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Ice Core Record of Polycyclic Aromatic Hydrocarbons over the Past 400 Years

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Combustion-derived polycyclic aromatic hydrocarbons (PAHs) have been studied in environmental samples such as wet precipitation [1–3], aerosols [4, 5], and seawater [6] as well as marine [7] and lacustrine [8] sediments. Recent ice core studies have shown that some chemical species were useful tracers to reconstruct a past change in environments [9]. However, little attention has been paid to organic compounds in the ice core studies despite their potential usefulness. We have studied molecular distributions of PAHs in an ice core taken from Greenland by using combined gas chromatography and mass spectrometry (GC-MS). This report presents organic geochemical evidence in the ice core for the enhanced anthropogenic emissions from Northern Hemisphere countries and discusses the atmospheric transport of organic pollutants to Arctic regions.

An ice core (205 m long) was taken from Site-J, Greenland (66°51.9′N, 46°15.9′W, altitude 2030 m) in 1989 with a mechanical shallow drill by the Japanese Arctic Glaciological Expedition 1989 [10]. The ice core chronology was determined by electrical conductivity and volcanic eruption records: the 205-m layer was estimated to be ca. 450 years old [11]. The ages of the surface layers were confirmed by the determination of tritium (K. Izumi, pers. commun.). Twenty-six sections collected from the core samples were used in this study. The length of each section was 0.2–1.5 m, which corresponds to less than 6 months to 4 years. Most of the ice sections were less than the averaged annual accumulation rate (42 cm of ice or 38 cm of water [11]. To avoid potential contamination, the surfaces of each ice section were mechanically removed at –20 °C. The samples were then melted in a precleaned Teflon container in a clean room (20 °C). The meltwater was poisoned with mercuric chloride to avoid a microbial degradation of organic compounds. The samples were stored at 4 °C in a precleaned brown glass bottle with a Teflon-lined screw cap prior to analysis, which prevents gas exchange with the ambient air. A procedural blank was prepared using pure water.

The meltwater sample (ca. 350 ml) was extracted three times with a methylene chloride/ethyl acetate (2:1) mixture. The combined extracts were concentrated and then saponified with a 0.5 *M* KOH/methanol solution. Neutral compounds were separated from the acidic components in the saponified fraction by using a solvent extraction with n-hexane/methylene chloride (2:1). PAHs in the neutral fraction were further isolated by silica gel column chromatography and determined by a computerized capillary GC-MS system (Finnigan-MAT ITS 40). A fused silica capillary column (DB-5, 0.25 mm i.d., 30 m long, film thickness 0.25 μm) was used with the column oven temperature programmed from 50 °C (2 min) to 120 °C at 30 °C/min and then to 310 °C (20 min) at 6 °C/min. Quantification was performed based on the peak areas of the mass chromatogram at m/z M^+ (molecular ions) by using the authentic PAHs as external standards. The recoveries of 26 PAHs [from naphthalene to benzo(*ghi*)perylene] were 77–99 % (av. 93 %) in the analytical procedures from the solvent extraction to GC-MS measurement. Duplicate analyses showed that analytical error was within 7 %. The concentrations reported here are corrected for the procedural blanks, which include the processes from the melting of ice samples to the GC-MS determination. All the organic solvents were redistilled in the laboratory prior to use.

More than 40 PAHs, ranging from naphthalene (mw 128) to 2,9-dimethylpicene (mw 306), were identified in the ice samples. Major nonalkylated PAH species detected include dibenzothiophene, phenanthrene, fluoranthene, and pyrene. Other PAHs such as fluorene, anthracene, benzo(*b*)fluorene, benz(*a*)anthracene, benzo(*k*)fluoranthene, benzo(*e*)pyrene, and benzo(*ghi*)perylene were also detected in the samples as minor species. The PAH constituents detected in the ice samples have been reported in the fossil fuel combustion products (e.g., [12]) as well as in crude oils [13]. Alkylated PAHs such as methylphenanthrene were also detected in the samples and were sometimes more abundant than their parent compounds. The alkylated PAHs have been abundantly reported in the exhausts from internal combustion engines [14]. Similar distributions of the PAH constituents have been reported from the polluted atmosphere in gas and particulate phases [15]. These results indicate that organic pollutants emitted to the atmosphere in the mid-latitudes of the Northern Hemisphere are transported long distances over the Arctic regions, being similar to the cases of sulfate and nitrate [16].

