Motor vehicles contribution to atmospheric bifunctional carbonyl compounds

R. Ortiz[1], S. Shimada[1], K. Sekiguchi[1], Q. Wang[1], and K. Sakamoto[1,2]*

[1] Institute for Environmental Science and Technology / Graduate School of Science and Engineering, Saitama University, 255 Shimo-Okubo, Sakura, Saitama 338-8570, Japan, ortiz@mail.saitama-u.ac.jp
[2] Center for Environmental Science in Saitama, 914 Kami-tanadare, Kazo, Saitama 347-0115, Japan

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.

Keywords: Bifunctional carbonyl compounds; Atmospheric sampling; Vehicle emissions of carbonyl compounds; Diurnal variation of semivolatile compounds; Suburban pollution

Introduction

Due to their ubiquitous nature, 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 (Destaillats et al., 2002). These compounds are potential mutagenics and carcinogenics, *i.e*. glyoxal, methylglyoxal and glycolaldehyde produce adverse effects that promote cellular oxidation by attacking the antioxidative mechanisms of cells (Shangari et al., 2003; Al-Enezi et al., 2006; Shangari et al., 2007; Mehta, et al., 2009). Additionally bifunctional carbonyls have the capacity to increase aerosol mass in the atmosphere through thermodynamical sorption processes as well as through heterogeneous reactions (Volkamer et al., 2007). In the aerosol phase they can reach the lungs, increasing their harmful potential. Understanding the behaviours of their gaseous and particulate concentrations in the atmosphere is necessary to evaluate their real contribution to atmospheric aerosol and their potential effects on human health, especially in urban and suburban regions. Nevertheless measurements of their concentrations are sparse. In this paper we report the measurements of seven bifunctional carbonyls in gaseous and particulate phases at a roadside and a suburban site. We believe that the effect of variables like wind speed and wind direction, which do not have diurnal cycles, can be understood better with higher time resolution measurements. In order to find the effect and contribution of vehicle emissions, bifunctional carbonyls were measured at a roadside and at a suburban site nearby for the first time with a time resolution of 2 h.

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. 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., 2012) 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).

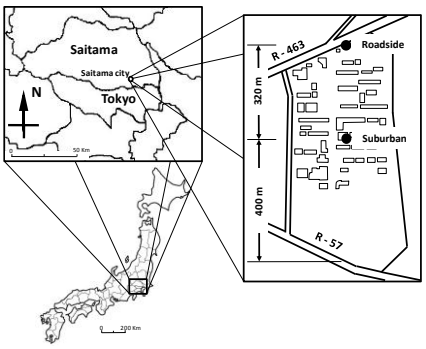

Figure 1. Sampling sites location.

Samples were collected with a set of 2 annular denuder-filter pack systems. The 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 fibre filters (47 mm Ø) (Pallflex, 2500 QAT-UP) impregnated with the same 40 mM PFBHA solution to collect the particulate phase compounds. Ozone was denuded using a denuder coated with potassium iodide that was set before the PFBHA-coated denuders. 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. 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%. 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.

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 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

Glycolaldehyde showed the highest total concentrations (gaseous plus particulate concentrations) followed by methylglyoxal. Concentrations showed 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}. Following a long period of rainy days, in the period from 19 to 22 August, the concentrations raised considerably peaking around 3000 ng m^{-3}. All compounds increased but especially pyruvic acid (Figure 2) in particulate phase. Concentrations were higher in early morning (from 2 to 8 a.m.). This second period was marked by higher oxidants concentrations and lower relative humidities.

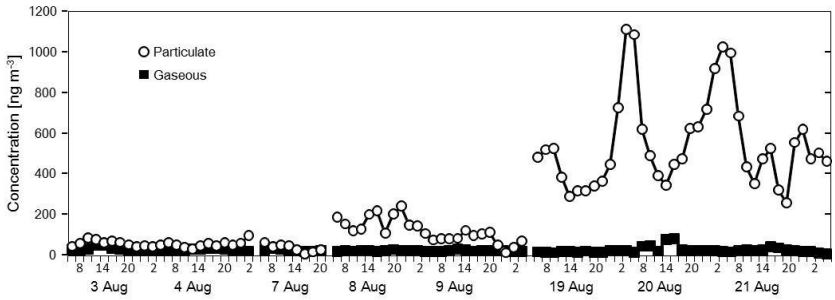

Figure 2: Pyruvic acid concentrations measured at the roadside site in both phases

Higher concentrations from 19 to 22 August increased the average values over the whole samplings. Bifunctional carbonyls were not measured in the suburban site in that period. Hence, 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).

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.

These bifunctional carbonyls concentrations are quite similar in a wide area around Tokyo Metropolis. Hence, measured values are not expected to show big differences between both sites, nevertheless gaseous concentrations at the roadside showed higher concentration levels than at the suburban site, the average values for the concentration differences (ΔCi = [concentration at the roadside site] – [concentration at the suburban site]) in both phases are reported in Table 2.

