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Importance of wet precipitation as a removal and transport process for atmospheric water soluble carbonyls

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Abstract

Carbonyl compounds exist in the atmosphere as either gases or aerosols. Some of them are water soluble and known as oxidation products of biogenic and/or anthropogenic hydrocarbons. Five carbonyl compounds, glyoxal (GO), 4-oxopentanal (4-OPA), glycolaldehyde (GA), hydroxyacetone (HA) and methylglyoxal (MG) have been identified in a temporal series of 12 rain samples. The concentrations of the compounds in the samples were high at the beginning of the rain event and decreased with time to relatively low and fairly constant levels, indicating that the compounds were washed out from the atmosphere at the start of the rain event. Possibly, these compounds also existed in the cloud condensation nuclei (CCN). Wet deposition rates of the carbonyl compounds were calculated for nine samples collected during a 20 h period. The deposition rates ranged from 0 (4-OPA) to $1.2 \times 10^{-1}\,\mathrm{mg\,C\,m^{-2}\,h^{-1}}$ (MG) with the average of $2.9 \times 10^{-2}\,\mathrm{mg\,C\,m^{-2}\,h^{-1}}$. Production rates of isoprene oxidation products (GA, HA and MG) in the area surrounding the sampling site were estimated with a chemical box model. The deposition rates exceeded the production rates in most samples. This indicates that the rainfall causes a large net flux of the water soluble compounds from the atmosphere to the ground. Insoluble carbonyl compounds such as *n*-nonanal and *n*-decanal were expected to be present in the atmosphere, but were not detected in the rain during the sampling period, suggesting that an aerosol containing these insoluble compounds does not effectively act as a CCN.

1. Introduction

Numerous types of organic compounds are found in the wet precipitation samples and have been studied for several decades (Kawamura and Kaplan,

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1986; Matsunaga et al., 1999; Matsunaga and Kawamura, 2000; Satsumabayashi et al., 2001). Wet precipitation samples contain almost all of the organic compounds that have been detected in the atmosphere; however, their distributions are quite different from the atmospheric gas and aerosol samples due to the difference in water solubility (Satsumabayashi et al., 2001). Water soluble carbonyls, such as glyoxal (GO), methylglyoxal (MG),

4-oxopentanal (4-OPA), glycolaldehyde (GA) and hydroxyacetone (HA), make up a major component of the oxidation products of atmospheric hydrocarbons. These soluble compounds are abundant in rain and snow samples. The GA, HA and MG are known as oxidation products of isoprene (Atkinson, 1990) which has the largest hydrocarbon emission rate on a global scale (Guenther et al., 1995). The GO and 4-OPA are also oxidation products of atmospheric organics. The GO and MG have many precursors derived from either biogenic or anthropogenic sources (Tuazon et al., 1984; Atkinson, 1989; Tuazon and Atkinson, 1989; Tuazon and Atkinson, 1990; Atkinson, 1990). The 4-OPA is known as an oxidation product of 6-methyl-5-hepten-2-one, which is also oxidation product of biogenic hydrocarbons (Fruekilde et al., 1998; Matsunaga et al., 2004a). Previous studies have shown that all of these five compounds exist in both gas and aerosol phases (Matsunaga et al., 2004b; Liggio et al., 2005).

In most previous studies, the target compounds measured in wet precipitation samples were carboxylic acids, dicarboxylic acids, alkanes, amines, amino acids and low molecular weight and single function carbonyls. These compounds provide little or no information regarding their origin due to their small carbon number and simple structure. Satsumabayashi et al. (2001) have shown a predominance of pinonaldehyde in rain and snow, which is a known oxidation product of monoterpenes (Yokouchi and Ambe, 1985), and revealed that biogenic polar compounds are also important as a constituent of wet precipitation.

Deposition rates of GO, MG, GA, HA and 4-OPA in rain water were obtained from measured concentrations and precipitation rates at Hokkaido University in Sapporo, Japan. The GO and MG have multiple major sources, while GA, HA and 4-OPA have only limited sources. At the site, isoprene is the most important precursor for GA and HA, and isoprene emission rates were estimated with a biogenic emission model. Chemical production rates of GA, HA and MG from isoprene were calculated with a chemical box model. Here, we report the deposition of compounds due to rainfall and we evaluate these fluxes by comparison with production rates. In this study, we examined the importance of wet precipitation as a sink for the water soluble carbonyl compounds. The results indicate that wet deposition is an important sink for these compounds even compared to chemical degradation and dry deposition.

2. Experiment

2.1. Sample collection

Rain samples were collected on the top of the building of Institute for Low Temperature Science in Hokkaido University at Sapporo in northern Japan (43°04′58.41″N 141°20′17.95″E). Sapporo has a population of 1.88 million and is located on the southern edge of the subarctic region. The sampling site was in the northern part of the city and surrounded by vegetation and residential area. The sampling was started with the beginning of a rain event and conducted from July 10th to 12th, 2002 during which time 12 rain samples were collected. There was no rain event for 3 days before the first sampling. Rain samples were collected with a rain collector made with stainless steel (sampling area; $0.307\,m^2$) and into 1100 ml of glass bottles. The collector and glass bottles were flushed with a purified methylene chloride, methanol and water prior to the sampling. The precipitation rate ranged from 2.9 to 5.7 mm h^{-1} (average of 4.2 mm h^{-1}). The rain event was continuous, excluding the period between 22:30 on July 10th and 08:30 on 11th (average precipitation rate of 0.3 mm h^{-1}). Carbonyl analysis was conducted for nine samples collected from 16:30 (local time) July 10th to 14:30 July 11th.

