ORGANIC COMPONENTS OF ANTARCTIC SNOW AND ICE PART 1. VOLATILE FATTY ACIDS IN SNOW DRIFT

Keiichi Ohta[1], Fumihiko Nishio[2] and Kazuo Osada[1]

[1]*Water Research Institute, Nagoya University,*
Furo-cho, Chikusa-ku, Nagoya 464-01
[2]*National Institute of Polar Research,*
9–10, Kaga 1-chome, Itabashi-ku, Tokyo 173

Abstract: Snow drift samples collected on Mizuho Plateau, Antarctica, were analyzed for volatile fatty acids including formic, acetic, propionic and butyric acids. Formic (2.3–11.7 ppb) and acetic (11.4–59.8 ppb) acids were detected as major components. Their concentrations were far lower than those reported in rain and snow samples from urban, rural and remote areas. However, the concentrations were higher than those of formic and acetic acid concentrations reported in the ice core sample collected from the coast of East Antarctica.

The concentrations of volatile fatty acids in snow drift samples showed a marked seasonal variation, *i.e.*, low levels in winter and high levels in summer, correlating with solar radiation. Based on this seasonal variation, we concluded that these volatile fatty acids were produced by photochemical oxidation of atmospheric hydrocarbons. The contribution of these volatile fatty acids to the acidity of snow drift was indicated to be small.

1. Introduction

A large number of organic compounds have been identified in rain and snow samples collected from urban, rural and marine areas (Lunde *et al.*, 1977; Graedel and Weschler, 1981; Meyers and Hites, 1982; Kawamura and Kaplan, 1986). These organic compounds provide useful information on the origin, atmospheric reactions, scavenging processes and transport of organic materials.

The origin of organic compounds in Antarctic snow and ice is of special interest since Antarctica is the most remote continent from areas with human activities and vegetation, which significantly contribute to the chemical composition of precipitation. Methane in bubbles enclosed in Antarctic ice has been investigated by several groups (Stauffer *et al.*, 1985; Pearman *et al.*, 1986; Khalil and Rusmussen, 1987). Other organic compounds found in Antarctic ice include formic, acetic and methanesulfonic acids, which were identified by Legrand and Saigne (1988) in the ice core sample collected from the coastal area in East Antarctica. The same authors suggested atmospheric methane and marine biogenic volatiles as possible precursors of formic and methanesulfonic acids, respectively.

In the katabatic wind region in Antarctica, drifting snow particles play an important role in the transport of materials. These particles settle down on the concave surface. The snow mass thus settled is called snow drift. Osada *et al.* (1989) recently reported the inorganic chemical composition of snow drift samples collected

on Mizuho Plateau. The organic composition of these samples has been examined by us. This paper describes some findings on volatile fatty acids which have been studied from the following viewpoints: (1) to understand organic chemical cycles in the Antarctic atmosphere and (2) to evaluate the contribution of organic acids to the acidity of Antarctic snow and ice.

2. Experimental

The snow drift samples were collected in 1986 at Mizuho Station (70°42'S, 44°20'E, 2230 m a. s. l.) and three other locations on Mizuho Plateau (Fig. 1). The sampling procedure was described by OSADA *et al.* (1989). The samples were kept frozen and transported to our laboratory.

The sample (100–150 g) was melted prior to analysis in a dessicator, to which a trap packed with KOH pellets was connected, to avoid contamination of the sample by volatile atmospheric acids in the laboratory. The resultant aqueous solution was spiked with isocaproic acid as an internal standard for quantification. The solution was adjusted to pH 8.5–9.0 and then concentrated. Fatty acids in the concentrate were derivatized to their *p*-bromophenacyl esters according to the method of KAWA-MURA and KAPLAN (1984). The *p*-bromophenacyl esters were purified by silica gel thin-layer chromatography, using *n*-hexane and dichloromethane (1: 1).

