

Atmospheric Concentrations of Semivolatile Bifunctional Carbonyl Compounds and the Contribution from Motor Vehicles

Ricardo Ortiz^{1),2)}, Satoru Shimada²⁾, Kazuhiko Sekiguchi^{1),2)}, Qinyue Wang^{1),2)} and Kazuhiko Sakamoto^{1),2),3),*}

¹⁾Institute for Environmental Science and Technology, Saitama University, 255 Shimo-Okubo, Sakura, Saitama 338-8570, Japan

²⁾Graduate School of Science and Engineering, Saitama University, 255 Shimo-Okubo, Sakura, Saitama 338-8570, Japan

³⁾Center for Environmental Science in Saitama, 914 Kami-tanadare, Kazo, Saitama 347-0115, Japan

*Corresponding author. Tel: +81-480-73-8331, E-mail: sakakazu@env.gse.saitama-u.ac.jp

ABSTRACT

Seven potentially harmful bifunctional carbonyls were measured in particulate and gaseous phases at a roadside site and a suburban site in an area about 30 km north-northwest from Tokyo metropolitan area in the Kanto region in Japan. For the first time, these compounds were measured in both phases with a time resolution of 2 h. We found that wind direction is an important parameter that affects the collection of these compounds near the source, and it can cover the effects of other important variables. Our results confirmed that motor vehicles and especially diesel fuelled vehicles are important sources of these compounds. Photochemical generation is also an important source of these compounds in the gaseous phase. Transportation from the urban area is also important, particularly in the aerosol phase.

Key words: Bifunctional carbonyl compounds, Atmospheric sampling, Vehicle emissions of carbonyl compounds, Diurnal variation of semivolatile compounds, Suburban pollution

1. INTRODUCTION

Bifunctional carbonyls are formed from the oxidation of numerous VOCs (Volkamer *et al.*, 2001). Carbonyl compounds have been measured in the rural (DiGangi *et al.*, 2012), forestal (Matsunaga *et al.*, 2004), suburban (Ortiz *et al.*, 2009) and urban atmosphere (Volkamer *et al.*, 2005) near busy roads (Destailats *et al.*, 2002), having been found in such sites, make carbonyls to be taken as ubiquitous in the atmosphere and therefore of primary importance. Additionally their mutagenic and carcinogenic properties make them a potential risk for human health. Glyoxal toxic

city has been thoroughly reviewed by Kielhorn *et al.* (2004) and its toxicity, together with that of other dicarbonyls has been studied from long ago (Destailats *et al.*, 2002; Ueno *et al.*, 1991). Glyoxal, methylglyoxal and glycolaldehyde produce adverse effects that promote cellular oxidation by attacking the antioxidative mechanisms of cells (Mehta, *et al.*, 2009; Shangari *et al.*, 2007; Al-Enezi *et al.*, 2006; Shangari *et al.*, 2003). Bifunctional carbonyls capacity to increase aerosol mass in the atmosphere through thermodynamical sorption processes as well as through heterogeneous reactions (Volkamer *et al.*, 2007), increase their threat on human health since when they are absorbed in ultrafine particles can reach more easily the lungs. The production of methylglyoxal alone has been estimated around 140 Tg per year globally (Fu *et al.*, 2008). Understanding the behaviors of their concentrations in gaseous and particulate phases in the urban and suburban atmosphere is necessary to evaluate their real contribution to atmospheric aerosol and their potential effects on human health. Nevertheless those measurements are sparse. In this paper we report the measurements of seven bifunctional carbonyls (glycolaldehyde, hydroxyacetone, glyoxylic acid, pyruvic acid, dihydroxyacetone, glyoxal and methylglyoxal) in gaseous and particulate phases at a roadside and a suburban site. To our knowledge, there are no conclusive studies on the health effects of hydroxyacetone, dihydroxyacetone, or glyoxylic and pyruvic acids, however we selected those compounds because our method showed good sensitivity to those compounds and our results demonstrated that they are of atmospheric relevance and perhaps these results may attract attention for future studies about their health effects as well as atmospheric measurements. Our previous measurements (Ortiz *et al.*, 2013a, b) were carried out with a 6 h time resolution, which did not allow us to observe the effects of atmospheric variables or traffic

volume at the roadside. This effect is particularly marked for variables like wind speed and wind direction, which do not have diurnal cycles. In order to find the concentrations behavior near a busy road, as well as the differences with the concentrations measured at a suburban site nearby, the automobiles contribution to atmospheric levels of these compounds in the suburban air, we measured for the first time their distribution in phases with a resolution time of 2 h.

