Atmospheric partitioning of bifunctional carbonyl compounds near a roadside in a suburban area

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Abstract:

Bifunctional carbonyls are ubiquitous in the atmosphere production of methylglyoxal alone has been estimated around 140 Tg per year globally. Bifunctional carbonyls are also important contributors to atmospheric aerosol through heterogeneous reactions; however their real contribution to atmospheric aerosol in the atmosphere has been little measured due to their capacity to coexist in gaseous and particulate phases which increases the difficulty to sample them in both phases simultaneously. We measured the atmospheric partitioning of semivolatile species in order to understand their contribution to atmospheric aerosol with a shorter time-resolution (2 h.). Our results indicate that equilibrium between phases is owed to several processes and not only to thermo-dynamical partitioning. Fresh emissions affect the partitioning and hence the stabilization on the variation of the partitioning coefficients is reached with aerosol aging. Our results also corroborate that bifunctional carbonyl compounds contribution to atmospheric aerosol is 3 to 8 orders higher than that estimated by thermo-dynamical predictions.

Keywords: Bifunctional carbonyls, Atmospheric secondary aerosol, Semivolatile species partitioning.

Introduction

Organic volatile compounds emitted in the gaseous phase undergo atmospheric oxidation, forming semivolatile compounds that condense to form aerosol. Also freshly emitted organic aerosol is oxidized, either by heterogeneous oxidation or when this primary organic aerosol evaporates as it is diluted during transport (Lipsky and Robinson, 2006). If evaporated compounds are oxidized, they may become into compounds with lower volatility that will afterward re-condense mainly on existing particles (Robinson et al., 2007). This process can be repeated and then subsequent gas-phase oxidation appears to be the principal responsible for most of the aging of organic aerosol (Lambe et al., 2009). Glyoxal is an important contributor to organic aerosol (Volkamer et al., 2007). Numerical models tend to under-predict organic aerosol concentrations in the atmosphere. Li et al. (2011) reported that modelled concentrations corresponded to 21 % and 25 % of the observed organic aerosol. This discrepancy is especially bigger under high photochemical activity (Volkamer et al., 2006; Karydis et al., 2007). We believe that to improve numerical models predictions, more information about the partitioning under real atmospheric conditions is necessary. Nevertheless, sampling of semi-volatile organic compounds is a difficult task, and long collection times are needed to accurately measure their concentrations. In this study we shortened the time resolution (2 h.) by applying a time-delayed set of two low-volume samplers, and this helped to analyse more clearly the effect of meteorological variables which do not have a clear diurnal pattern, like wind speed and direction.

Experimental

Seven bifunctional carbonyl compounds were sampled in ambient air between 28 July and 22 August 2009 at two sites, a suburban site and a roadside site. Both sites are situated in a suburban area c.a. 30 km north-northwest from the center of Tokyo metropolitan area. At the roadside site, the sampler inlet was located at 1.5 m above ground level in the south walk side of national road 463. The suburban site was located 320 m south from the roadside site; in this site the sampler inlet was located on the balcony of the 10th floor of the General Research Building in the campus of Saitama University at 37 m above ground level (Fig. 1).

Samples were collected with a set of 2 annular denuder-filter pack systems, which allow collection of gaseous and particulate phases simultaneously. The sorbent technique was applied using *O*-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine hydrochloride (PFBHA, Sigma-Aldrich Chemie, Steinheim, Germany) as sorbent. A detailed description of the sampling system

can be found in Ortiz et al. (2009). Coarse particles were removed with a cyclone (URG-2000-30EN) (*D*p >2.5 µm, 50% cut-off point at a flow rate of 10 L min^{-1}) set at the inlet of the system. Samples were extracted with dichloromethane. The extraction efficiencies ranged between 82% and 93% in the gaseous phase. In the particulate phase, extraction efficiencies ranged from 94% to 99%. Collection efficiencies in the gaseous phase ranged from 96% to 98%. In the particulate phase collection efficiencies are estimated above 99%. Non-refractory particulate matter below 1 µm ($NRPM_1$) was measured with a time-of-flight aerosol mass spectrometer (Q-AMS, Aerodyne Research Inc., Billerica, MA, USA) at the roadside site. The samples were collected via a stainless steel inlet using a $PM_{2.5}$ cyclone (URG-2000-30EN, University Research Glassware, Chapel Hill, NC) at a flow rate of 10 L min^{-1}. Meteorological variables (temperature, relative humidity, solar radiation, UV radiation, wind speed, wind direction, etc.) were measured at the Saitama Institute of Public Health monitoring site, which is located about 700 m east of the roadside sampling site.

