



Measurements of changes in the atmospheric partitioning of bifunctional carbonyls near a road in a suburban area



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HIGHLIGHTS

- Carbonyl compounds were measured every 2 h at a roadside and a background sites.
- Experimental and theoretical partitioning coefficient values were compared.
- Partitioning coefficients stabilized when the aerosols aged.
- Equilibrium between gaseous and particulate phases depends also to an aging process.
- Bifunctional carbonyls aerosol production was 3–8 orders higher than predicted.

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ABSTRACT

Bifunctional carbonyls are ubiquitous in the atmosphere and are important contributors to atmospheric aerosols through heterogeneous reactions. However, the actual contributions of bifunctional carbonyls to atmospheric aerosols have been little measured because of their capacity to coexist in both the gaseous phase and the particulate phase, making it difficult to sample them in both phases simultaneously. Using a short time resolution (2 h), we measured the atmospheric partitioning of semivolatile species to understand their contributions to atmospheric aerosols. Our results indicate that equilibrium between the gaseous phase and the particulate phase was due not only to thermodynamic partitioning but also to an aging process. Fresh emissions from motor vehicles affected the partitioning, and partitioning coefficients stabilized when the aerosols aged. The contribution of bifunctional carbonyl compounds to atmospheric aerosols was 3–8 orders of magnitude higher than that estimated by thermodynamic predictions, corroborating previous findings.

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1. Introduction

Globally, organic compounds make up 50% of aerosol mass, and in polluted areas this amount can be as high as 90% (Zhang et al., 2007). Usually, organic volatile compounds emitted in the gaseous phase undergo atmospheric oxidation or photooxidation, forming semivolatile compounds that condense to form aerosols. Freshly

emitted organic aerosols are oxidized either by heterogeneous oxidation or when they evaporate as they are diluted during transport (Lipsky and Robinson, 2006). If these evaporated compounds are oxidized, they may form compounds with lower volatility that recondense mainly on existing particles (Robinson et al., 2007). This process can be repeated, and subsequent gas-phase oxidation appears to be responsible for most of the aging of organic aerosols (Lambe et al., 2009).

The smallest α -dicarbonyls, glyoxal and methylglyoxal, are ubiquitous in the atmosphere, and the production of methylglyoxal alone has been estimated to be 140 Tg per year globally (Zhang et al., 2005). Because α -dicarbonyls are highly volatile, they cannot condense into the organic phase of particles through traditional gas-particle partitioning. For a long time, glycolaldehyde, hydroxyacetone, and methylglyoxal were not considered to be significant constituents of aerosols due to their

Abbreviations: OOA, oxidized organic aerosol; HOA, hydrocarbon-like organic aerosol; SOA, secondary organic aerosol; PFBHA, *O*-(2,3,4,5,6-pentafluorobenzyl) hydroxylamine hydrochloride; NRPM₁, nonrefractory particulate matter smaller than 1 μ m; BSTFA, *N,O*-bis(trimethylsilyl)trifluoroacetamide; SPM, suspended particulate matter; GAD, glycolaldehyde; HAC, hydroxyacetone; GAC, glyoxylic acid; PYR, pyruvic acid; DHA, dihydroxyacetone; GLY, glyoxal; MGY, methylglyoxal.

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relatively high vapor pressure (Matsunaga et al., 2005b). More recent studies, however, have shown that at least glyoxal is an important contributor to organic aerosols (Volkamer et al., 2007). Glyoxal and methylglyoxal can efficiently partition into water by forming hydrated structures (Loeffler et al., 2006; Zhao et al., 2012). Moreover, in the aqueous phase, glyoxal and methylglyoxal can undergo photooxidation to form pyruvic acid and glyoxylic acid (Zhao et al., 2012), and depending on the aerosol conditions, their loss by this mechanism can be comparable to that by gaseous photooxidation (Lim et al., 2010; Tan et al., 2010). These facts reveal a lack of knowledge of the evolution and partitioning of these and many other semivolatile compounds in the atmosphere. Although numerical models are frequently used to predict aerosol formation, model predictions tend to underpredict organic aerosol concentrations in the atmosphere. Li et al. (2011) reported that modeled concentrations of glyoxal and methylglyoxal corresponded to 21% and 25% of the organic aerosol. This discrepancy is especially large under high photochemical activity (Volkamer et al., 2006; Goldstein and Galbally, 2007; Karydis et al., 2007). For example, in Mexico City, Volkamer et al. (2006) found high mass loadings of oxidized organic aerosol (OOA)¹ in photochemically young air masses, indicating that secondary organic aerosol (SOA) formation is sufficiently rapid that OOA can be the dominant component of organic aerosol locally at certain times of the day. This result confirms that the contribution of semivolatile compounds is still not completely understood. We believe that measuring the partitioning under actual atmospheric concentrations will provide important information for improving numerical model predictions. However, sampling semivolatile organic compounds is difficult, and collecting sufficient amounts of samples to accurately measure their concentrations takes a long sampling time. Recently, the analysis by aerosol mass spectrometry to determine the amounts of OOA and hydrocarbon-like organic aerosol (HOA) with a short time resolution is becoming more widely used. We believe that the information provided by species-resolved sampling, together with the high-time-resolution bulk composition, can provide important insights into the evolution of organic aerosols. In this study, we shortened the time resolution (2 h) by applying a time-delayed set of two low-volume samplers to analyze the effects of meteorological variables that do not have a clear diurnal pattern such as wind speed and wind direction.

