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Distribution of dicarboxylic acids and carbon isotopic ratios in aerosols from 1997 Indonesian forest fires

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Abstract. Fine aerosol particles collected in Southeast Asia during 1997 Indonesian forest fires were studied for the concentrations of total carbon (TC), water-soluble organic carbon (WSOC) and low molecular weight dicarboxylic acids (C_2-C_{12}) as well as carbon isotopic ratios of TC ($\delta^{13}C_{TC}$). TC and WSOC showed a large increase during the heavy forest fire event. At the same period, dicarboxylic acids, dominated by oxalic (C_2) followed by succinic (C_4) and malonic (C_3) acids, also showed a concentration increase. Furthermore, the $\delta^{13}C_{TC}$ showed a decrease from ca. –25.5 to –27.5‰ during an intensified forest fire event, suggesting an addition of organic aerosols derived from C_3 plants whose $\delta^{13}C$ are lower. These results indicate that the aerosol particles in Southeast Asia were significantly affected by the combustion processes of vegetations during the 1997 Indonesian forest fires that were extensively induced by El Ninõ event.

Introduction

During a dry season of Southeast Asia, forest fires frequently occur and cause changes in the concentration and composition of aerosols in the tropical atmosphere. Such changes in the atmosphere should alter the optical and microphysical properties of tropical clouds and have a strong impact on radiation balance [*Andreae and Crutzen*, 1997]. *Novakov and Corrigan* [1996] reported that water-soluble organic components in smoke particles from smoldering biomass combustion are responsible for their intrinsic cloud condensation nuclei (CCN) activity. However, there are no detailed reports on the molecular composition of water-soluble organic fraction in aerosols associated with biomass burning. Characterization of water-soluble organic aerosols at molecular levels is necessary to better understand the changes in the atmospheric composition caused by forest fires.

Water-soluble organic aerosols that account for 20-67% of total carbon in aerosols [*Saxena and Hildemann*, 1996], have capability to act as CCN [*Novakov and Penner*, 1993; *Cruz and Pandis*, 1997; *Matsumoto et al.*, 1997]. Low molecular weight dicarboxylic acids are one of the most abundant water-soluble organic compound classes identified in aerosols [*Sempéré and Kawamura*, 1994], and may strongly contribute to CCN due to the hydrophilicity of their carboxyl groups. Dicarboxylic acids have been reported abundantly in aerosols from the urban [*Kawamura and Kaplan*, 1987; *Kawamura and Ikushima*, 1993;

Sempéré and Kawamura, 1994], marine [*Kawamura and Sakaguchi*, 1999] and polar atmosphere [*Li and Winchester*, 1993; *Kawamura et al.*, 1996].

A large-scale forest fire has occurred over Indonesia from August to October, 1997, that were induced by dry atmospheric condition associated with the large El Ninõ event in that year. In this study we collected fine aerosol particles in Southeast Asia and analyzed for total carbon (TC), water-soluble organic carbon (WSOC) and low molecular weight dicarboxylic acids as well as carbon isotopic ratios of TC ($\delta^{13}C_{TC}$). $\delta^{13}C$ analysis has been shown to be a useful approach to identify the origin of atmospheric carbonaceous aerosols, which are derived from either natural or anthropogenic sources [*Cachier et al.*, 1986]. Here, we report results of dicarboxylic acids and $\delta^{13}C_{TC}$ in aerosols collected during and after the large-scale forest fire and discuss the origin and production process of the organic aerosols.

Samples and Methods

Aerosol particles (diameters <2.1 μm) were collected on pre-combusted (450ºC, 3 hrs) quartz fiber filters (Pallflex, 2500QAT) using an Andersen low volume air sampler (Dylec, AN-200) on ground base. Figure 1 shows a map of sampling locations, with major forest fire sites. Samples were collected in Singapore (1°17'N, 103°51'E; October 17 to November 12, 1997), Pulau Seribu (6°02'N, 106°45'E; November 12-19, 1997) and Serpong (6°22'N, 106°39'E; November 19 to December 10, 1997). The Singapore samples were collected during the large-scale forest fires, whereas other samples were collected after major forest fires were over.

