemically inert but providing a surface for the accumulation of volatile compounds which later destroy ozone through gas phase reactions, or as being chemically active in the destruction of ozone through heterogeneous reactions. Chemical analysis of bulk snow and ice samples provide supporting evidence but are insufficient by themselves to distinguish between these cases. If reactions do occur on crystal surfaces in the snow pack, or if the snow crystals serve as a medium for accumulating highly reactive compounds, then the effects are more likely to be seen in air within the snow pack or free air that has been in close contact with the snow.

2. Experimental

Electro-polished canister samples of whole air were collected during the April 1994 Polar Sunrise Experiment (PSE94) at camp NARWHAL (84°N, 63°W) on an ice floe on the Arctic Ocean (Hopper *et al.*, 1997), and analyzed for C_2 - C_7 hydrocarbon concentrations by GC-FID (Ariya, 1996). Identification and quantification of non-methane hydrocarbon species were made using reference

gas mixture blends (Conservation and Protection Service, Environment Canada). The standard mixtures, containing 5 ppbv of C₂-C₇ alkanes, alkenes, and alkynes were loaded onto the GC system exactly in the same way as the samples. The quantitation limit based on FID response and baseline noise was approximately 5 pptv for the C₅ hydrocarbons in a 1 L sample. Most species (C₂-C₅ alkanes) were at mixing ratios well above the quantitation limit for a major part of the sampling period and therefore the precision was of the order of 1%. Our laboratory participated in few rounds of International Hydrocarbon Intercomparison Experiments since November 1991. Results for most species were within about 10% of those of the National Institute for Standards and Technology (NIST) and the National Center for Atmospheric Research (NCAR). To note that the generation of alkenes in sample canisters has been observed by our group previously and appears to be related to canister sampling history, being more noticeable for canisters that have been used in urban air sampling (Ariya *et al.*, 1998). The free air samples were collected at heights of 0.5 m – 1 m above the snow surface using a portable pump at various locations around the camp (selected at sampling time to be upwind of the camp) through approximately 1.5 m of 6.25 mm OD stainless steel tubing.

Snow pack interstitial air was sampled at two fixed sites using the same pump. Stainless steel tubing (6.25 mm OD) was buried to depths of 1 m and 1.5 m. Snow was excavated using an aluminum shovel which had been washed and then plunge-cleaned in clean snow many times before use. The snow pits were back-filled with snow in approximately the same order it had been removed. The snow surface was smoothed and the pit allowed to consolidate several days before the first samples were taken. Upper ends of the sample lines above the surface were capped between samples. The buried ends were covered by loosely fitting stainless steel fittings and, for one line, wrapped loosely in a small sheet of clean teflon foil (no difference was observed between results from the two pits). This was sufficient to prevent the drawing of loose snow crystals into the buried sample lines, although formation of ice crystals inside the steel lines did occur over the sampling period.

Sampling thin snow packs presents problems because of the sample volume required (for PSE94, 3.2 l canisters, pressurized to 35 psig) which may entrain free tropospheric air during sample collection. At NARWHAL, the interstitial air sampling sites were located in snow accumulated between the ice blocks of an old pressure ridge. While these sites were not entirely characteristic of the snow pack, the deeper snow here had an appearance and physical properties most similar to the upper layer of snow over the ice floe. These sites had the additional advantages of minimal entrainment of free air, minimal contamination from camp and vehicle activities, slower exchange between free air and interstitial air, a larger volume of snow similar to the

relatively fresh top layer of low density snow on most of the floe, i.e., at the snow - atmosphere interface.