The PAH compositions in the ice core samples are characterized by a predominance of relatively low molecular weight PAHs (such as phenanthrene, mw 178). This is in contrast to the molecular distributions of PAHs in aerosol samples collected from mid-latitudes, which usually indicate the predominance of higher molecular weight PAHs such as fluoranthene (mw 202), pyrene (mw 202), and benzo(*a*)pyrene (mw 252) [4]. The PAH distributions in wet precipitations, however, have shown the abundant presence of lower molecular weight species such as naphthalene (mw 128) and phenanthrene (mw 178) [2]. Further, lower aromatic hydrocarbons are important constituents of gaseous PAHs in the ambient atmosphere [15]. These considerations indicate that the PAHs detected in the Greenland ice sheet are scavenged from the atmosphere largely by wet (snow) precipitation, which efficiently removes PAHs present in both gaseous and particulate forms. Alternatively, dry deposition may also be important during the winter season when temperature is low enough to allow the adsorption of gaseous hydrocarbons on the aerosol particles.

Total concentrations of the major nonalkylated PAHs (dibenzothiophene, phenanthrene, fluoranthene, and pyrene) detected in the ice core sampes ranged from less than 1 pg/g ice to 230 pg/g ice. Figure 1 plots the individual PAH concentrations in the ice core as a function of age on the basis of running three-point means. The PAH concentrations were generally very low in the 16th to 18th century (hereafter, referred as C). They were still low in the 19th C, however, became higher in the early 20th C and very high in the late 20th C. Their total PAH concentrations (av. 103 pg/g ice) in the late 20th C is ca. 50 times more abundant than those (av. 2.3 pg/g ice) before the 18th C. The concentrations obtained for the late 20th C are comparable to those reported in the wet precipitations from urban areas (e.g., 60–1200 pg/g, av. 270 pg/g for Los Angeles rain [1, 2]). The historical trend of the PAH concentrations recorded in the ice core demonstrates that atmospheric transport of anthropogenic organic matter was enhanced after the 1930s, probably due to an enhanced atmospheric emission of fossil fuel combustion products in the Northern Hemisphere.

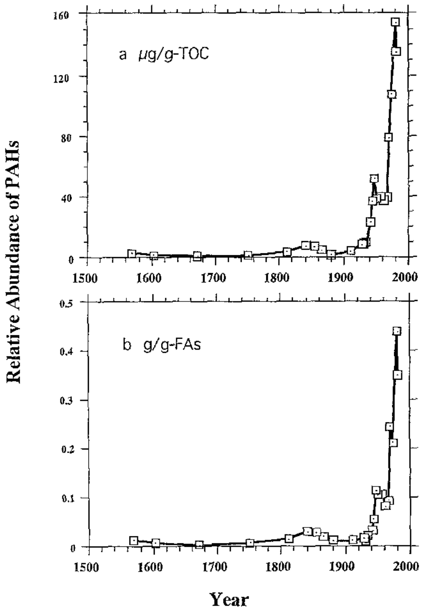

Fig. 2. Historical trend in the abundance of nonalkylated PAHs relative to a) total organic carbon (TOC) contents, b) long-chain fatty acids (C_{20}–C_{32}) of terrestrial higher plant origin in the Greenland (Site-J) ice core. The nonalkylated PAHs include dibenzothiophene, phenanthrene, fluoranthene, and pyrene. TOC data were from [18]. Fatty acid data were provided from Kawamura et al. (unpubl. results). The relative abundances are presented as three-point running means

A similar trend was obtained when the PAH concentrations (pg/g ice) were normalized by total organic carbon (TOC) contents (Fig. 2 a), whose concentration ranged from 0.7 to 5.7 ppm with no increasing trend in the late 20th century [18]. The same historical trend was also recognized in the concentration of the PAHs relative to those of fatty acids (C_{20}–C_{32}) of terrestrial higher plant origin (Fig. 2 b). These results demonstrate that contributions of anthropogenic PAHs relative to biogenic organic materials over the Greenland ice sheet have significantly increased since the 1930s. In other words, the anthropogenic emission

