

VERTICAL PROFILES OF TOTAL ORGANIC CARBON AND POLAR ORGANIC COMPOUNDS IN THE ICE CORE FROM SITE-J, GREENLAND

Kimitaka KAWAMURA¹, Kazuhisa YOKOYAMA¹ and Yoshiyuki FUJII²

¹*Department of Chemistry, Faculty of Science, Tokyo Metropolitan University,
1-1, Minami-Ohsawa, Hachioji-shi, Tokyo 192-03*

²*National Institute of Polar Research,
9-10, Kaga 1-chome, Itabashi-ku, Tokyo 173*

Abstract: Forty two sections from a 206 m long ice core (*ca.* 450 yr old at the bottom) were studied for total organic carbon (TOC) content and distributions of polar organic compounds including C₂-C₁₀ dicarboxylic acids, C₂-C₄ oxocarboxylic acids, C₂-C₃ aldehydes and C₁₄-C₁₈ fatty acids. TOC contents in the ice core samples ranged from 0.7 to 5.7 ppm ($\mu\text{g/g-ice}$): however, no clear trend was observed in the vertical profile. Concentration ranges of total diacids, oxoacids, aldehydes and fatty acids were 3.1-32.4, 0.1-2.6, 0.09-1.7 and 0.01-11.1 ng/g-ice, respectively. Vertical profiles of diacids and fatty acids showed peaks at 6.9 and 32-35 m depths.

1. Introduction

Our preliminary study of ice core samples collected from Site-J, Greenland showed that polar organic compounds are present in the ice at concentration levels detectable by capillary gas chromatography and mass spectrometry (KAWAMURA and YASUI, 1991). These organic compounds have been considered to originate from biogenic sources such as marine phytoplankton as well as photochemical oxidation of both biogenic and anthropogenic organic compounds (KAWAMURA and KAPLAN, 1991). We extended the study to analyze 42 ice samples sectioned from a 206 m long ice core collected from Site-J, for polar organic compounds including dicarboxylic acids, oxocarboxylic acids, aldehydes and fatty acids. In this report, we present vertical profiles of their concentrations in the ice core as well as total organic carbon.

2. Samples and Analytical Methods

A 206 m long ice core was collected at Site-J, Greenland (66°51.9'N, 46°15.9'W, altitude: 2030 m) from May to June, 1989 (WATANABE and FUJII, 1990). The accumulation rate at Site-J was estimated by electric conductivity and volcanic eruption records: the 206 m layer has been estimated to be *ca.* 450 yr old (SHOJI *et al.*, 1991). Forty two sections were taken from the core and used in this study. The length of each section was 20-150 cm, which corresponds to from

ca. half to 4 yr. Core sample surfaces were removed from each section to avoid potential contamination before melting. The melt water samples were poisoned with mercuric chloride to prevent biodegradation and stored at 4°C in a pre-cleaned brown glass bottle with a Teflon-lined cap which prevents gas exchange during storage before analysis.

For TOC measurement in ice samples, a 4 ml melt water sample was taken in the pre-heated (450°C) glass screw vial (7 ml) with a Teflon-lined cap. After acidification with 1.2 M HCl solution (50 μ l), the sample was bubbled with helium gas for 3 min to purge dissolved carbon dioxide. A water sample (80 or 200 μ l) was injected to a Shimadzu TOC-500 carbon analyzer to determine total organic carbon by the high temperature catalytic oxidation (HTCO) method. Organic carbon in the ice melt sample was combusted with oxygen at 680°C in a platinum-coated alumina column, and the resulting carbon dioxide was determined by a non-dispersive infrared (NDIR) detector. Injection was repeated five times for each sample. Two data sets having the highest and lowest numbers were discarded. The remaining three values were averaged. Only averaged TOC values are presented here. The analytical error of this procedure was within 5 %. The TOC data presented here are corrected for the blanks.