2.2. Sample preparation and analysis

The analytical procedure applied to determine the concentrations of the target carbonyls is described in detail by Matsunaga and Kawamura (2000). The rain samples were poisoned with 1 ml of chloroform to avoid microbial degradation and stored at a temperature of 4 °C. Approximately 100 ml of sample was then removed into a separate glass flask. Approximately 5 ml of derivatization reagent (5% of O-benzylhydroxylammonium chloride (BHA) in methanol) was added to the samples. The benzylhydroxyl oxime derivatization for carbonyls in the rain samples required one night (at least 4 h) for completion at room temperature, and the derivatives were extracted 3 times from the sample water with approximately 10 ml of ethyl acetate using a separation funnel. Finally, the derivatives in the extracts were concentrated and further derivatized with 30 μl of N,O-bis(trimethylsilyl)-acetamide (BSTFA, SUPELCO). The oxime derivative of hydroxy carbonyls such as GA and HA is derivatized into its trimethylsilyl ether. These derivatization

processes allow a better separation for the compounds and enhance the sensitivity. Two microliters of the derivative solution was injected into a GC/FID (Carlo Erba GC6000 with a flame ionization detector) equipped with a cold on column injector. A DB-1701 capillary column (0.32 mm i.d. × 60 m length, film thickness of 0.25 μm, J&W Scientific) was used as a separation column.

3. Results and discussion

3.1. Concentrations and deposition rates of the water soluble carbonyls in the rain sample

As shown in Fig. 1 and Table 1, the first sample (No. 1) showed the highest concentrations for all measured compounds, and then the concentrations decreased to less than half of the first sample. The deposition rates of the compounds showed the same pattern as that of the concentrations, indicating that the sample collected at the beginning of the rain (No. 1) contains a large amount of the compounds (in gas phase or coarse aerosol, not in accumulation mode particles) that were "washed out" from the atmosphere. These water soluble and biogenic carbonyls have been identified also in remote and urban atmosphere, not only in gas phase but also in aerosols (Matsunaga et al., 2004b, 2005). It is very likely that the samples (Nos. 2–9) contain compounds that were "washed out" from the atmosphere, but the compounds in the rain samples could also be explained as a composition of the cloud condensation nuclei (CCN). The compounds detected in the rain sample can originate from several processes (e.g. CCN, washout, production in the raindrop, etc.). However, Henry's law constants of those compounds are large (see Table 1). This means these compounds have a potential to play an important role to change the CCN activity of the aerosols due to their high Henry's law constant (see Table 1).

3.2. Estimation for the production rates of GA, HA and MG

The GA, HA and MG are known as major oxidation products of isoprene. Production yields of these compounds from isoprene have been calculated using a chemical box model, NCAR Master Mechanism (NMM; Bey et al., 1997; Aumont et al., 2000). Because not all of the data needed for the NMM calculation (e.g. hydrocarbon concentrations)

were obtained in this experiment, we estimated the yields based on the measured ambient concentrations of isoprene, NO_x and ozone. In our previous study which focused on a global production of GA, HA and MG (Matsunaga et al., paper in preparation), we found that the yields have a linear relationship with those concentrations: therefore, the yields are empirically predictable using isoprene, NO_x and ozone concentrations. Monthly averaged isoprene concentrations output from a chemical global model (the model for ozone and related chemical tracers, MOZART; Horowitz et al., 2003) were applied in the calculations. The NO_x and ozone concentration data were provided by the Environmental Bureau, Eco-City Promotion Department, Environmental Pollution Control Section, Sapporo City (ozone concentration was obtained as a total oxidant concentration). Averaged production yields of GA, HA and MG from isoprene for 8–11 July 2002 were estimated to be 3.4%, 7.3% and 1.1%, respectively. The isoprene emission rate (used in the MOZART simulations; Guenther et al., 1995) at the site is estimated to be 8.9×10^{-2} mg C m^{-2} h^{-1}. A more recent isoprene emission model (MEGAN) developed by Guenther et al. (2006) uses high resolution (<1 km) land cover data and region-specific emission factors predicts an isoprene emission of 3.6×10^{-1} mg C m^{-2} h^{-1}. Therefore, the production rates of GA, HA and MG can be estimated as products of the yields and isoprene emission rate (see Table 2). Because there are two different estimates for site-specific isoprene emission rate, the estimated production rates of the compounds have two different values for each compound.