The esters were determined by a Shimadzu GC-9A gas chromatograph equipped with an FID and SE-52 (25 m×0.25 mm) capillary column. Nitrogen was used as a carrier gas at a flow rate of 1 ml min^{-1}. The split ratio was 3: 1. The column oven temperature was programmed from 180 to 280°C min^{-1}. Analytical repro-ducibility was better than ±15%. The detection limit was 0.1 ppb. Mass spectra were measured for the identification of the *p*-bromophenacyl esters on a GC/MS system (JEOL, JMS-D-300) combined with an on-line computer (JEOL, JMA-2000E).
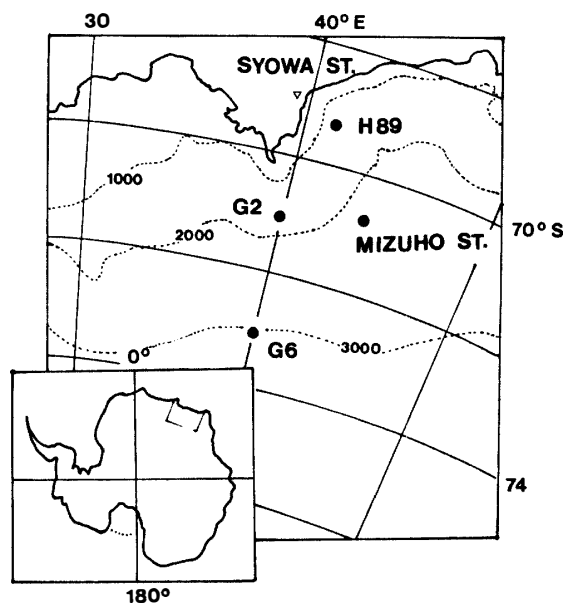

Fig. 1. Locations of snow drift sampling on Mizuho Plateau.

Operating conditions of the MS were as follows: electron energy, 20 eV; emission current, 330 A; scanning 150–500 m/z in 2.5 s.

3. Results and Discussion

Eight snow drift samples collected at Mizuho Station and three samples from other locations (G2, G6 and H89; Fig. 1) were analyzed.   Volatile fatty acids having carbon atom numbers from 1 to 4 (C_1 to C_4) were identified.   The C_3 and C_4 acids have not been reported in Antarctica.   A typical gas chromatogram of these fatty acids (as their p-bromophenacyl esters) is illustrated in Fig. 2.

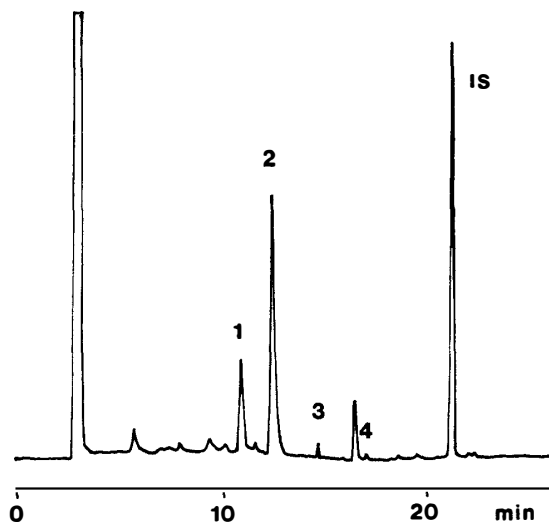Table 1 lists concentrations of four fatty acids in the snow drift samples.   Formic

Fig. 2.   A gas chromatogram of volatile fatty acids (as their p-bromophenacyl esters) in snow drift samples collected at Mizuho Station.   Peak number 1=formic, 2=acetic, 3= propionic, 4=butyric acids.   IS=internal standard (isocaproic acid).

Table 1.   Concentrations of volatile fatty acids in snow drift samples collected from Mizuho Plateau in 1986.

Sampling site	Date	Concentration (ppb)			
		Formic (C_1)	Acetic (C_2)	Propionic (C_3)	Butyric (C_4)
H89	2/04	7.54	55.3	1.51	0.29
Mizuho Station	2/11	9.50	59.8	2.41	ND
〃	3/02	5.91	20.5	1.72	ND
〃	3/17	2.30	16.9	1.20	0.90
〃	4/02	4.77	19.2	0.73	0.25
〃	7/29	4.40	11.4	1.90	0.39
〃	8/29	2.96	15.8	1.78	0.46
〃	9/04	11.4	35.2	1.70	0.21
〃	10/05	8.65	31.3	1.32	ND
G2	11/09	11.7	39.5	1.99	ND
G6	12/03	6.03	44.8	2.30	0.26

