



Volatile organic compounds in ambient aerosols

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ABSTRACT

In order to investigate the concentration levels of volatile organic compounds (VOCs) in ambient aerosols, monocyclic aromatic hydrocarbons (MAHs) and chlorinated hydrocarbons (CHs) in the particulate phase were measured simultaneously with those in the gas phase in the urban atmosphere. Six compounds were detected in the aerosols at concentrations from 0.051 (1,2-dichloroethane) to 1.75 ng m⁻³ (benzene). Benzene was detected as the most dominant compound in the aerosols, although toluene was the most dominant compound in the gas phase. The VOCs in the aerosols had concentrations comparable to those reported for some semi-volatile organic compounds (SOCs) in the aerosols. The concentrations of the VOCs in the aerosols were primarily controlled by the aerosol mass loading. Temperature and relative humidity had no significant effect on the gas/particle partitioning of the VOCs. Our results also suggested that the hygroscopic properties of the aerosols should be considered to discuss the partitioning of the VOCs.

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1. Introduction

Atmospheric volatile organic compounds (VOCs) have been recognized to have significant impacts on atmospheric chemistry and human health. Although there are a number of VOCs in the ambient atmosphere, monocyclic aromatic hydrocarbons (MAHs) and chlorinated hydrocarbons (CHs) have been often focused on in atmospheric environmental studies due to their toxic effects on human health. MAHs have also been significant contributors to the formation of ozone (Carter, 1994; Chiang et al., 2007) and secondary organic aerosols (Koo et al., 2003; Volkamer et al., 2006) in the urban atmosphere.

Most of the studies concerning these VOCs have targeted the gas phase because almost all of these VOCs exist in the gas phase. Recent studies, however, demonstrated that some VOCs were detected in the particulate phase in the ambient atmosphere (Hamilton et al., 2004; Khanal and Shooter,

2004; Odabasi et al., 2005) at the same concentration levels as the semi-volatile organic compounds (SOCs) such as polycyclic aromatic hydrocarbons (PAHs), although the VOCs were mostly found in the gas phase. For instance, Odabasi et al. (2005) reported that 27 VOCs with the concentrations of 1–933 pg m⁻³ were detected in the aerosols, although 99.9% of the VOCs were found in the gas phase. The existence of VOCs in the particulate phase could be potentially important for discussing their effects on human health because submicron particles have significant influences on respiratory organs (Dockery et al., 1993; Pope et al., 1995). In addition, removal efficiency of atmospheric species through dry and wet processes are largely different between gas and particulate phases, which suggests potential impact of the VOCs in the aerosols on the transport of the VOCs from atmosphere to earth surface including hydrosphere and biosphere. The concentration levels of the VOCs in the particulate phase and their partitioning between the gas and particles, therefore, are interesting in the discussion concerning the environmental effects of the VOCs. This paper shows the measurements of the MAHs and CHs in the ambient aerosols in the urban atmosphere and discusses the factors controlling the gas/particle partitioning of these VOCs.

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2. Experiment

Gas and aerosol samples were simultaneously collected on the roof of a six-story building on the campus of Kanagawa University in Yokohama, a large industrial and commercial city with a population of 3.6 million. The sampling site is surrounded by a residential area at a distance of about 3 km from a large industrial area near the ocean. Collections of the samples were conducted on 37 days randomly selected from September 2006 to August 2007. The sampling intervals of the particle samples were generally 24 or 48 h. Gas samples were collected simultaneously with aerosol samples but the sampling intervals of them were generally 3 h.

Monocyclic aromatic hydrocarbons (MAHs) and chlorinated hydrocarbons (CHs) were targeted in this study. The gaseous MAHs and CHs were collected on an adsorbent consisting of Carboxen 1000 (Supelco Inc., 140 mg, 60/80 mesh size) and Carbopack B (Supelco Inc., 190 mg, 60/80 mesh size), which was filled in a glass thermal desorption tube (Shimadzu GLC, Ltd., 6.35 mm o.d. × 4 mm i.d. × 8.89 cm), at the flow rate of 50 ml min⁻¹. The glass tubes were previously conditioned at 100, 200, 300, and 350 °C for 2 h (30 min for each temperature step) by purging them with high-purity helium (>99.9999%) at 150 ml min⁻¹, and then heating again at 300 °C for 30 min just before sampling. To avoid water condensation on the adsorbent and the destruction of the collected VOCs by ozone during the air sampling, a polypropylene tube filled with Mg(ClO₄)₂ and an ozone scrubber (Waters Corp., Sep-Pak ozone scrubber) were connected in series to the inlet of the glass tube, although interferences of the Mg(ClO₄)₂ and ozone scrubber on the collection of the VOCs were not investigated in this study.