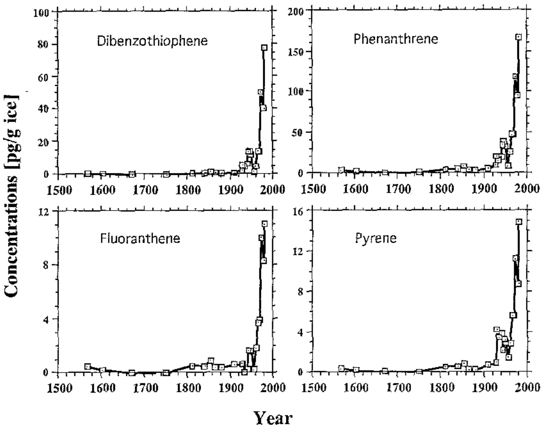

Fig. 1. Concentration changes in major nonalkylated PAHs in the Greenland (Site-J) ice core for the last 400 years. The original data were treated by three-point running means and plotted as a function of the year

levels found in the preindustrial period are less than 2% of the present level (Figs. 1 and 2), indicating a very low background level of PAH emission. An enhanced activity of human beings has been recorded in the acidity of the same ice core samples (Fujii and Kamiyama, in prep.): the pH decreased from 5.3 (1910 A.D.) to 5.15 (1980 A.D.). The Greenland ice core (Dye 3) study also showed that concentrations of nonsea salt sulfate and nitrate increased during the last 100 years, however, only by a factor of three [19]. In contrast to PAH, natural sources of excess sulfate and nitrate are significant due to volcanic activity and lightning in the atmosphere as well as photochemical oxidations of biogenic dimethyl sulfide, nitrogen oxides, etc. These considerations indicate that PAHs in the ice are powerful tools to reconstruct the enhanced activities of human beings.

The general trend of the PAH concentrations in the ice core is in good agreement with the historical record of the world petroleum production. A record of the world crude oil productions shows an exponential increase from 1900 to 1980 A.D. [17]. These comparisons clearly demonstrated that organic pollutants were transported over great distances to the Arctic regions and preserved in the ice layers with information of historical fossil fuel usage. Alkylated PAHs, which are constituents of crude oils [13] and are emitted to the atmosphere from internal combustion engines [14] as described above, were more abundant in the ice core samples than nonalkylated PAHs (see Table 1). Interestingly, the ratios of the alkylated to nonalkylated PAHs increased from 3.8 (before 1800 A.D.) to 9.9 (1950 A.D.). Changes in the qualitative distributions of PAHs suggest that the source of PAHs transported over the Greenland ice sheet has shifted from biomass burning, such as forest fires and wood burning, to fossil fuel combustion in the last 200 years.

The PAH concentrations fluctuated, showing lower values in 1880–1920 and 1950–1960 A.D. (Figs. 1 and 2). In general, a fluctuation of the PAH concentrations in the ice core can be caused by changes in snow accumulation rate, PAH emission rate to the air, and/or atmospheric circulation and the transport mechanism. There is no evidence to support a significant change in the snow accumulation rate in the ice core. On the other hand, the world crude oil production record suggests that atmospheric emission from combustion sources have exponentially increased in the 20th C [17]. Thus, the fluctuations might be associated with a past meteorological change. In fact, during 1880–1920 A.D., when lower PAH concentrations were observed (Fig. 2a), the Greenland winter temperatures were reported to be much lower than average [21]. In addition, a small decrease in PAH concentration in 1950–1960 A.D. seems to be consistent with the lower winter temperature recorded for the period [21]. These considerations lead to the suggestion that the distributions of chemical species preserved in the Greenland ice core may reflect a change in the atmospheric transport of chemical species caused by a change in the air circulation pattern at high latitudes.

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Table 1. Concentrations (pg/g ice) of nonalkylated and alkylated PAHs in the ice core from Greenland, Site-J. Nonalkylated PAHs include dibenzothiophene, phenanthrene, fluoranthene, and pyrene. Alkylated PAHs include methyl-, dimethyl-, and trimethylphenanthrenes, and methyldibenzothiophenes. The alkylated PAHs were tentatively quantified using the peak areas of M^+ ion and (M–15) or (M–1) ions relative to the M^+ ion of authentic standards

	1500–1799 (*n* = 5)	1800–1899 (*n* = 5)	1900–1950 (*n* = 8)	1951–1982 (*n* = 8)
Nonalkylated PAHs	2.3 ± 1.9	5.5 ± 2.9	26 ± 19	103 ± 77
Alkylated PAHs	9.4 ± 11	29 ± 27	190 ± 220	1000 ± 1490
Total	11 ± 13	34 ± 28	220 ± 240	1100 ± 1510
Alkylated/Nonalkylated Ratios	3.8	5.8	8.2	9.9

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Light-Induced Oxidation of Bisulfite-Aldehyde Adducts in Real Fog Water