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

	Gaseous ΔCi (3-10 Aug.)			Particulate ΔCi (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 ΔCi values for gaseous concentrations are higher with northerly wind since the sampling point was located on the southern sidewalk of the road and therefore sampling under northerly winds reflect better the influence of vehicles emissions. High values of standard deviation are expected since there is an additional effect of dilution when winds became stronger. As for particulate concentrations, ΔCi showed that at the roadside particulate concentrations 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. Nevertheless methylglyoxal showed consistently an opposite behaviour in this change of phases.

The highest total gaseous concentrations (the sum of all compounds in gaseous phase) were measured under soft northerly winds (Figure 3). For example, on early morning 3 August the highest concentrations were observed in the period, with a peak 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 after 2:00 pm. Under winds from other directions, the roadside site is influenced from background air and the concentrations decrease and there is little influence of wind speed over the concentrations.

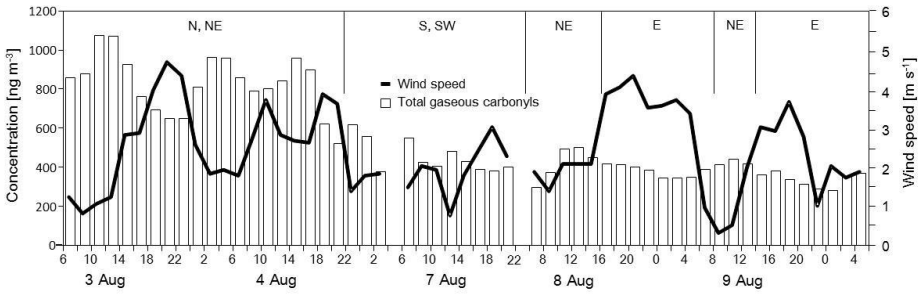

Figure 3: Variation of total gaseous concentrations and wind speed at the roadside site.

Wind did not show a clear effect over particulate concentrations. However they show a good correlation with $NRPM_1$, especially compounds with higher concentrations. $NRPM_1$ could only be measured on the period from 7 to 22 August. Figure 4 shows the correlation of glycolaldehyde, pyruvic acid and glyoxal concentrations on particulate phase with $NRPM_1$. Pyruvic acid shows a behavior close to that of glycolaldehyde, except when its concentrations were higher (19 to 22 August), when it shows a different slope. Higher particulate pyruvic acid did not increase $NRPM_1$ concentrations in a period when winds came exclusively from the south (19 and 20 August). These results indicate that pyruvic acid emitted in the metropolitan area was transported to the sampling site in aged and larger particles.

If all carbonyls measured in the particulate phase were on the $NRPM_1$ mode, the contribution would be of 12.3 ± 4.9 % of $NRPM_1$. 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.

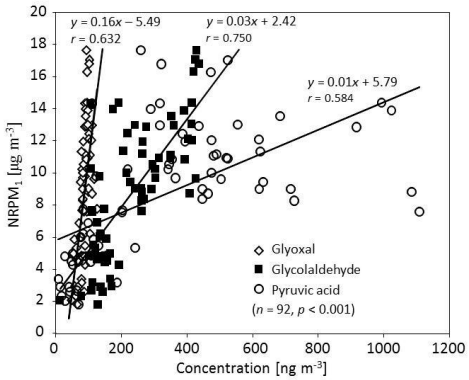

Figure 4: Glycolaldehyde pyruvic acid and glyoxal concentrations on particulate phase at roadside site and their correlations to $NRPM_1$.

Oxidized organic aerosol (OOA) was calculated by deconvolution method (Zhang et al., 2006). In Figure 5 we can see the diurnal variations of particulate carbonyls and OOA. There are two well marked periods separated by 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 these experiments. Nevertheless, during the second period, the lower

concentrations of carbonyls are higher than the highest concentrations measured in the first period of Figure 5 (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.