Dicarboxylic acids, oxoacids, aldehydes and fatty acids were measured by the methods reported previously (KAWAMURA and YASUI, 1991). Briefly, an aliquot of the samples (100–150 ml) was concentrated by a rotary evaporator under a vacuum and dried with 14 % borontrifluoride in n-butanol to derive carboxyl groups and aldehyde groups to butyl esters and dibutoxy acetals, respectively. The ester and/or acetal derivatives were purified and analyzed by capillary gas chromatography (HP5890) and capillary GC-mass spectrometry (Finnigan-MAT ITS-40). Recoveries for diacids (C₂–C₉) were better than 70 %. Analytical errors in the procedures were within 25 % for diacids (C₂, C₃, C₄, C₅ and C₆), 15 % for ω -oxoacids (C₂–C₄), 15 % for aldehydes (C₂–C₃), and 28 % for fatty acids (C₁₆, C₁₈). The data presented here are corrected for blanks.

3. Results and Discussion

In all ice core samples, we detected dicarboxylic acids, ω -oxoacids, aldehydes and fatty acids. Table 1 gives concentration ranges and average concentrations of the compound classes as well as total organic carbon contents.

3.1. Total organic carbon

TOC contents in the ice core fluctuated from 0.7 to 5.74 ppm with an average concentration of 1.7 ppm. The average value is much lower than those reported in urban rainwater samples (5–10 ppm, LILJESTRAND and MORGAN, 1981; KAWAMURA and KAPLAN, 1991), but are on a similar level with the concentrations (1.2–1.3 ppm) reported for a rural site in New Hampshire (LIKENS *et al.*, 1983) and the remote marine atmosphere in the North Pacific (ZAFIRIOU *et al.*, 1980) although the lowest values (0.16–0.41 ppm) have been reported for the North Pacific atmosphere during the wet season (ZAFIRIOU *et al.*, 1980).

Table 1. Concentration ranges and average concentrations of polar organic compounds and total organic carbon in the 200 m ice core from Site-J, Greenland.

Compound classes	Concentrations (ng/g-ice)	
	Range	Average
Polar organic compounds		
Dicarboxylic acids (C ₂ -C ₁₀)	3.12-32.4	10.6
ω -Oxoacids (C ₂ -C ₄)	0.13-2.62	0.59
Aldehydes (C ₂ -C ₃)	0.09-1.72	0.46
Fatty acids (C ₁₄ -C ₁₈)	0.01-11.1	2.57
Total organic carbon	700-5740 (0.70-5.74 ppm)	1730 (1.73 ppm)

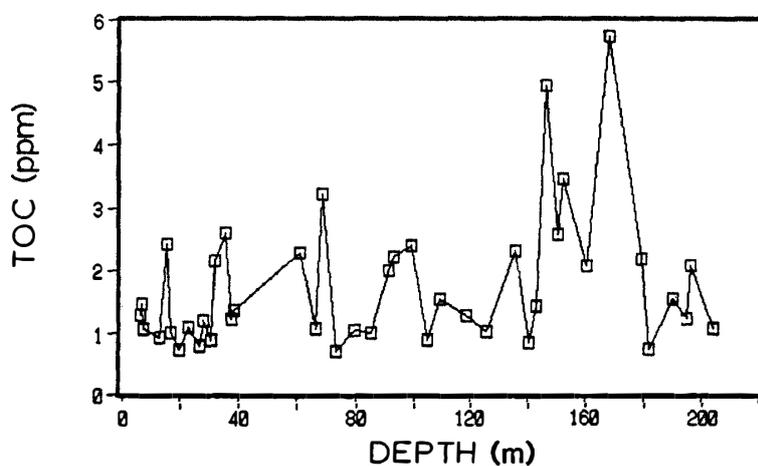


Fig. 1. Vertical profile of total organic carbon (TOC) content in an ice core from Site-J, Greenland.

Lower values (0.03–0.32 ppm) have been reported for dissolved organic carbon (DOC) contents in the snow samples collected from Dye 3, Greenland (TWICKLER *et al.*, 1986). The difference in carbon content between the Site-J ice core and Dye 3 snow samples is probably due to different sampling location and/or different sample preparation and analytical methods: the Site-J samples were measured for both particulate and dissolved organic carbon by the HTCO method whereas Dye 3 samples were analyzed only for dissolved organic carbon by wet oxidation under UV irradiation. The UV wet oxidation methodology is now realized to underestimate the carbon content values due to incomplete oxidation of organic carbon to carbon dioxide (SUGIMURA and SUZUKI, 1988).