ND: not determined.

acid (C_1) and acetic acid (C_2) are major constituents of volatile fatty acids. Their concentrations fluctuated from sample to sample. The concentrations of formic (2.3–11.7 ppb) and acetic (2.3–11.7 ppb) acids were far lower than those reported for rain in urban areas (C_1: 100–1840 ppb, C_2: 154–6120 ppb; BARCELONA et al., 1980; KAWAMURA and KAPLAN, 1984) and remote continental and marine areas (C_1: 170–1630 ppb, C_2: 50–600 ppb; GALLOWAY et al., 1982; KEENE et al., 1983).

Recently LEGRAND and SAIGNE (1988) have reported very low concentrations of formic and acetic acids for the ice core sample collected near the coast of East Antarctica. They noticed that the concentration of formic acid (0.1–1.2 ppb) was higher than that of acetic acid (<0.15 ppb) throughout all ice core sections by using an ion chromatographic technique. In the snow drift samples (Table 1), acetic acid was a dominant constituent accounting for 60–85% of the total concentration of volatile fatty acids in each sample, whereas formic acid accounted for 10–25%, being different from the acetic to formic acid ratio reported in the ice core sample.

A similar difference in this ratio exists between rain samples in urban and remote areas. In urban areas such as Pasadena, California (BARCELONA et al., 1980) and Los Angeles (KAWAMURA and KAPLAN, 1984), acetic acid was a predominant constituent. In several rain samples in Los Angeles, the acetic acid concentration was more than ten times higher than the formic acid concentration. In remote continental and marine areas, however, the concentration of acetic acid was 2 to 6 times lower than that of formic acid (GALLOWAY et al., 1982). Explanations have not yet been given for this difference between urban and remote areas. It is difficult also for us to offer complete explanations for the different distribution pattern between Antarctic snow drift and ice core samples. The differences in the sampling location and analytical methods between the snow drift and ice core samples may contribute to the discrepancy between the two samples. Apart from these differences, preferential evaporation of formic acid from snow drift due to its high volatility may occur during the deposition, wind erosion and re-deposition of snow drift.

Formic and acetic acids in the snow drift samples showed a seasonal variation in their concentrations (Fig. 3). The acetic acid concentration decreased rapidly from February to April, and increased after September. The formic acid concentration also showed a similar trend. Figure 3 includes data from four sampling sites (Mizuho Station, G2, G6 and H89) on Mizuho Plateau. Among these sites, the volatile fatty acid concentration in snow drift varies little from site to site, since these sampling sites are in similar meteorological and chemical environments (OSADA et al., 1989). Although data are lacking in several months, it is clear that the concentrations of volatile fatty acids are high in summer and low in winter. We will discuss possible factors causing this seasonal variation as follows.

Volatile fatty acids are emitted directly into the atmosphere from anthropogenic and biogenic sources as primary products (GRAEDEL, 1978). This direct emission contributes to a small portion of volatile fatty acids in the atmosphere. Most are believed to be transformed photochemically from atmospheric hydrocarbons (GRAEDEL and WESCHLER, 1981; CHAMEIDES and DAVIS, 1983; ATKINSON, 1985). EHHALT et al. (1986) proposed a detailed process for this photochemical transformation. It consists of the following steps: (1) the gas-phase oxidation of paraffinic and olefinic hy-
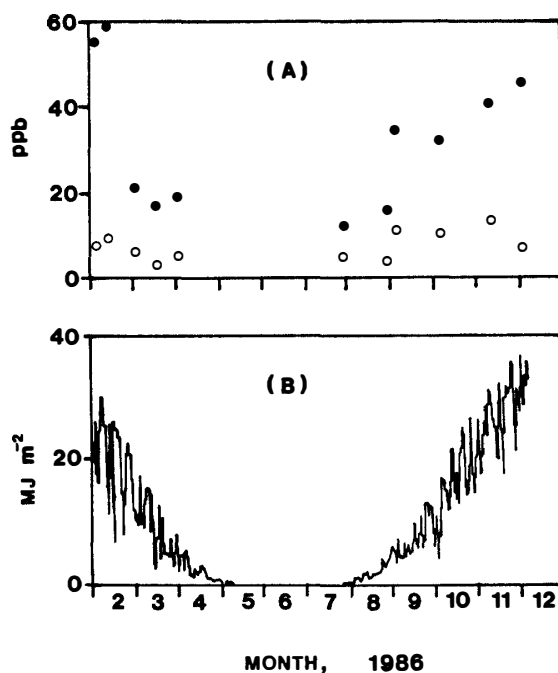
Fig. 3. Seasonal variations of formic (open circle) and acetic (closed circle) acid concentrations in snow drift from Mizoho Plateau (A), and solar radiation (B) monitored at Syowa Station (JAPAN METEOROLOGICAL AGENCY, 1988).