2. EXPERIMENTAL

2.1 Sampling Sites

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. Under southerly winds this suburban area is impacted by the influence of air pollution generated in Tokyo. Nevertheless, under winds coming from other direction they have the influence of pollution generated in surrounding industrial areas. Previous measurements (Ortiz *et al.*, 2013a) have shown that the concentration levels of bifunctional carbonyls are quite similar in a wide area around the sampling sites. 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).

2.2 Sampling System

Samples were collected with a sampling system which was consisted of a set of 2 annular denuder-filter pack systems. Their annular denuders (URG-2000-30B) were coated with a 40 mM solution of *O*-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine hydrochloride (PFBHA, Sigma-Aldrich Chemie, Steinheim, Germany), to collect gaseous phase compounds. A filter pack (URG-2000-30F, #47) was set with a tandem of 3 quartz fiber filters (47 mm ϕ) (Pallflex, 2500 QAT-UP) impregnated with the same 40 mM PFBHA solution to collect the particulate phase compounds. The first filter collected fine particles and a fraction of the 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 sampling air using a denuder (URG-2000-30B) coated with potassium iodide that was set before the PFBHA-coated

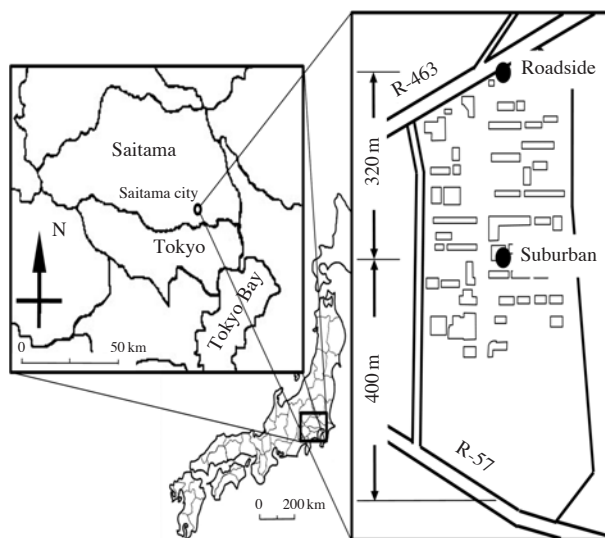


Fig. 1. Sampling sites location.

denuders. Coarse particles were removed with a cyclone (URG-2000-30EN) ($D_p > 2.5 \mu\text{m}$, 50% cut-off point at a flow rate of 10 L min^{-1}) set at the inlet of the system. The system details are described in detail elsewhere (Ortiz *et al.*, 2009). The extraction efficiencies in the gaseous phase ranged from 82% for glycolaldehyde to 93% for glyoxal. In the particulate phase, extraction efficiencies 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 are estimated above 99%. Blank samples were taken twice daily per site. To take a blank sample, filters and denuders underwent the exact same process than sampling filters and denuders, except by the exposition to the flow of air. Non-refractory particulate matter below $1 \mu\text{m}$ (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 $\text{PM}_{2.5}$ 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.

