Gas-aerosol partitioning of semi volatile carboxyls in polluted atmosphere in Hachioji, Tokyo

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1 Atmospheric fine particles are known to have an important role in the ambient atmosphere [Bidleman, 1988; Andreae and Crutzen, 1997]. However, their production processes and the factors controlling gas particle partitioning are not well known and still have large uncertainties. Recent laboratory experiments have revealed some of the production processes and the gas particle partition mechanism. Jang and Kamens [2001] proposed that sulfuric acid can act as a catalyst to change carboxyls to lower vapor pressure forms such as acetal, hemi-acetal and polymers [see also Jang et al., 2003; Berndt et al., 2004]. Indeed, oxidation products of monoterpenes and isoprene and other carbonyl compounds have been observed in ambient aerosols in spite of the relatively high vapor pressures [Kavouras et al., 1998; Kavouras and Stephanou, 2002; Limbeck et al., 2003; Matsunaga et al., 2003, 2004a]. The gas particle partition of these semi volatile compounds includes adsorption onto the aerosol, dissolution into the liquid water phase and absorption into the organic matter phase in the aerosol [Finizio et al., 1997; Finlayson-Pitts and Pitts, 1999]. The partition of polar and low molecular weight compounds such as semi volatile organic compounds (SVOCs) is thought to be mainly controlled by dissolution and absorption. Therefore, their partitioning could be changed by the composition of the ambient aerosol. Some equations for the gas-aerosol equilibrium constant have been proposed [Yamasaki et al., 1982; Pankow, 1987, 1994a; Odum et al., 1996; Seinfeld and Pandis, 1998]. The equilibrium constant Kp is given below:

\[ K_p = \frac{[\text{Gas}]/[\text{Particle}]/\text{TSP}}{F/A/\text{TSP}} \]

where, TSP, F and A are total suspended particulate matter, fraction of the compound in organic matter phase in the aerosol and gas phase concentration of the compound, respectively.

2 The chemical and physical properties of gases and particles can be substantially different, even if they have the same chemical composition. Therefore, studies on the gas particle partitioning are very important for understanding climate and air quality. This means that the physical state of atmospheric constituents can be as important as their chemical composition. Atmospheric carboxyls are a major component of atmospheric semi volatile constituents but there are few reports which describe the gas particle partitioning of SVOCs in real ambient air. Here we discuss the variation of gas particle partition coefficients of semi volatile organic compounds obtained in a field experiment, and its relationship with air quality.

2. Experiment

The field experiment was conducted from May 12th to May 15th, 2004. The sampling site was a faculty of engineering building on the campus of Tokyo Metropolitan University, Hachioji, Tokyo (35°37’03”N, 139°23’09”E). Hachioji is a moderately populated city located 30 km west of central Tokyo. The SVOCs and NMHCs were collected on the roof of the 6th floor, and other instruments were deployed in a laboratory on the 3rd floor of the building.

3 Gaseous and particulate SVOCs were collected with an annular denuder sampling system (ADSS) which consists of a 1st denuder tube, a quartz fiber filter and a backup denuder tube. These annular denuder tubes were coated with O-benzylhydroxylammonium chloride (BHA). The SVOCs trapped on the inner wall of the denuders are immediately derivatized to their benzylhydroxyl oximes by the coated BHA. The derivatives in the denuder tubes were extracted with methanol at the site. The extract from

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Figure 1. $K_p$ values of semi volatile dicarbonyls (glyoxal, methylglyoxal and 4-oxopentanal) against the concentrations of anthropogenic pollutants. (a) benzene, (b) isopentane and (c) SO$_2$. Vertical bars indicate uncertainty of the $K_p$ values due to change in the aerosol density and analytical error. Horizontal bars indicate uncertainty of measured value. See color version of this figure in the HTML.

3. Results and Discussion

[a] The TSP is estimated from the number concentration and diameter of aerosols obtained by a particle counter by assuming that aerosols are spherical and that their averaged density is 1.5 g cm$^{-3}$ [Stein et al., 1994; Pitz et al., 2003]. The aerosol density also has a variability of approximately ±33% [Pitz et al., 2003], vertical error bars in Figures 1a–1c indicates uncertainties of the $K_p$ values due to change in the density. Although the site was dry (relative humidity at the site was less than 60% during the field experiment.), it is likely that some part of the aerosols had liquid water phase due to deliquescence. In addition, a major part of the aerosols probably had a liquid organic matter phase which can absorb the SVOCs. Therefore, we expect that the gas particle partition of the SVOCs includes not only adsorption but also dissolution and absorption into the liquid phase. Indeed, Henry’s law constants of glyoxal and glycolaldehyde are very large (3.6 × 10$^5$ (in seawater) [Zhou and Mopper, 1990] and 4.1 × 10$^4$ mol kg$^{-1}$ atm$^{-1}$ [Betterton and Hofmann, 1988], respectively).