The vertical profile of TOC in the ice core did not show a clear trend although higher concentrations were observed at some layers including 145–167 m depth (Fig. 1). We had expected TOC values to be higher in the surface layers due to enhanced emission in the 20th century of anthropogenic carbon to the atmosphere by fossil fuel combustion. However, no increase of TOC content in the upper ice layer was observed, suggesting that the major source of the organic carbon is not of anthropogenic origin. Rather, a significant portion of organic

carbon in the ice core may be derived from marine organic materials through sea-to-air emission and subsequent atmospheric transport.

3.2. Dicarboxylic acids

A homologous series of dicarboxylic acids were detected throughout the ice core from Site-J, as shown in Fig. 2. Interestingly, distributions of diacids in the ice samples are generally recognized by a predominance of succinic acid (C_4), following oxalic (C_2) acid as the second to third dominant diacid. This is in contrast to urban aerosol and rainwater samples, in which oxalic acid is always the major diacid species (KAWAMURA *et al.*, 1985; KAWAMURA and KAPLAN, 1987). This discrepancy between Greenland ice samples and urban atmospheric samples suggests that diacids in the ice samples are not directly derived from urban areas; rather, they are contributed from biogenic sources, probably associated with atmospheric photochemical activity.

Concentrations of total diacids ranged from 3.12 to 32.4 ng/g-ice in the 206 m ice core, as shown in Fig. 3a. Although they significantly fluctuated in the core with higher concentrations at 6.9, 31.8–35.2, and 167 m depth, the concentrations seem to increase at shallower depths. The diacids have been considered to be

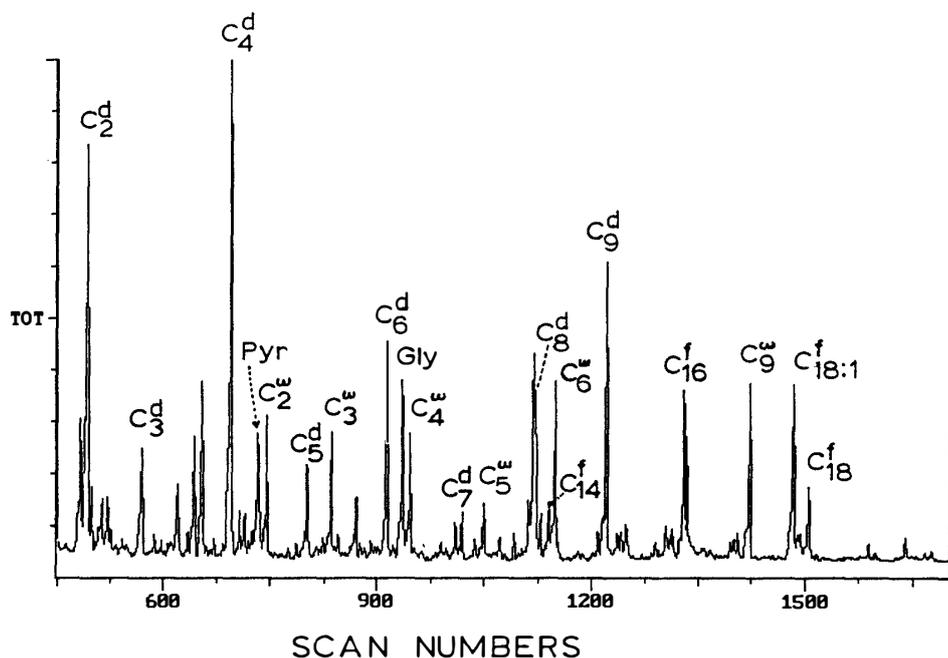


Fig. 2. Reconstructed total ion chromatogram (TOT) of polar organic compounds isolated from an ice core sample (#58, 26.4 m in depth: 1949 AD) collected at Site-J, Greenland.

GC-MS conditions; column: fused silica DB-5 capillary column (30 m \times 0.32 mm), column oven temperature: programmed from 50°C (1 min) to 120°C (30°C/min) then to 300°C (6°C/min), injection: splitless injector, data acquisition: every one second, mass range: m/z 35–500.