2.3 Samples Treatment and Analysis

The bifunctional carbonyls were sampled in gaseous and particulate phases. Because the carbonyls compounds collected must be in an amount enough to be

detected by our analysis method, we put a set of two sampling systems at each site. Each system collected the sample for a period of 4 h but the sampling was delayed 2 h between systems, allowing a time resolution of 2 h. All samples were taken on sunny days. A total of 80 samples were taken at the suburban site and 92 samples at a roadside site, from which 51 samples were taken simultaneously at both sites. Gaseous samples were extracted 3 times with 5 mL of a dehydrated dichloromethane. The extracted solutions were added 20 μL of 40 nmol PFBHA solution and stored at -18°C in amber vials. The filters were put in individual petri slides, which were put into individual unipack bags, and the set of three filters were put into alumipack bags to be stored at -40°C . Before analyses, filter samples were put into 50 mL amber vials and 6 mL of dehydrated dichloromethane were added; the samples were then ultrasonicated for 20 min for extraction. The extraction solutions were filtered with PTFE syringe filters and the filter rinsed twice with 3 mL dichloromethane.

The samples were derivatized in situ to their PFBHA-oximes, however to ensure their total derivatization, particularly of those carbonyls that underwent polymerization in the aerosol (Yu *et al.*, 1997), the extracted solutions were left at room temperature 20 to 24 h. The samples were then dried with a gentle nitrogen stream and reconstituted to 100 μL with 50 μL of a mixture of 1 : 1 dehydrated hexane and dehydrated dichloromethane, and 50 μL of *N,O*-bis(trimethylsilyl) trifluoroacetamide (BSTFA), which was used to silylate hydroxyl groups. 5 μL of *n*-dodecylbenzene were added as internal standard. Bifunctional carbonyls were then analyzed by GC-MS (GC-2010, Shimadzu, Kyoto, Japan) with a DB-5 capillary column (30 m \times 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.

3. RESULTS

3.1 Variations of Concentrations of the Bifunctional Carbonyls

The total concentrations of bifunctional carbonyls are shown in Fig. 2a and 2b. Total concentrations in this figure are defined as the sum of gaseous and particulate concentrations of each bifunctional carbonyl. As it can be seen, glycolaldehyde was the most abun-

dant compound, followed by methylglyoxal. Concentrations show a clear diurnal pattern, with higher concentrations during daytime, when the human activities and photochemical reactions produce more of these compounds. There is a clear difference between two periods in the roadside concentrations. From 3 to 9 August, the sum of the concentration of all compounds peaks around 1700 ng m^{-3} . From 19 to 22 August the concentrations raised considerably peaking around 3000 ng m^{-3} . During this second period all compounds increase but especially pyruvic acid, which shows higher concentrations in early morning (from 2 to 8 a.m.). This second period followed a long period of rainy days, from 10 to 18 August, and it was marked by higher oxidants concentrations and lower relative humidities.

The concentrations in the suburban sites are lower than in the roadside. However, the suburban site shows a larger diurnal variation, influenced by higher concentrations in the gaseous phase during daytime and lower during nighttime compared to roadside 6 days concentrations.

The average concentrations during the whole period showed higher concentrations in both phases at the roadside. These average values were influenced by the higher concentrations measured in the last period (19 to 22 August). Bifunctional carbonyls were not measured in the suburban site during that last period. Hence, average values over the whole period cannot be compared. To compare differences between both sites, Table 1 shows the average values over the period in which measurements were simultaneously made at both sites (3 to 10 August).

During the simultaneous period, gaseous concentrations were higher at roadside, indicating that automobiles are an important source of these compounds in the gaseous phase. Particulate concentrations though, showed a mixed behaviour and it depended on the species. Concentrations changed in similar patterns sometimes being slightly higher at one site or another. Among the 7 measured species, methylglyoxal and glycolaldehyde had the higher total concentrations. The most abundant by far in the gaseous phase was glycolaldehyde throughout the analyzed period and at both sites.