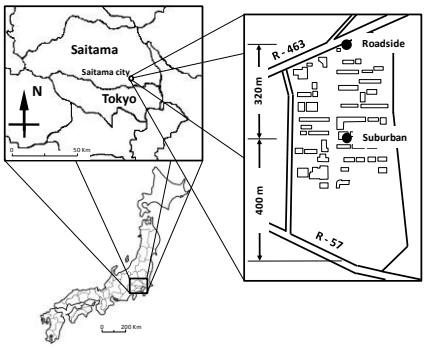

Figure 1. Sampling sites location.

The extracted samples were derivatized with *N,O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA), which was used to silylate hydroxyl groups. All samples were analyzed by GC-MS (GC-2010, Shimadzu, Kyoto, Japan) with a DB-5 capillary column (30 m x 0.32 mm (i.d.); 0.25 µm film thickness; J & W Scientific, Folsom, CA) in electron ionization mode. The values which indicate the concentrations of the compounds in the manuscript have been already subtracted the blank values and corrected by extraction and collection efficiencies. Identification of the compounds measured in this study was conducted by comparison with authentic standards.

Results and discussion

Table 1 shows the average concentrations found during the measurements. The gaseous phase concentrations measured at the roadside were higher than at the suburban site; meanwhile particulate phases were somehow similar at both sites. The concentrations of these compounds in both phases are affected by equilibrium, which determines their distribution in gaseous and particulate phases. According to this principle, any variation in the amount of a given compound in one phase will affect the amount of that compound in the other phase.

Table 1: Average concentrations measured and their standard deviations [ng m^{-3}]

	Roadside		Suburban	
	Gas	Particles	Gas	Particles
GAD	250 ± 113	112 ± 35	186 ± 41	120 ± 33
HAC	84 ± 48	47 ± 15	22 ± 17	51 ± 24
GAC	33 ± 16	49 ± 34	20 ± 4	43 ± 14
PYR	27 ± 6	83 ± 53	22 ± 7	105 ± 41
DHA	39 ± 19	23 ± 10	28 ± 10	20 ± 6
GLY	32 ± 15	77 ± 18	21 ± 6	68 ± 18
MGY	84 ± 70	121 ± 35	93 ± 72	98 ± 28

*GAD: Glycolaldehyde; HAC: Hydroxyacetone; GAC: Glyoxylic acid; PYR: Pyruvic acid; DHA: Dihydroxyacetone; GLY: Glyoxal; and MGY: Methylglyoxal.

A better approach to understand contribution to aerosol can be made through their partitioning coefficients (K_p). Pankow's model (Pankow, 1994) was used to calculate the experimental K_p

values (Eq. 1) and theoretical K_p values were calculated with Eq. 2 considering that partitioning is mainly owed to absorption.

$$K_{\mathrm{p}} = \left[\frac{F/A}{\mathrm{TSP}}\right] \quad (1)$$

$$K_{\mathrm{p}} = \frac{1}{p_{\mathrm{L}}^{\mathrm{o}}}\left[\frac{f_{\mathrm{om}}760RT}{MW_{\mathrm{om}}\zeta 10^{6}}\right] \quad (2)$$

where F is the particulate and A the gaseous concentrations, TSP is the total suspended particles (PM_7 was used as an approximation), $p^o{}_L$ is the liquid vapor pressure, f_{om} is the organic matter fraction, MW_{om} is the organic matter average molecular weight, and ζ is the activity coefficient. Liquid vapor pressure values were estimated using the SPARC online calculator (Version 4.5) (Hilal et al., 1995). The values of f_{om} and ζ were assumed to be 1 since we consider that the compounds are mainly absorbed in the organic phase of the aerosol. This assumption has been used in previous studies (Healy et al., 2008; Johnson et al., 2006; Kamens et al., 1999), and MW_{om} is estimated arbitrarily to be 120 for all measurements in this study, since we cannot measure this factor, this assumption has been used before (Healy et al., 2008, Jang and Kamens, 2001).

Table 2: Average Log K_p values.

	Log K_p		
	Roadside	Suburban	Theoretical
GAD	-1.74 ± 0.34	-1.61 ± 0.24	-6.96 ± 0.08
HAC	-1.60 ± 0.34	-0.99 ± 0.44	-6.93 ± 0.07
GAC	-1.25 ± 0.34	-1.10 ± 0.19	-8.79 ± 0.03
PYR	-0.99 ± 0.29	-0.74 ± 0.23	-6.98 ± 0.06
DHA	-1.64 ± 0.35	-1.56 ± 0.23	-4.82 ± 0.10
GLY	-0.99 ± 0.24	-0.90 ± 0.21	-8.97 ± 0.04
MGY	-1.13 ± 0.36	-1.26 ± 0.38	-8.64 ± 0.05

Experimental partitioning coefficients are 3 to 8 orders higher than predicted. These results are consistent with values obtained in previous measurements in the same sites (Ortiz et al; 2012a), and also in other sites in the Kanto area (Ortiz et al., 2012b). Values of K_p's exceeding their theoretical predictions have also been found by Matsunaga et al. (2005a) in a suburban area of Tokyo. Experimental K_p values obtained in chambers by Jang et al. (2003) and Healy et al. (2008) are considerably lower than our atmospheric measurements, nevertheless their measurements also exceeded by several orders the predicted values.