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Aqueous-phase oxidation of sulfur dioxide or S(IV) forming sulfuric acid/sulfate ion is considered an important process in the generation of atmospheric acidified precipitation. Both laboratory and model studies have shown hydrogen peroxide, ozone, and O_2 in the presence of trace-metal catalysts to be the dominant oxidants [1–4]. In acidic atmospheric water droplets (below pH 5), the oxidation by H_2O_2 is believed to be a major pathway for the oxidation of dissolved SO_2 in the atmosphere [1, 3, 5]. The kinetics of this reaction have been examined by a number of researchers and are rapid under acidic conditions [3, 6]. However, field observations of fog, rain, and cloud water, in which H_2O_2 and a S(IV) species coexist, indicate that an inhibitor is present to reduce the rate of the oxidation of S(IV). This inhibition is caused by the formation of the adducts, hydroxyalkanesulfonates (HASA), between aldehydes, especially formaldehyde, and sulfite/bisulfite ions in atmospheric droplets [7–9]. Most HASA are resistant to oxidation by H_2O_2 and O_3 as well as by O_2/Fe^{3+} [7, 10–12]. Although studies have been done on both the occurrence of HASA in atmospheric waters and the mechanism and kinetics for the formation of HASA, little work addresses the oxidation of HASA in atmospheric waters [7–9, 13, 14]. We have conducted a study on the photochemical behavior of real fog waters, and present here a light-induced oxidation of S(IV)-aldehyde adducts and outline its probable mechanisms. The evidence for the coexistence of H_2O_2 and S(IV) is also shown.

Fog-water samples were collected in October 1989. A Teflon screen sampler was situated on the roof of the EAWAG building in Dübendorf (Switzerland) for the collections. After collection, the fog samples were filtered (0.45 µm) and analyzed. Table 1 presents values for selected parameters for the sampling periods in which S(IV) and H_2O_2 were measured in the fog water. Both S(IV) and H_2O_2, at significant concentrations, were found in these samples. The first three samples in Table 1 are characterized by high pH values with high concentrations of S(IV), and the following samples with both low pH and S(IV) concentrations, indicating that the S(IV) oxidation processes determined the acidity of the fog waters. To study the stability of H_2O_2 and S(IV) in these fog waters, the fog samples were kept in the dark at 4 °C and analyzed at intervals of time. No detectable change in the concentration of H_2O_2 or S(IV) was observed at least within 48 h (Fig. 1). Previous studies have shown that the oxidation of dissolved SO_2 by H_2O_2 is very fast. The depletion of H_2O_2 obeys the following empirical rate law [2]:

$$-d[H_2O_2]/dt = k[H^+]\ [H_2O_2]\ [\text{dissolved } SO_2], \quad (1)$$

where $k = 7.2 \pm 2.0 \times 10^7\ M^{-2}\ s^{-1}$. The lifetime of H_2O_2 is in the order of a few seconds under the conditions observed for these fog waters. The observed high stability of H_2O_2 and S(IV) indicated that S(IV) does not exist as dissolved SO_2 in these samples, but is combined

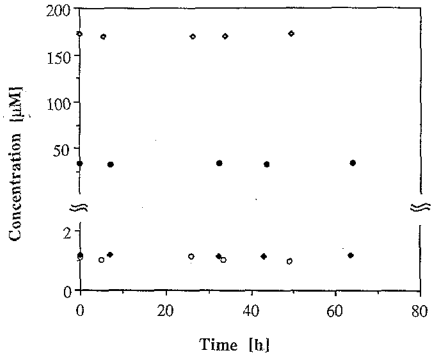

Fig. 1. Stability of H_2O_2 and S(IV) in fog waters. ◇, ● S(IV); ◆, ○ H_2O_2

Table 1. Concentrations of S(IV), H_2O_2, and other selected constituents in fog waters. The analytical methods have been reported elsewhere [16, 18]. S(IV) and CH_2O were determined as total S(IV) and CH_2O by adding a solution of NaOH to dissociate the HASA into bisulfite and aldehydes

Date	Start time	pH	S(IV) [µ*M*]	CH_2O [µ*M*]	H_2O_2 [µ*M*]	Dissolved Fe [µ*M*]
22 Oct.	07:30–08:30	4.32	206	55	0.51	31
27 Oct.	07:40–10:00	5.21	172	82	1.1	8.9
28 Oct.	02:20–03:30	4.89	109	68	0.38	2.8
	03:30–04:30	3.03	34	78	1.2	10
	04:30–05:45	3.03	44	80	1.2	5.4
	05:45–07:25	3.05	2	45	1.3	15
	07:25–10:30	4.18	31	63	0.82	17