A part of the filter sample was cut off and subjected to an elemental analyzer (Calro Erba, NA1500) for the determination of TC. Aerosol samples were not decarbonated prior to the measurements because fine aerosols exclude calcium carbonate from soil and are acid by sulfate and nitrate. The combustion furnace was maintained at 850℃ and the resulted CO_2 was isolated on a gas chromatograph (GC) installed in the elemental analyzer system. The CO_2 was measured with a TCD detector and then introduced to isotope ratio mass spectrometer (Finnigan MAT, DeltaPlus) through an interface (Finnigan MAT, ConFloⅡ) for $\delta^{13}C$ measurement. The carbon isotopic ratios are expressed as $\delta^{13}C$ relative to PDB standard; $\delta^{13}C = [(^{13}C/^{12}C)_{sample}/(^{13}C/^{12}C)_{PDB}-1]\times 10^3$. The reproducibility of TC was 6% and the standard deviation of δ^{13}C measurements for laboratory standard was 0.1‰. For the WSOC measurement, a part of the filter sample was cut in pieces and extracted with pure water. The water extracts were then filtered on Pallflex quartz fiber filter to remove particles and filter debris, and acidified with 1.2M HCl. After purging dissolved inorganic carbon with pure air, WSOC was measured with a carbon analyzer (Shimadzu, TOC-5000). The reproducibility of WSOC measurements was 9%. By operational definition, WSOC excludes volatile organic carbon that may be removed during the HCl acidification of the water extracts.

An aliquot of the filter sample was also extracted for the isolation of dicarboxylic acids with pure water. The extracts were concentrated and then esterified with 14% borontrifluoride in n-butanol to derive dicarboxylic acid dibutyl esters. The dibutyl esters were determined by a capillary GC (Hewlett-Packard, HP6890) equipped with a split/splitless injector, fused silica capillary column (HP-5, 25m × 0.2mm i.d. × 0.5μm film thickness) and an FID detector. For the peak identification, authentic diacid dibutyl esters were used as external standards. The compounds were also identified with a GC/mass spectrometer (ThermoQuest, Voyager). Detailed analytical procedures for the diacids are described elsewhere [*Kawamura and Ikushima*, 1993]

Results and Discussion

Temporal variations of aerosol TC and WSOC concentrations are shown in Figure 2. Concentration ranges of TC and WSOC were 9.1–81 μgCm^{-3} and 0.42–25 μgCm^{-3}, respectively. Highest concentrations of TC and WSOC were observed during the intensified haze events, whereas lowest values (background) were obtained after major forest fires were over. TC and WSOC concentrations during the haze events were ca. 10 and 20 times higher than the background, respectively. Although the Singapore data appear to be influenced by local urban pollution, these results clearly indicate that the forest fires largely affect TC and WSOC contents in the aerosols. The amplitude of WSOC peak relative to the background is greater than that of TC (Figure 2), suggesting that the production of water-soluble organic carbon is heavily involved with the combustion of vegetations.

WSOC was found to account for 5–32% of TC. WSOC/TC ratios (av. 29%) during the haze events were found to be higher than the background (av. 16%). *Novakov and Corrigan* [1996] reported that WSOC/TC ratios are more than 40% for smoldering combustion of vegetation, whereas the ratio is only 5% for the flaming combustion. Our results suggest that the increased WSOC contents during the haze events were mainly derived from smoldering combustion process of the vegetation. However, flaming combustion should also contribute to the production of WSOC, because hot spots of the fires have been seen over Indonesia by satellite.

In accordance with the TC increase as described above, $\delta^{13}C_{TC}$ were found to decrease from ca. –25.5 to –27.5‰ (Figure 3), indicating that the aerosol carbon sources were significantly changed. An anti-correlation obtained between TC concentration and $\delta^{13}C_{TC}$ suggests that isotopically lighter carbon was emitted to the atmosphere during the forest fires and attached to the aerosols. Indonesian tropical rain forests consist of C_3 plants, which are generally depleted in ^{13}C ($\delta^{13}C$ range: –20 to –30‰; mean: –26‰) than C_4 plants ($\delta^{13}C$ range: –10 to –18‰; mean: –12‰) [*Deines*, 1980]. *Turekian et al.* [1998] reported that carbon isotopic fractionation in the organic aerosols during combustion of C_3 plants was not pronounced. The depletion of ^{13}C observed during the forest fire events might be caused by the atmospheric emission of organic particles derived from combustion of C_3 plants.