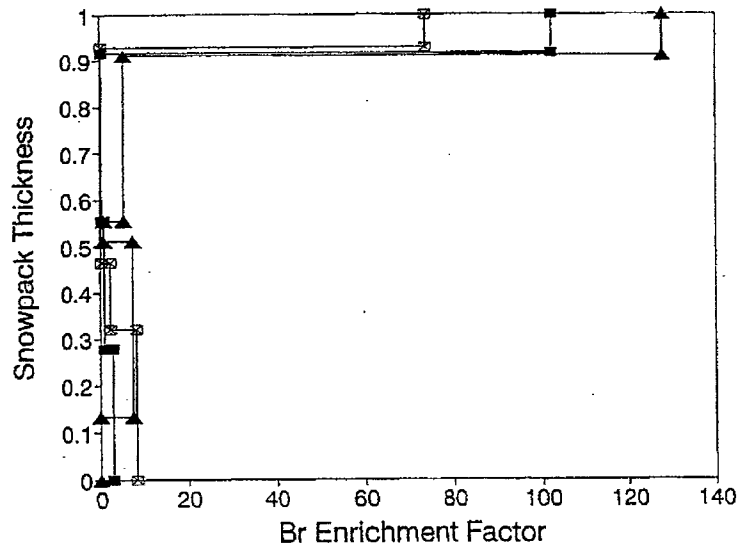


Figure 1. Br enrichment factors relative to Na (calculated using a Br/Na mass ratio of 0.0043 in bulk sea-salt aerosol (Sturges and Barrie, 1988) observed in layers of 3 snow sampling pits, as a function of normalized snow pack thickness (0 = base of snow pack, i.e., the sea ice - snow interface; 1 = top of snow pack, i.e., the snow - atmosphere interface). Snow pack depth on the NARWHAL ice floe was typically 20 cm - 30 cm.

Snow cover on large ice floes in this area of the Arctic Ocean was typically 20 cm - 30 cm in depth. Above the sea ice surface, the snow pack consisted of combinations of various layers including large hoar frost crystals, dense consolidated old snow crystals, and frequently a 1 cm - 2 cm layer of low density fresh snow easily moved by light winds. This top layer was highly enriched relative to seawater in Br⁻ (as determined by ion chromatography; Figure 1) and some halocarbons such as CHBr₃ and CHBr₂Cl (factors of 20-40 and 8-10, respectively) but not enriched in Cl⁻, CH₂Br₂, CHBrCl₂, or CH₂ClI. The association of enriched Br with relatively fresh snow, but not in older snow in the snow pack, indicates that Br in some form was being scavenged from the atmosphere in April.

3. Results and Discussion

The Arctic air mass is very homogeneous during winter time (e.g., Jobson *et al.*, 1994; Ariya *et al.*, 1998) and the variability in mixing ratios for many hydrocarbons in ambient air was small. In Figure 2, average mixing ratios of interstitial samples at Narwhal Ice Camp during April 1994 are compared to free air measurements made during the same period at the site (Ariya *et al.*, 1998), as well as to those measured at Alert during winter (January and February) and spring (April) (Jobson *et al.*, 1994) and those taken in March at Spitsbergen (Hov *et al.*, 1983) and Barrow (Doskey and Gaffney, 1992). The NARWHAL interstitial air mixing ratios were comparable to winter measurements from other Arctic sites but higher on average than those in free air samples from NARWHAL (Figure 2). Despite the precautions taken, contamination of the interstitial samples must be considered. The same pump and procedures were used for all samples, with only the sample lines and the source of the air being different. Sample lines for both interstitial air sampling locations were from the same length of prepared tubing as used for the portable free air sampling unit, and results from both fixed locations were comparable. These factors suggest that the difference in average mixing ratios between free air and interstitial air samples were real.

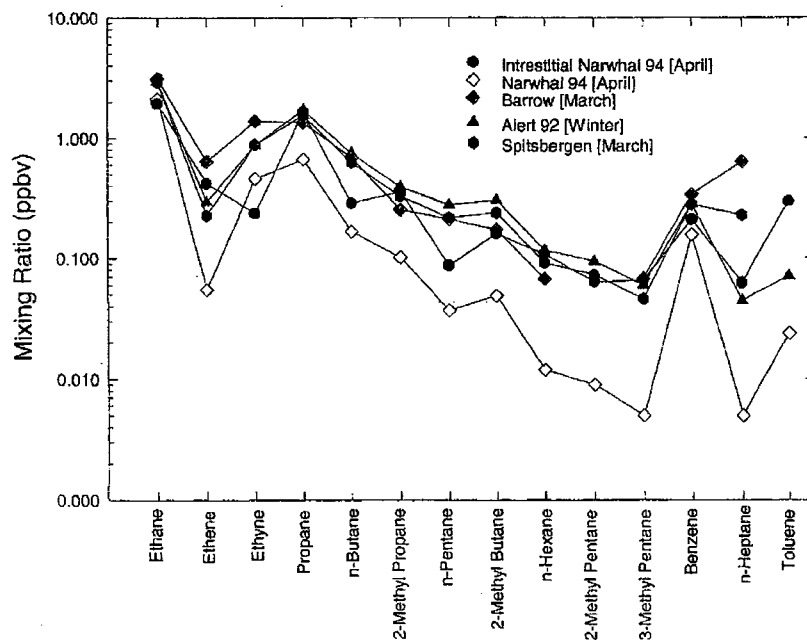


Figure 2.