Ambient aerosols with diameters smaller than 10 μm were collected on a quartz fiber filter (Toyo Roshi Kaisha, Ltd., QR100) by a high-volume air sampler equipped with a preseparator (Shibata Scientific Technology, Ltd., HV-1000F). To investigate the size distributions of the VOCs in the aerosols, two size-fractionated aerosol samples with diameters smaller than 2.0 μm (fine mode) and of 2.0–10 μm (coarse mode) were also collected on the filters using a NILU filter holder with a two-stage impactor (Tokyo Dylec Corp., NL Series). After the aerosol collections, the filter was finely cut and inserted into the empty glass thermal desorption tube. The ends of the glass tube were plugged with inert silica wool. Analytical blank of the MAHs and CHs including the filter blank ranged from 6.5% (toluene) to 33.3% (ethylbenzene) of the sample measurements. These blanks were subtracted from the sample measurements. In order to check the adsorption of the gaseous VOCs on the filter, a back-up filter was set behind the aerosol collection filter. The amounts of m,p-xylene and o-xylene found in the back-up filters reached 40–50% of the sample measurements. Except for both compounds, the VOCs amounts in the back-up filters were similar to the levels of those in the analytical blanks. These results indicate that the adsorption of the gaseous VOCs on the filter can be negligible except for m,p-xylene and o-xylene, but the measurements of both compounds would be overestimated.

For analysis of the MAHs and CHs in the samples, a gas chromatograph/mass spectrometer (GC/MS) system (Shimadzu Corp., GCMS-QP2010) connected to a thermal desorption (TD) system (Shimadzu Corp., TDTS-2010) was used.

The chromatographic column was VOCOL (Supelco Inc., 60 m × 0.25 mm i.d., 1.5 μm film thickness) and the carrier gas was helium at 3.0 ml min⁻¹. Desorption of the MAHs and CHs from the adsorbent or sample filter in the glass tube was conducted by the TD system at 280 °C with helium at 50 ml min⁻¹. The temperature program of the GC was as follows: 40 °C for 5 min, 40–140 °C at 8 °C min⁻¹, 140–200 °C at 15 °C min⁻¹, and then 200 °C for 7 min. Quantification of each compound was achieved by using the areas of them relative to an internal standard (fluorobenzene).

3. Results and discussion

3.1. Measurements of VOCs in the gas and particulate phase

During the observation period, 31 aerosol samples, including 7 size-fractionated samples, were simultaneously collected with 231 gas samples. Table 1 summarizes the measurements of the MAHs and CHs in the gas phase. Sixteen compounds were detected in the gas phase, of which the concentrations ranged within the values reported by the other recent investigations at urban sites in Japan (Yamamoto et al., 2000; Sato et al., 2006). Toluene was determined as the most dominant compound in the gaseous MAH and CH groups, which is similar to past studies in urban atmospheres (Yamamoto et al., 2000; Ho et al., 2004; Sato et al., 2006).

In this study, 6 compounds were detected in the particulate phase, of which the concentrations are also summarized in Table 1. The mean concentrations of the VOCs in the aerosols ranged from 0.051 (1,2-dichloroethane) to 1.75 ng m⁻³ (benzene). Benzene was detected as the most dominant compound in the aerosols, followed by toluene. The VOCs in the aerosols had comparable concentrations to those reported for some SOCs such as polychlorinated biphenyls (PCBs) and PAHs (Tasdemir et al., 2004; Vardar et al., 2004). The concentration ratio of the VOCs in the aerosols to those in the gas phase ranged from 10^{-4.8} (ethylbenzene) to 10^{-2.9} (benzene). The VOCs were mostly found in the gas phase.

Large portions of the VOCs in the aerosols were detected in the fine mode range. The ratios of the VOC concentrations in the fine mode to their sum in both modes are also summarized in Table 1. Mass concentrations of fine particles were nearly twice as high as those of coarse particles at the site (Takeuchi et al., 2004), which would lead the VOCs to be distributed mainly in the fine mode range because the VOC concentrations were largely dependent on aerosol mass concentrations as discussed later. In addition, higher aerosol surface concentrations in the fine mode range compared to those in the coarse mode range, which has been generally found in urban atmosphere (Whitby and Sverdrup, 1980), can be also attributable to the size fractionation of the VOCs in the aerosols.

3.2. Factors controlling the concentrations of the VOCs in the aerosols

Comparisons of the concentrations of benzene in the aerosols to those of gaseous benzene and aerosol masses are shown in Fig. 1a and b, respectively. Mass concentrations of the aerosols with diameters less than 10 μm by a β-ray absorption technique were obtained from an ambient air

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