A homologous series of diacids (C_2-C_{12}) dominated by oxalic acid (C_2) followed by succinic (C_4) and malonic (C_3) acids were detected in the aerosol samples with the maximum concentrations during the intensified haze events. Diacids except for adipic acid (C_6) showed temporal variations similar to TC and WSOC. Concentration range of total diacids (TDA) was 87-3800 ngm^{-3} (Figure 4a). TDA were found to account for 2-8 % of WSOC in this study. These values are less than those (4-15%) reported in the Tokyo atmosphere, where photochemical production of diacids is important by gas-to-particle conversion of volatile organic compounds and heterogeneous reactions on aerosol surface [*Kawamura and Ikushima*, 1993; *Sempéré and Kawamura*, 1994]. Also, diacids are directly emitted by an incomplete combustion of fossil fuels [*Kawamura and Kaplan*, 1987]. These results suggest that major portion of the diacids were not likely produced in the haze by the secondary photochemical process. Rather, diacids might be formed by the combustion processes of vegetation. Photochemical evolution of organic aerosols might be not significant in the haze.

Oxalic acid whose distributions ranged from 22 to 2400 ngm^{-3} (Figure 4b) was found to be the most abundant diacids. Oxalic acid has been suggested to be formed in the atmosphere as a secondary product by the oxidation of aromatic hydrocarbons [*Norton et al.*, 1983]. Large enhancement of tropospheric ozone has been observed during 1997 Indonesian forest fires [*Tsutsumi et al.*, 1999] and hydrocarbons are known to be emitted by biomass burning [e.g., *Ferek et al.*, 1998]. Thus, it is likely that diacids are formed in the hazy atmosphere by gas-to-particle conversion of the volatile hydrocarbons emitted during forest fires. However, as stated above, we consider that combustion processes of the tropical plants primarily control the distribution of diacids in the atmosphere during the Indonesian forest fire event.

Although most diacids showed a temporal variation similar to oxalic acid, adipic acid showed a different variation. Adipic acid whose concentration ranged from 1.2 to 340 ngm^{-3} (Figure 4c) gave a maximum concentration during a weakened forest fire period. Adipic acid has been reported as one of the oxidation products of cyclohexene [*Hatakeyama et al.*, 1985], however, it is also a precursor of 6,6-nylon, a synthetic polymer used for fiber materials. This temporal variation suggests that adipic acid was not derived from forest fires. Rather, it might have originated from local anthropogenic source near the sampling location. In contrast, azelaic acid (C_9) whose concentration ranged 1.2 to 58 ngm^{-3} (Figure 4d), is known to derive from the atmospheric oxidation of biogenic unsaturated fatty acid containing a double bond predominantly at C-9 position [*Yokouchi and Ambe*, 1986; *Kawamura and Gagosian*, 1987; *Stephanou*, 1992]. This acid showed a temporal variation similar to oxalic acid. It is likely that azelaic acid was formed by the oxidation of unsaturated fatty acid during combustion processes, and that combustion of vegetation was the main source of the enhanced haze in Southeast Asia.

In summary, total carbon, water-soluble organic carbon and low molecular weight dicarboxylic acids were found to be significantly produced in the atmosphere of Southeast Asia during forest fires. Apparent depletion of ^{13}C of aerosol carbon suggested that particulate carbon was added to fine aerosol particles as a result of combustion of C_3 plants. This study also suggested that photochemical evolution of organic aerosols was not significant in the haze during the forest fire events.

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Captions

Figure 1. Map of sampling locations in Southeast Asia with major forest fire sites.

Figure 2. Temporal variations of concentrations of (a) total carbon (TC) and (b) water-soluble organic carbon (WSOC) in aerosol samples (D_p<2.1 μm) collected in Southeast Asia, 1997; ●: Singapore, □: Pulau Seribu, ×: Serpong. Shaded areas mean that Singapore was heavily covered with thick haze according to TOMS aerosol index, and lay on the down winds from fire hot spots.

Figure 3. Correlation of carbon isotopic ratio ($\delta^{13}C_{TC}$) and concentration (μgCm^{-3}) of TC in aerosol samples (D_p<2.1 μm) collected in Southeast Asia, 1997; ●: Singapore, □: Pulau Seribu, ×: Serpong.

Figure4. Temporal variations of concentrations of (a) total dicarboxylic acids (TDA), (b) oxalic acid (C2), (c) adipic acid (C6) and (d) azelaic acid (C9) in aerosol samples (D_p<2.1 μm) collected in Southeast Asia, 1997; ●: Singapore, □: Pulau Seribu, ×: Serpong. For shaded area, see Figure 2.