Mean C₂-C₇ hydrocarbon mixing ratios from high Arctic locations.

After polar sunrise the free air alkane mixing ratios systematically decrease, because of increased photochemical activity with the larger, more reactive alkanes displaying the largest concentration change (Figure 2). Hence, measurements in which there are relatively lower concentrations of more reactive species correspond to more photochemically processed air masses. In comparison to the free air samples from NARWHAL, the interstitial air samples had higher mean mixing ratios for most hydrocarbons (Figure 2). The mixing ratios of alkanes and toluene in the interstitial samples are similar to those taken during the winter and early spring in the different locations in the Arctic region. This would suggest that the interstitial air samples represent less photochemically processed air masses trapped in the snow during dark months.

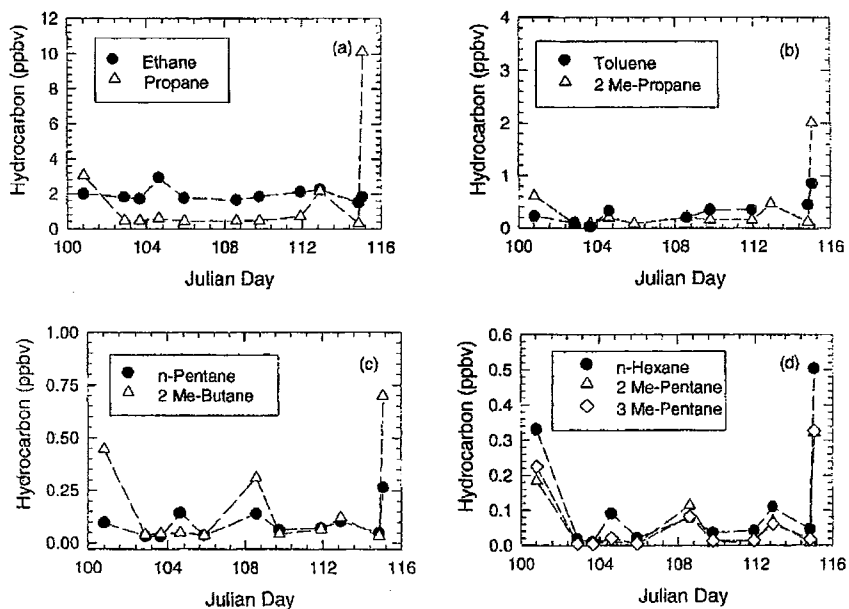


Figure 3 Time series for some C₂-C₇ hydrocarbons at ice camp NARWHAL: (a) ethane, propane; (b) 2-methyl propane and toluene; (c) n-pentane and 2-methyl butane; (d) n-hexane, 2-methyl pentane and 3-methyl pentane.

Ethane and benzene mixing ratios were similar in both interstitial and free air. Ethane is the slowest reacting non-methane alkanes with respect to atmospheric oxidation by HO or halogens. Benzene is also a relatively slow

reactant, particularly towards halogens (Ariya, 1996). While mixing ratios of most hydrocarbons in free air exhibit moderate to high variability at polar sunrise, benzene mixing ratios are remarkably constant with only a slow decrease over long periods (Jobson *et al.*, 1994), thus the similar mixing ratios for the slow reacting species in the free and interstitial air is to be expected.

Figure 3 shows the time series for measured C₂-C₇ hydrocarbons in snow pack interstitial air, while Figure 4 a-c shows both the interstitial and free air data for ethyne, n-butane, and benzene as well as the surface layer ozone mixing ratio. N-butane was chosen as a representative alkanes which react with Cl-atoms almost at every collision, (Ariya and Niki, 1996), but very slowly (almost 10⁶ times slower) with Br than with Cl. Benzene in contrast, as mentioned above, reacts slowly with both Cl and Br atoms, while ethyne is very reactive toward both Cl and Br atoms. Thus, in the presence of Cl-atoms, alkanes and ethyne mixing ratios are expected to decrease, whereas benzene mixing ratios should not be significantly affected. However, in the presence of active bromine, ethyne should be the only tracer among these three molecules which should decrease in concentration.