[7] Figures 1a–1c shows for the relationship between log $K_p$ of three dicarbonyls and the concentrations of three anthropogenic species. Glyoxal is an oxidation product of numerous precursors, methylglyoxal also has many precursors including isoprene, 4-oxopentanal is mainly derived from biogenic precursors [Fruekilde et al., 1998; Matsunaga et al., 2004b]. Both benzene and isopentane are typical hydrocarbons derived from fossil fuel combustion [Hewitt, 1999]. Because Tokyo city currently has a limited SO$_2$ source, the concentration of SO$_2$ at the site does not control the acidity of the aerosols. If the SO$_2$ concentration indicated the acidity of the aerosol, then the $K_p$ values should increase with SO$_2$ concentration, because high acidity can change carbonyls to their lower vapor pressure forms with acid catalyzed reactions [Jang and Kamens, 2001; Berndt et al., 2004]. In addition, sulfuric acid is deliquescent, therefore, sulfuric acid should drive the gas particle equilibrium of the polar carbonyls to particle phase. However, the results show the opposite trend. Therefore, we can regard the SO$_2$ concentration only as a tracer of anthropogenic pollution at the site. Indeed, SO$_2$ concentration also showed a good positive correlation with CO and NO$_2$. Because the source of SO$_2$ in Tokyo is primarily limited to the Tokyo Bay area and because the sampling site is located 40 km from the coast, SO$_2$ concentrations are unlikely to be disturbed by local emission. This might lead to a better correlation between SO$_2$ and a cryo focus GC/FID system [Kato et al., 2001]. CO and SO$_2$ concentrations were measured with commercial analyzers (Model 48C, Model 43C and Thermo Electron, respectively). Particle number concentration and size distribution were also monitored with a commercial particle counter (Model 237A, Met One). Particles were counted as a pulse of scattered laser light, and their diameters were distinguished to 5 diameter classes by the intensity of the scattered light. NO$_2$ was measured by photolytic conversion followed by ozone chemiluminescence. The ambient NO$_2$ was converted to NO using a photolytic converter (PLC760, Eco Physics) and then detected by ozone chemiluminescence (CLD770AL ppt, Eco Physics).
concentration and the $K_p$ values than that of benzene, isopentane, CO and NO$_2$.

The log $K_p$ was inversely proportional to the concentrations of these anthropogenic pollutants. Hydroxycarbonyls show the same trend as dicarbonyls. As mentioned above, the partitioning coefficient $K_p$ should be significantly affected by efficiencies of the dissolution into the liquid water phase and/or absorption into the organic matter phase of the aerosol. However, the $K_p$ value did not show a clear relationship with relative humidity. It is likely that the increase in [Particle]/[Gas] may be canceled out by the increase in the TSP value ($\mu$g m$^{-3}$) with higher relative humidity because of growth of the aerosols by the deliquescence, thus we could not see a positive relationship between the $K_p$ value and humidity. On the other hand, a larger fraction of the anthropogenic pollutants in the atmospheric particles may lead the average polarity (including external mixing of polar and non-polar aerosols) of the ambient aerosols to be non-polar (e.g. an increase in the amount of elemental carbon, semi volatile and non-polar hydrocarbons). Dicarbonyls and hydroxycarbonyls generally have high polarity and also can exist as acetal, hemi-acetal and other derivatives, which also have polar molecules [Jang and Kamens, 2001]. Therefore, it is likely that the lower polarity of the organic matter phase in the aerosol could decrease the solubility of the SVOCs. Assuming that the gas and particulate SVOCs had achieved equilibrium, the results presented in Figures 1a–1c suggest that an increase in the anthropogenic pollutants drove the gas particle equilibrium of the SVOCs to the gas phase. However, this trend was not observed in the case of aliphatic aldehydes, which may be caused by the large non-polar component of their structure. The aliphatic aldehydes may be able to be absorbed in the non-polar organic phase like a surfactant with their long alkyl chain.

In this manuscript, we have discussed the gas particle partition of SVOCs and proposed the possibility that polluted air quality can drive the gas particle equilibrium of the SVOCs to the gas phase. We also observed an interesting relationship between the $K_p$ and particle number concentration. Because the concentration of SO$_2$ was proportional to fine particle number concentration (see Figure 2a, this trend was also observed in other pollutants), the $K_p$ values also showed an inverse correlation with the particle number (see Figure 2b). Hydroxycarbonyls also showed almost the same trend. Figure 3 shows a temporal variation of the $K_p$ of glyoxal, total concentration of VOCs and SVOCs, ambient temperature, relative humidity, concentrations of NO$_x$ and ozone concentration through the experiment. CO concentration ranged from

![Figure 2](image1.png)

**Figure 2.** (a) Plot of SO$_2$ concentration against fine particle number concentration (500–700 nm and 700–1000 nm). (b) The $K_p$ values of dicarbonyls against the particle number concentration same as (a). The vertical bars indicate uncertainty of the $K_p$ due to variability of the aerosol density. See color version of this figure in the HTML.

![Figure 3](image2.png)

**Figure 3.** Temporal variations of the $K_p$ of glyoxal, total concentration of VOCs and SVOCs, ambient temperature, relative humidity, concentrations of NO$_x$ and ozone. See color version of this figure in the HTML.
150 to 1780 ppbv (average; 469 ppbv, median; 422 ppbv). The $K_{sp}$ showed a decrease despite the high relative humidity in the afternoon on the 14th. These results were totally different from observations in the forest atmosphere where gas particle partition depended on the number concentration and relative humidity [Matsunaga et al., 2004a]. It is very likely that this is because the seed aerosol in the forest atmosphere mainly contains water and the oxidation products of biogenic organics [Kavouras et al., 1998] which can effectively absorb the polar SVOCs and their derivatives. These results suggest that the process where an aerosol seed accumulates semi volatile compounds is very different in polluted urban air and remote air due to differences in the average aerosol properties. This could be a very important factor in determining the processes controlling aerosol production and growth and requires additional studies.

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