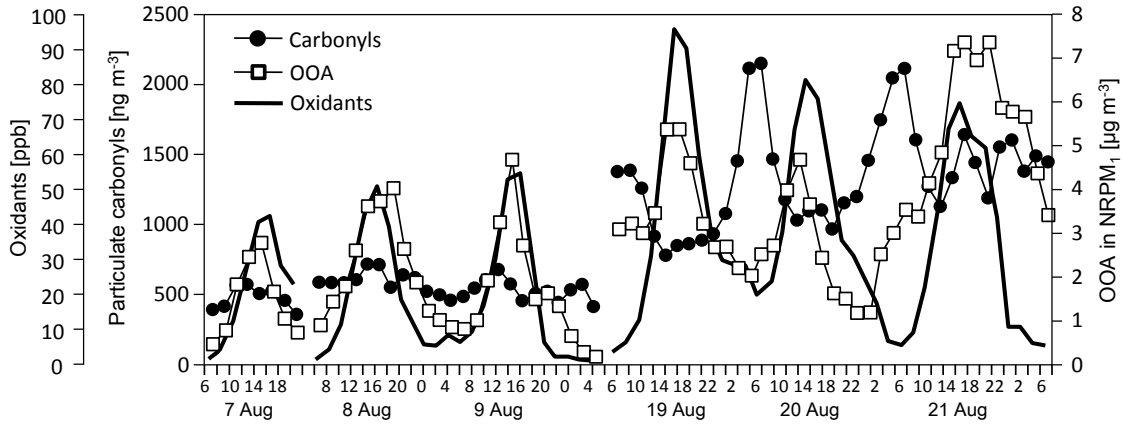

Figure 5: Variation of total carbonyls concentrations in particulate phase, OOA and oxidants at roadside site.

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 (Destaillats 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.

Conclusions

Seven bifunctional carbonyls were measured in gaseous 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. Concentrations measured are highly affected by wind direction, and its effect 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.

References

Al-Enezi, K.S., M. Alkhalaf and L.T. Benov (2006), Glycolaldehyde induces growth inhibition and oxidative stress in human breast cancer cells, *Free Radical Bio. Med.*, 40 (7), 1144–1151.

Destaillats, H., R. Spaulding and M.J. Charles (2002), Ambient air measurement of acrolein and other carbonyls at the Oakland-San Francisco Bay Bridge Toll Plaza, *Environ. Sci. Technol.*, 36, 2227–2235.

DiGangi, J.P., S.B. Henry, A. Kammrath, E.S. Boyle, L. Kaser, R. Schnitzhofer, M. Graus, A. Turnipseed, J.H. Park, R.J. Weber, R.S. Hornbrook, C.A. Cantrell, R.L. Maudlin III, S. Kim, Y. Nakashima, G.M. Wolfe, Y. Kajii, E.C. Apel, A.H. Goldstein, A. Guenther, T. Karl, A. Hansel and F.N. Keutsch (2012), Observations of glyoxal and formaldehyde as metrics for the anthropogenic impact on rural photochemistry Atmospheric *Chem. Phys. Discuss*., 12, 6049–6084.

Jiang, Z., Q. Wang, K. Sekiguchi and K. Sakamoto (2006), Investigation of variations in Suspended particulate matter with enforcement of regulations on diesel vehicle exhaust in suburban Japan, *JSME Int. J. B*, 49, 2–7.

Matsunaga, S., M. Mochida and K. Kawamura (2004), Variation on the atmospheric concentrations of biogenic carbonyl compounds and their removal processes in the northern forest at Moshiri, Hokkaido Island in Japan, *Geophys. Res.*, 109, D04302

Mehta, R., J. Wong and P.J. O'Brien (2009), Cytoprotective mechanisms of carbonyl scavenging drugs in isolated rat hepatocytes, *Chem.-Biol. Interact.*, 178 (1–3), 317–323.

Ortiz, R., K. Enya, K. Sekiguchi and K. Sakamoto (2009), Experimental testing of an annular denuder and filter system to measure gas–particle partitioning of semivolatile bifunctional carbonyls in the atmosphere, *Atmos. Environ.*, 43 (2), 382–388.

Ortiz, R., N. Yoshida, A. Sorimachi, K. Sekiguchi and K. Sakamoto (2012), Transport of semivolatile bifunctional carbonyls from urban to rural areas and their contribution to downwind atmospheric aerosol, (Under Review)

Shangari, N., W.R. Bruce, R. Poon and P.J. O'Brien (2003), Toxicity of glyoxals – role of oxidative stress, metabolic detoxification and thiamine deficiency, *Biochem. Soc. T.*, 31, 1390–1393.

Shangari, N., R. Mehta and P.J. O'Brien (2007), Hepatocyte susceptibility to glyoxal is dependent on cell thiamin content, *Chem.-Biol. Interact.*, 165 (2), 146–154.

Volkamer, R., L.T. Molina and M.J. Molina (2005), DOAS measurement of glyoxal as an indicator for fast VOC chemistry in urban air, *Geophys. Res. Lett.*, 32, L08806.

Volkamer, R., F. San Martini, L.T. Molina, D. Salcedo, J.L. Jimenez and M.J. Molina (2007), A missing sink for gas-phase glyoxal in Mexico City: Formation of secondary organic aerosol, *Geophys. Res. Lett.*, 34, L19807.

Yu, J.Z., H.E. Jeffries and K.G. Sexton (1997), Atmospheric photooxidation of alkylbenzenes−I. Carbonyl product analyses, *Atmos. Environ.*, 31, 2261−2280.

Zhang, Q., M.R. Alfarra, D.R. Worsnop, J.D. Allan, H. Coe, M.R. Canagaratna and J.L. Jimenez (2006), Deconvolution and quantification of hydrocarbon-like and oxygenated organic aerosols based on aerosol mass spectrometry, *Environ. Sci. Technol.*, 39, 4938-4952.