Of greatest interest are the ethyne mixing ratios observed in the interstitial air samples. The lower mean ethyne interstitial air mixing ratio for the entire period (Figure 2) can be seen from Figure 4a to arise because there were relatively fewer interstitial samples from the period when ozone was present and therefore when ethyne mixing ratios were higher. A comparison of ethyne mixing ratios in individual samples (Figure 4a) shows that during depleted ozone conditions, ethyne was often higher in interstitial air. Ethyne mixing ratios in both interstitial and free air were highly correlated with ozone (Figure 4a), much more so than alkanes. The same time series response in both free air and interstitial air shows that ethyne in interstitial air may have been similarly affected by reaction with Br. Note that, based on the higher mean alkane mixing ratios in interstitial air as compared to the free air samples at NARWHAL, we tentatively conclude that the exchange time between these reservoirs is fairly long. Thus the depletion of ethyne in the snow pack air may suggest that the Br chemistry is at least in part occurring in or on the snow pack itself.

As seen in Figure 4c, benzene mixing ratios in interstitial samples are similar to those taken in the free air during this period and show very little variability consistent with its low reactivity towards atmospheric oxidants (Ariya *et al.*, 1998). The behaviour of n-butane does not follow that of ozone or of free air samples, and no clear signature of Cl atom chemistry can be deduced either from its behaviour (see Figure 4b), or from the other alkanes shown in Figure 3. Note that Ariya *et al.* (1997) demonstrated a clear Cl atom signature in the free air samples during the initial prolonged period of ozone depletion at NARWHAL (JD 98 - 107). That there were no similar trends

observed in interstitial mixing ratios during the same ozone-depleted period may indicate that Cl chemistry occurred in the free air but not in interstitial air, and may relate to the fact that the snow pack was enriched relative to sodium in total bromine but not in total chlorine.

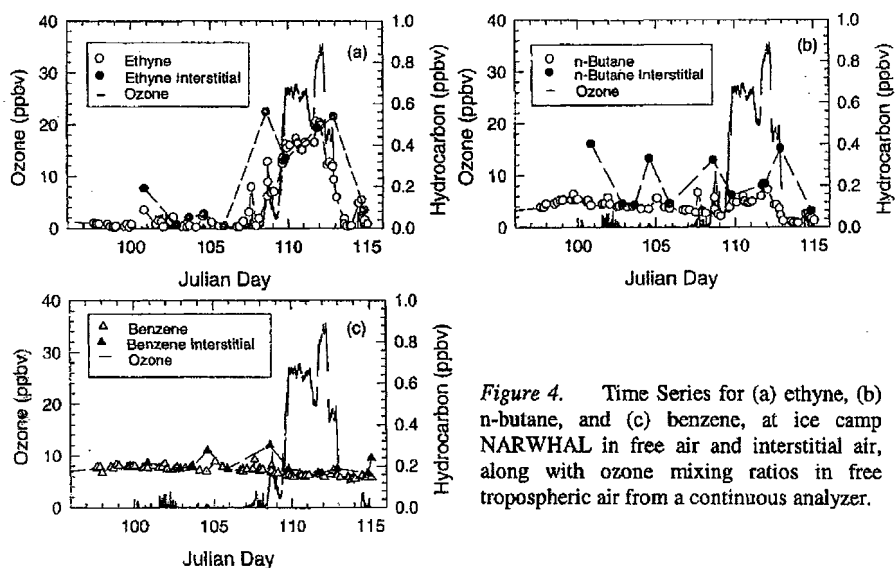


Figure 4. Time Series for (a) ethyne, (b) n-butane, and (c) benzene, at ice camp NARWHAL in free air and interstitial air, along with ozone mixing ratios in free tropospheric air from a continuous analyzer.

A fundamental problem for further interpretation of our data is that it is not clear whether the variations in ethyne mixing ratios, for example, were due to reactions with Br occurring within the snow pack, or whether the observations could be explained by reactions in free air which subsequently replaced the interstitial air. Qualitatively, a short turnover time will lead to no significant difference between interstitial and free air concentrations of hydrocarbons. However, the higher mean mixing ratios for many C_2 - C_7 hydrocarbons were observed in the interstitial samples compared to the air samples, indicating that the turnover time is not short. Although, we have no quantitative measure of the turnover time for the interstitial air, which will be a function of snow pack porosity, ambient wind speed, and atmospheric pressure [Massman *et al.*, 1997]. Further measurement on interstitial hydrocarbon mixing ratios is highly desirable and will be particularly useful if the turnover time of the interstitial air can be quantified.

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