3.2 Gaseous Concentrations of the Bifunctional Carbonyls and Roadside Emission

Measured values are not expected to show big differences between both sites since the concentrations of these bifunctional carbonyls are quite similar in a wide area around Tokyo metropolitan area. Previous measurements made simultaneously in the region at

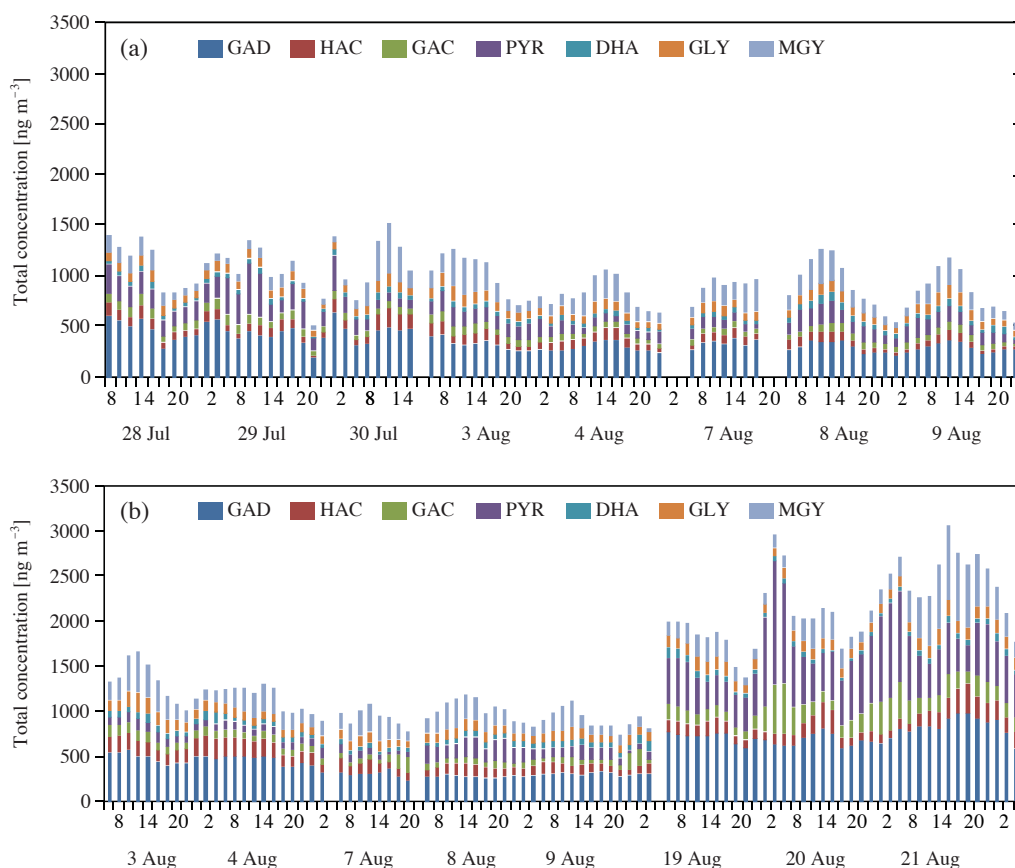


Fig. 2. (a) Total concentrations variation on the suburban site. (b) Total concentrations variation on the roadside site. *GAD: Glycolaldehyde; HAC: Hydroxyacetone; GAC: Glyoxylic acid; PYR: Pyruvic acid; DHA: Dihydroxyacetone; GLY: Glyoxal; and MGY: Methylglyoxal.

Table 1. Average concentrations measured and their standard deviations [ng m⁻³].

	Roadside (3-10 Aug.)		Suburban (3-10 Aug.)	
	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

distances up to 73 km from the center of Tokyo Metropolitan Area, and the total concentrations showed differences within 10% between sites (Ortiz *et al.*, 2013a). Nevertheless, gaseous concentrations at the roadside showed higher concentration levels than at the suburban site. Concentrations of these compounds are influenced by several variables, carbonyls transported from the urban area, vehicles emissions contribu-

ing to the number of vehicles and the particular emissions from each vehicle, solar radiation, temperature, humidity, among others. Those variables influence in different ways the compounds concentrations. Under lower humidity and higher oxidants concentration conditions, the concentrations of these compounds increased considerably. Wind direction showed to be a very important parameter that markedly influences the variation on measured concentrations. This influence was owed to the location of the sampling site, in the southern sidewalk of the road, about 4 m from the traffic. Table 2 shows the average values for the concentration differences (ΔC_i). ΔC_i values calculated from the concentration at the roadside site after subtracting the concentration at the suburban site in each phase. These compounds are emitted in gaseous phase or generated through photochemical reactions in the gaseous phase. Average ΔC_i values reported are from all wind directions (average ΔC_i), and the directions the two directions which showed the more marked ΔC_i differences for gaseous concentrations.