Abbreviation; C_n^d : α , ω -dicarboxylic acids with n carbon numbers, C_n^o : ω -oxocarboxylic acids with n carbon numbers, C_n^f : fatty acids with n carbon numbers, $C_{18:1}^f$: monounsaturated fatty acid with 18 carbon numbers (oleic acids), Pyr: pyruvic acid, Gly: glyoxal.

produced by photochemical oxidation of both anthropogenic organic matter such as cyclic olefins (GROSJEAN *et al.*, 1978) and biogenic compounds such as unsaturated fatty acids (KAWAMURA and KAPLAN, 1991).

3.3 ω -Oxocarboxylic acids

Figure 3b shows a vertical profile of ω -oxocarboxylic acids (C_2 – C_4) in the ice core. Although their concentrations fluctuated from 0.16 to 2.84 ng/g-ice, they showed few peaks at depths of 6.9, 31.8 and 167 m. These peaks are consistent with those of diacids (Fig. 3a). Although the origin of ω -oxoacids is not clearly understood at present, they are probably derived from photochemical oxidation of both anthropogenic and biogenic organic compounds.

3.4 Aldehydes

Aldehydes (glyoxal and methylglyoxal) were also detected in the 206 m ice core samples with concentration range of 0.09–1.72 ng/g-ice. Their vertical profile shows peaks at around 6.9, 31.8 and 104 m in depth (Fig. 3c).

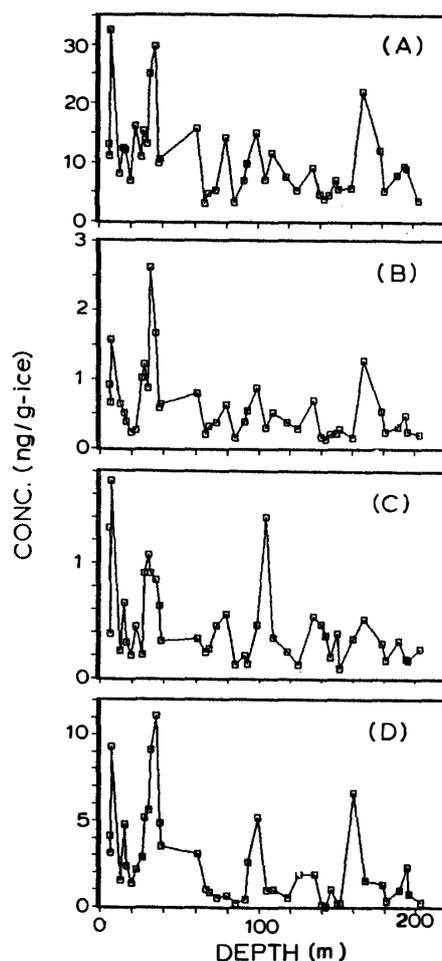


Fig. 3. Vertical profiles of (A) dicarboxylic acids (C_2 – C_{10}), (B) ω -oxocarboxylic acids (C_2 – C_4), (C) aldehydes (C_2 – C_3), and (D) fatty acids (C_{14} – C_{18}) in an ice core from Site-J, Greenland.

3.5. Fatty acids

Fatty acids (C₁₄–C₁₈) were detected in the ice core by the method used. These acids are of biogenic origin and are likely derived from marine sources such as phytoplankton (KAWAMURA and KAPLAN, 1991). Thus, vertical profiles of the acids may provide information on sea-to-air emission of biogenic organic matter and long-range transport over the Greenland ice sheet. The vertical profile of fatty acids showed four major peaks in the core at around 6.9, 35.2, 98.8, and 159.8 m depth (Fig. 3d). In the ages corresponding to above depths, it is probable that marine derived organic materials were abundantly supplied to the Greenland site through the atmosphere. The transport processes of marine organic matter are probably associated with changes in atmospheric circulation patterns in the past. The former two peaks are consistent with peaks of diacids, aldehydes and ω -oxoacids.

4. Concluding Remarks

Total organic carbon (TOC) was measured in a 206 m long ice core from Greenland with concentration range of 0.7–5.7 ppm. TOC contents did not show a clear trend with depth. Dicarboxylic acids, ω -oxocarboxylic acids, aldehydes and fatty acids were detected throughout the ice core. The vertical profiles of polar organic compounds did not show a clear increasing trend with time; rather, they showed significant fluctuations in the core with higher values at around 6.9 and 32–35 m depth. The study of these organic compounds in ice may provide information on past sea-to-air emission of marine derived organic matter and subsequent long-range transport over the Greenland ice sheet.

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