drocarbons by the OH radical or ozone, yielding water soluble aldehydes, (2) diffusion of the aldehydes into the aqueous layer such as cloud droplets and water film covering aerosols, and (3) transformation of the aldehydes to carboxylic acids by oxidation with OH radical.

An importance of the photochemical oxidation reaction in the Antarctic atmosphere is suggested by DELMAS et al. (1982). They concluded that a large portion of the SO_4 and NO_3 in Antarctic snow and ice was generated photochemically in the atmosphere. LEGRAND and SAIGNE (1988) suggested that formic acid in the Antarctic ice core sample would be transformed from atmospheric methane through the photochemical oxidation process.

High concentrations of formic and acetic acids, except for the case at the beginning of September, correlate with high levels of solar radiation (Fig. 3). This strongly suggests that volatile fatty acids in our snow drift samples are transformed photochemically in the Antarctic atmosphere from hydrocarbons with 1–4 or more carbon atoms. Except for high concentrations around September, the seasonal variations of formic and acetic acid concentrations resemble those of excess SO_4 (total minus sea salt-derived portion) and NO_3 anion concentrations for snow drift samples on Mizuho Plateau (OSADA et al., 1989). This supports the conclusion that most volatile fatty acids in our samples are photochemical products.

On the Antarctic Continent, there are no significant source points emitting hydrocarbons to be transformed to volatile fatty acids. Therefore, these hydrocarbons must originate from the ocean and partly from remote continental areas (DUCE et al., 1983) and are transported to Mizuho Plateau. ITO (1985) has observed that the atmospheric concentration of aerosols increases in the Antarctic summer. Liquid-

phase oxidation should act on these aerosols and on the quasi-liquid layer of snow particles and snow flakes. The fatty acid-containing aerosols can be removed from the atmosphere, directly or after in-cloud scavenging, by collision with drifting snow particles. Evaporation of some portion of volatile fatty acids from the aqueous layer on aerosols and snow particles and the re-diffusion into it are possible, modifying the relative abundance of each component.

KEENE et al. (1983) suggested that volatile fatty acids contribute significantly to the acidity of precipitation in the Southern Hemisphere. LEGRAND and SAIGNE (1988) found organic acids in the ice core sample in East Antarctica to be insignificant. In our snow drift samples, four fatty acids (C_1-C_4) taken together amount to 0.66 μE l^{-1} in annual mean. This concentration is less than 10% of the total inorganic anions (Cl^-, NO_3^-, SO_4^{2-}; 7.8 μE l^{-1}) determined by OSADA et al. (1989). This suggests that volatile fatty acids make a small contribution to the acidity in snow drift, if these acids are present in free form.

4. Concluding Remarks

Volatile fatty acids with carbon atom numbers from 1 to 4 were detected in the snow drift samples collected on Mizuho Plateau. This is the first report of the detection of C_3 and C_4 acids in Antarctica. Although these volatile fatty acids were in very low concentration, they showed a marked seasonal variation with a correlation to solar radiation. Based on this seasonal variation, we conclude that most volatile fatty acids are produced in the atmosphere by photochemical oxidation of hydrocarbons. This study suggests that a considerable amount of hydrocarbons should be transported into the inner regions of Antarctica from marine areas surrounding the Antarctic Continent. However, the information on hydrocarbons in the Antarctic atmosphere is not available at present. Studies on the hydrocarbons in the Antarctic atmosphere are required.

Acknowledgments

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