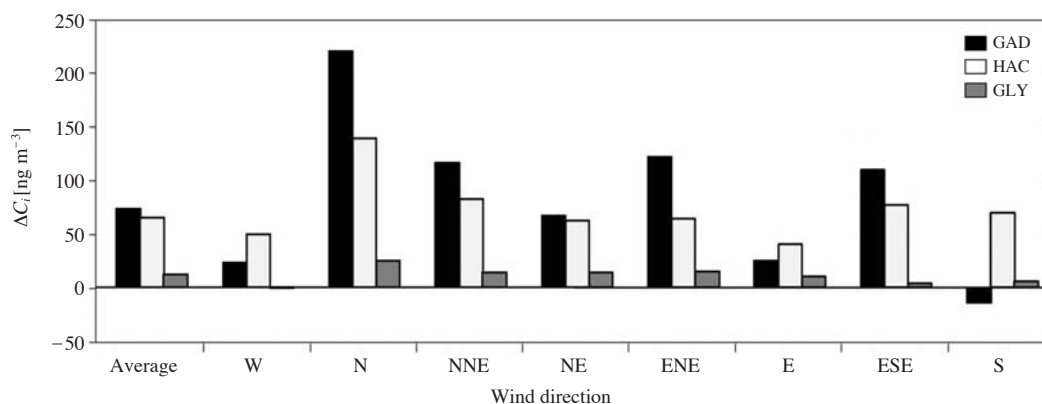


Fig. 3. ΔC_i for all recorded wind directions for 3 compounds (3-10 Aug.).

Table 2. ΔC_i between sites [ng m^{-3}].

	Gaseous ΔC_i (3-10 Aug.)			Particulate ΔC_i (3-10 Aug.)		
	Average	N*	S*	Average	N*	S*
GAD	70 ± 107	220 ± 17	-13 ± 24	-6 ± 38	-41 ± 17	-0.5 ± 24
HAC	65 ± 40	139 ± 20	69 ± 13	-4 ± 21	-11 ± 19	-33 ± 13
GAC	14 ± 17	42 ± 10	6 ± 22	-1 ± 16	-11 ± 10	6 ± 21
PYR	6 ± 10	12 ± 24	3 ± 14	-20 ± 50	-33 ± 24	-33 ± 14
DHA	11 ± 24	38 ± 5	1 ± 8	4 ± 8	-6 ± 5	-3 ± 7
GLY	11 ± 15	25 ± 30	6 ± 7	11 ± 17	-3 ± 30	21 ± 7
MGY	-3 ± 47	18 ± 31	-12 ± 24	27 ± 31	-17 ± 30	65 ± 24

*N: under northerly wind influence; S: under southerly wind influence ($n=51$).

The ΔC_i values for gaseous concentrations are higher with northerly wind since the sampling point was located on the southern sidewalk of the road. High values of standard deviation are expected since there is an additional effect of dilution when winds became stronger. In the case of particulate concentrations, ΔC_i showed that particulate concentrations at the roadside are lower under northerly winds. This result is expected and provides evidence that when these compounds are transported, the gaseous phase is absorbed by the particles. Hence, particulate concentrations at the suburban site are higher than at the roadside. However when wind came from the south, the behaviour is very different for each compound, while particulate hydroxyacetone and pyruvic acid decreased considerably, glyoxal, and more markedly methylglyoxal showed an increase in particulate phase, although methylglyoxal showed consistently an opposite behaviour in in this change of phases. Fig. 3 Shows the concentration differences under all recorded wind directions.