2. Experimental

2.1. Sampling sites

Ambient air samples were collected between 28 July and 22 August 2009 at a suburban site and a roadside site, and the concentrations of seven bifunctional carbonyl compounds in the samples were determined. Both sites are in a suburban area ca. 30 km north-northwest of the center of the Tokyo metropolitan area (Fig. 1). Under southerly winds, this area is impacted by air pollution generated in Tokyo, whereas under winds from other directions, the area is affected by pollution generated in surrounding industrial areas. Previous measurements (Ortiz et al., 2012a, 2012b) have shown that the concentrations of bifunctional carbonyls are quite similar over a wide area around the sampling sites. At the roadside site, the sampler inlet was located 1.5 m above ground level on the south side of national road 463. The suburban site was 320 m south of the roadside site; at this site, the sampler inlet was located 37 m above ground level on the balcony of the 10th floor of the General Research Building on the campus of Saitama University.

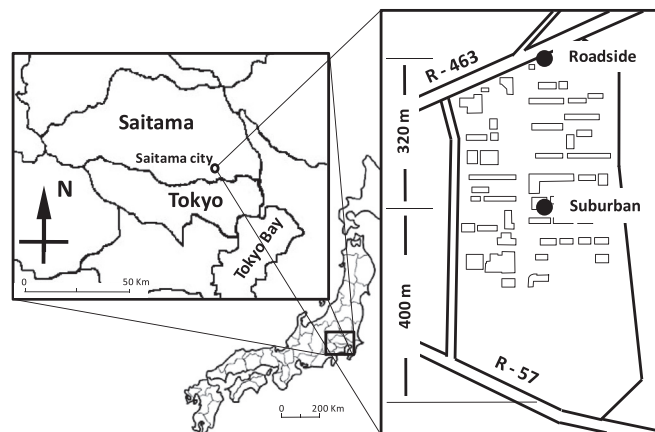


Fig. 1. Locations of sampling sites.

2.2. Sampling system

Samples were collected with a sampling system consisting of a set of two annular denuder-filter pack systems. Gas-phase compounds were collected in annular denuders (URG-2000-30B, University Research Glassware, Chapel Hill, NC, USA) coated with a 40 mM solution of *O*-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine hydrochloride (PFBHA, Sigma–Aldrich Chemie, Steinheim, Germany). Particulate-phase compounds were collected on the filter pack (URG-2000-30F, #47, University Research Glassware), which consisted of a set of three quartz fiber filters (47 mm diameter; Pallflex, 2500 QAT-UP, Pall Co., Port Washington, NY, USA) impregnated with a 40 mM solution of PFBHA. The first filter collected fine particles and the fraction of gas not collected in the denuders; and the second and third filters collected the carbonyl compounds that volatilized from the particles on the first filter during sampling. Ozone was denuded from the air sample by a denuder (URG-2000-30B) coated with potassium iodide that was set before the PFBHA-coated denuders. Coarse particles were removed with a cyclone (URG-2000-30EN, University Research Glassware; $D_p > 2.5 \mu\text{m}$, 50% cut-off point at a flow rate of 10 L min^{-1}) set at the inlet of the system. The system is described in detail elsewhere (Ortiz et al., 2009). Extraction efficiencies in the gaseous phase ranged from 82% for glycolaldehyde to 93% for glyoxal, whereas extraction efficiencies in the particulate phase ranged from 94% for glycolaldehyde to 99% for glyoxylic acid and hydroxyacetone. Collection efficiencies in the gaseous phase ranged from 96% for pyruvic acid to 98% for methylglyoxal; in the particulate phase, collection efficiencies were estimated to be above 99%. Non-refractory particulate matter smaller than $1 \mu\text{m}$ (NRPM₁) was analyzed 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) at a flow rate of 10 L min^{-1} . Meteorological variables (temperature, relative humidity, solar radiation, UV radiation, wind speed, and wind direction) and SPM (measured by beta attenuation method) were measured at the Saitama Institute of Public Health monitoring site, located about 700 m east of the roadside sampling site.

2.3. Sample treatment and analysis

The concentrations of the bifunctional carbonyl compounds were determined in both the gaseous and the particulate phases. Because the amount of carbonyl compound collected must be sufficiently high to be detected by our analytical method, we used two

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