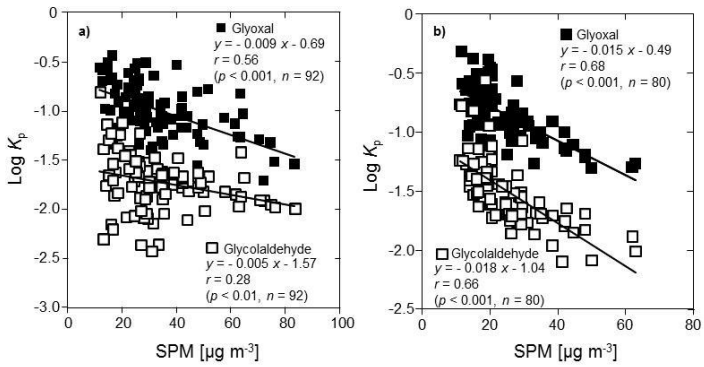

Figure 2: Correlation between SPM and Log K_p. (a) Roadside, (b) Suburban.

Figure 2 shows the correlations of the partitioning coefficients of glyoxal and glycolaldehyde to suspended particulate matter (nearly equal to PM_7). Glyoxylic acid and dihydroxyacetone at the suburban site also showed the same correlations. The correlation values are close for all these four compounds and show similar slopes. At higher SPM values the measured values show a narrower span of distribution, which means that at higher values of SPM the partitioning coefficients are more stable, and this does not happen under lower concentrations of SPM, a

similar behaviour is shown with oxidants concentration, conditions that indicate more aged air masses and hence more aged aerosols. These facts indicate that equilibrium is reached in time and not instantaneously. Matsunaga et al. (2005a) found a correlation of the particle concentration number with partitioning, a similar effect found in our results with SPM.

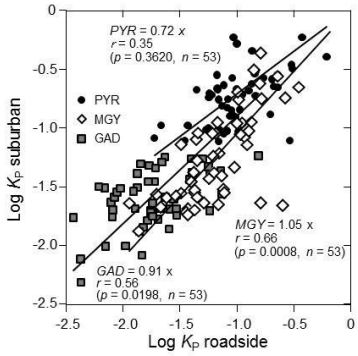

Figure 3: Correlation between Log K_p between sites.

Except for methylglyoxal, average K_p's are lower at the suburban site (Figure 3), which indicates that equilibrium displaced stronger to particulate phase at the suburban site, this has explanation on fresh emissions at the roadside which increases gaseous phase concentrations. However it also indicates that these compounds can be transported longer distances in both phases, and somehow, they prevail more in the particulate phase. Matsunaga et al. (2005b) found that particles that reached Duke Forest (Chapell Hill, NC) already contained bifunctional carbonyls. Figure 3 shows the scatter plot for the partitioning of 3 species in both sites, the slopes of regression lines confirm that species partitioned more towards the particle phase at the suburban site. The slopes close to the unity in the case of glycoladehyde and methylglyoxal indicate that contribution from transportation of these compounds is higher than in the case of pyruvic acid, which showed a stronger contribution from motor vehicles emissions. This fact is perhaps owed to the fact that pyruvic acid is more sensitive to photo-decomposition.

Carbonyl compounds are known to participate in aldol, acetal, and esterification reactions, forming new species which have lower volatility and remain in the particulate phase. Laboratory studies have proved the formation of high molecular weight products from carbonyls in the particulate phase (Gross et al., 2006; Denkenberger et al., 2007) and it is well known that glyoxal polymerizes in the water fraction of aerosol (Trainic et al., 2011). Our results demonstrate that not only glyoxal, but all the bifunctional carbonyls measured can contribute to aerosol formation in similar ways.

Remarks

Seven highly-abundant bifunctional carbonyl compounds were measured in gaseous and particulate phases at a suburban and a roadside site. The comparison between experimental and calculated partitioning showed a big discrepancy. Our results indicate that measured bifunctional carbonyl compounds contribute much more to the formation of secondary organic aerosol than predicted. Motor vehicles contribute to the concentrations of these compounds, and this contribution is particularly high in the gaseous phase. Motor vehicle fresh emissions alter the partitioning coefficients at the roadsite. Bifunctional carbonyls equilibrium between phases is owed not only to thermo-dynamical processes, but to an aging process which do not occur instantaneously. Partitioning coefficients had less variation at higher levels of SPM and higher levels of oxidants, which indicated that aging and equilibrium are reached through time.

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