3.3 The Wind Influence on Measurements

The effect of wind speed is shown in Fig. 4. The highest gaseous concentrations were measured under

soft northerly winds. On early morning 3 August slow winds contribute to the higher concentrations observed in the period, then the peak is reached around noon. In 4 August winds continue coming from the north, and become slow again in early morning, causing a peak from 2:00 to 6:00 am, and other peak in the afternoon, after 2:00 pm. Then, when winds change their direction, the roadside site is influenced from background air and the concentrations decrease. In the period from 7 to 10 August we can see little influence of wind speed in the concentrations. In this period the samplers are taking background air, and when wind speed increases, the diluting air is also background air which has similar concentrations. There are no vehicles fresh emissions to dilute, but already aged background air. Gaseous concentrations increase but not considerably when direction changes to NE and bring some fresh emissions from the roadside to the sampling site.

3.4 Influence on Non-refractory Particulate Matter below 1 μm

Gaseous concentrations of semivolatile compounds are supposed to be strongly linked to particulate con-

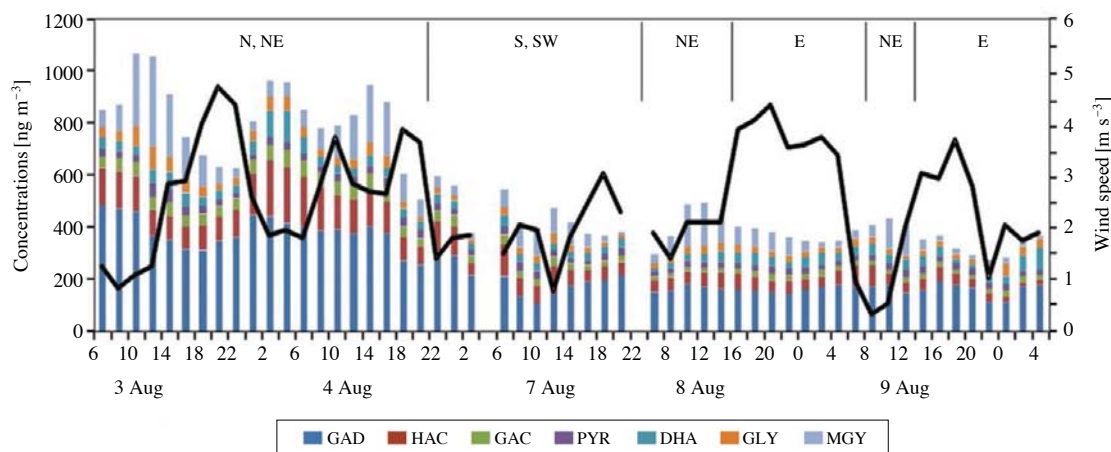


Fig. 4. Concentrations variation on gaseous phase at roadside site.

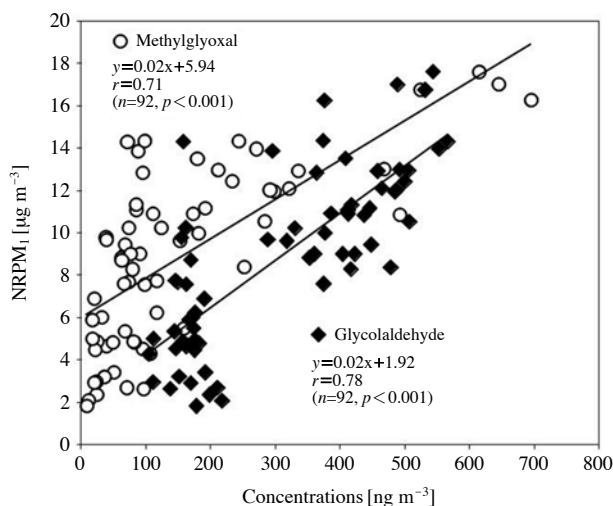


Fig. 5. Glycolaldehyde and methylglyoxal concentrations on gaseous phase at roadside site and their correlations to NRPM_{1} .

centrations, since they are governed by equilibrium between phases (Pankow *et al.*, 1993). Nevertheless, more than thermodynamical equilibrium, the governing equilibrium is driven by other phenomena, including heterogeneous reactions. Our analysis method forces the fraction of compounds that underwent heterogeneous reactions in the particulate phase to go back to the original carbonyl compound (Yu *et al.*, 1997). Hence, thermodynamical partition cannot be measured; instead, we can measure the real contribution to the generation of atmospheric aerosol by these species. Fig. 5 shows how the most abundant bifunctional carbonyls in gaseous phase are positively correlated to non-refractory particulate matter below $1 \mu\text{m}$ (NRPM_{1}). The more abundant among the measur-

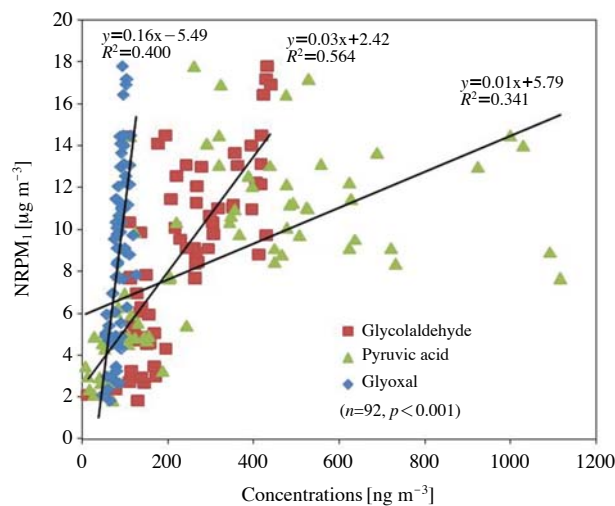


Fig. 6. Glycolaldehyde pyruvic acid and glyoxal concentrations on particulate phase at roadside site and their correlations to NRPM_{1} .

ed compounds show higher correlation coefficient values, indicating a clear influence.

On the other hand, a good correlation is also shown with the concentration in the particulate phase. Fig. 6 shows the correlation of glycolaldehyde, pyruvic acid and glyoxal concentrations on particulate phase with NRPM_{1} . It is noticeable how compounds with higher concentrations again showed better correlation values. Pyruvic acid shows a behavior close to that of glycolaldehyde, except when its concentrations are higher, in the last sampling period; it shows a different slope. This result indicates that at higher particulate pyruvic acid, there will be no increment in the NRPM_{1} concentrations. In this period with high concentrations of

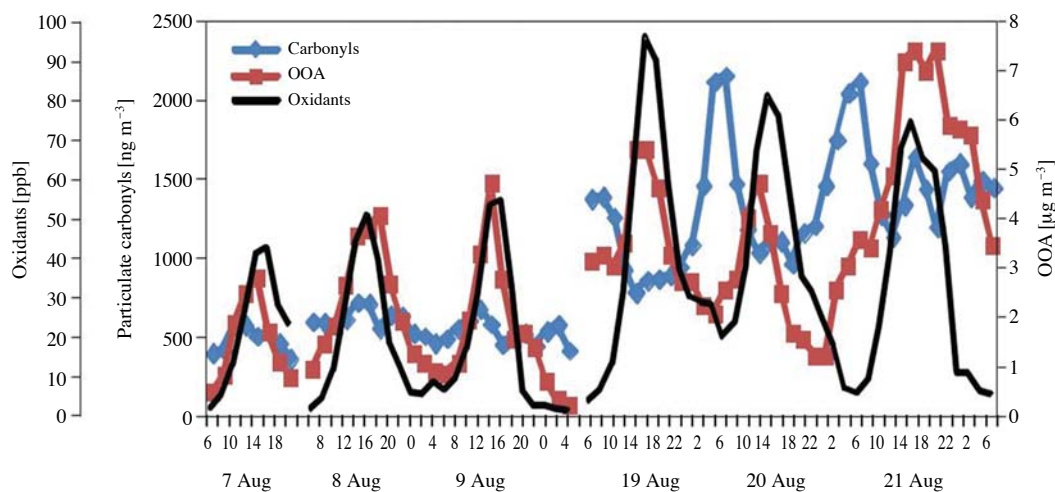


Fig. 7. Variation of the particulate concentrations of all measured carbonyls and OOA in NRPM₁ at the roadside site.

pyruvic acid, winds came exclusively from the south in 19 and 20 August. Therefore this lower influence on NRPM₁ may be owed to concentrations of pyruvic acids emitted in the metropolitan area and transported to the sampling site. Therefore the pyruvic acid was distributed on more aged aerosol, and therefore of larger particle diameter. Wind direction changed on 21 August to be predominantly northerly.

If all carbonyls measured in the particulate phase were on the NRPM₁ mode, the contribution would be of $12.3 \pm 4.9\%$ of NRPM₁. However an important fraction of particulate carbonyls is transported to the sampling sites, since the particulate concentrations measured in the suburban site are already high and frequently higher than at roadside.

The average difference of concentrations between sites indicates that only dihydroxyacetone, glyoxal and methylglyoxal had higher particulate concentration at the roadside, 4 ng m^{-3} , 11 ng m^{-3} and 27 ng m^{-3} respectively. These differences are low, and also consistent with previous results (Ortiz *et al.*, 2013b). Usually at the roadside the particulate concentrations are lower than at the suburban site, and especially considering the higher gaseous concentrations at the roadside, which would drive to higher absorption by preexisting particles.

NRPM₁ could only be measured on the period from 7 to 22 August. The oxidized organic aerosol (OOA) was calculated by deconvolution method (Zhang *et al.*, 2006). In Fig. 7 we can see the diurnal variations of particulate carbonyls and OOA. There are two well marked periods; the first, after the rain, and the second, after 8 days of rain. After rain oxidants increased and relative humidity decreased. In both periods, OOA showed a stronger variation compared to particulate

carbonyls variation, we surmise it on the presence of other compounds photochemically generated like other carbonyls and organic acids, which are also semivolatile and were not measured in this experiments. Nevertheless, during the second period, the lower concentrations of carbonyls are higher than the highest concentrations measured in the first period of Fig. 7 (7-9 Aug.). Carbonyls concentrations increase more with lower oxidants in this period, which may indicate less scavenging by ozone or OH radical. And it probably indicates that they are still emitted during nighttime by motor vehicles.

In the first period OOA and particulate carbonyls showed low concentrations. In the second period, concentrations of both increased. In the first period peaks are coincident for OOA and carbonyls. However in the second there is a delay on OOA peaks compared to those of carbonyls. Particulate carbonyls show peaks in the early morning 4:00 and 6:00 am, at those times there is already sunlight, however it might not be intense enough to produce these compounds photochemically. Nevertheless, at those times the traffic of heavy-duty diesel vehicles is higher compared to other times of the day (Jiang *et al.*, 2006). And the profile suggests that these compounds are emitted by diesel vehicles more vigorously than by gasoline vehicles (Destailats *et al.*, 2002). On the other hand, during 19 and 20 August, winds were soft and coming from the south. This means that aged aerosol transported from the city was richer in carbonyls under those conditions.

4. CONCLUSIONS

Seven bifunctional carbonyls were measured in gas-

eous and particulate phases at a roadside site and a suburban site during summer. The samples were taken with a time resolution of 2 h, and they allowed us to observe the influence of very important parameters like wind direction, which demonstrated to have a higher influence than expected on the collection of these very important compounds. Hence, concentrations measured are highly affected by wind direction, and this can cover the effect of other variables, like radiation, temperature or relative humidity. Results clearly showed that these compounds are emitted by vehicles, and diesel vehicles seem to have a stronger emission rates. However secondary generation is still an important factor in the gaseous phase. Nevertheless, in the particulate phase, transportation plays also a key role in the concentrations measured in this suburban area.

ACKNOWLEDGEMENT

This work was accomplished as part of a joint research program (Joint Research of Saitama University with the Japan Auto-Oil Program of the Japan Petroleum Energy Center), with funding from the Ministry of Economy, Trade and Industry in Japan (2008 and 2009). Additional support was provided by Grants-in-Aid from Saitama University.

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(Received 9 May 2013, revised 21 August 2013, accepted 23 August 2013)