3.3. Comparison of the production rate with the deposition rate

As shown in Table 2, the wet deposition rates of the compounds largely exceed the estimated production rates. The estimation for the production rates is limited only by chemical production from isoprene. Because MG is known to have major precursors other than isoprene such as aromatic hydrocarbons, the ratio between the wet deposition and production rate (D/P) showed the highest value of the three compounds, indicating underestimation of the chemical production rate. The GA is also known to be produced from 2-methyl-3-buten-2-ol, which is a biogenic volatile compound (Ferronato et al., 1998); therefore, the D/P ratio for GA is also relatively high. The HA does not have any known
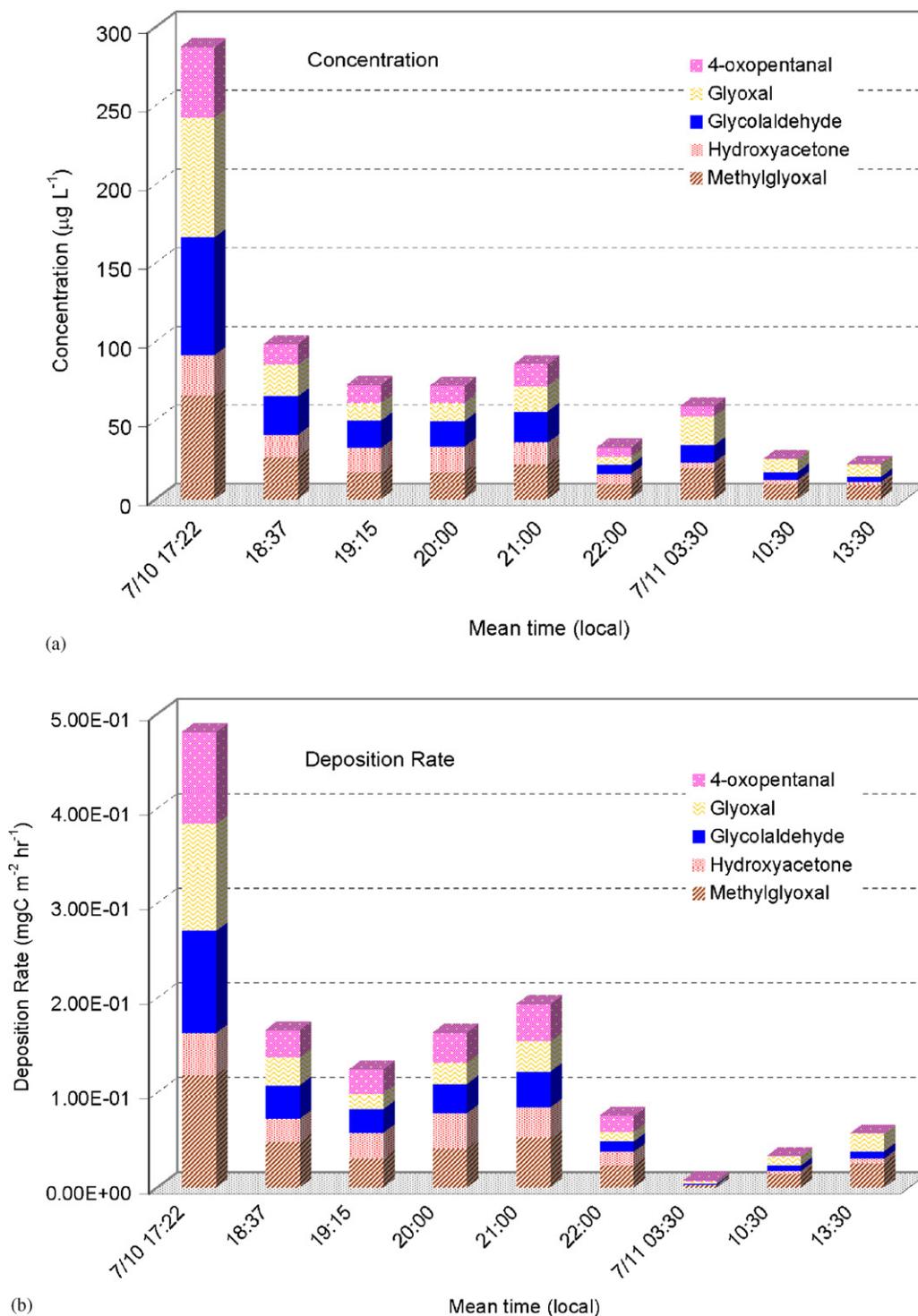
Fig. 1. Concentrations (a) and deposition rates due to the rain (b) of water soluble carbonyl compounds detected in temporal rain samples.

major precursors or sources other than isoprene. Yet, even in the case of HA, the deposition rate exceeded the production rate for most of the sampling periods. Therefore, wet precipitation is highly important as a removal process of the water soluble compounds from the atmosphere.

Table 1
Concentrations and deposition rates of the carbonyls in rain samples

No.	Sampling			GO	MG	4-OPA	GA	HA	GO	MG	4-OPA	GA	HA	Precipitation (mm h^{-1})
	Start[a]	End[a]	Time (h)	Concentrations (µg l^{-1})					Deposition rates (mg C m^{-2} h^{-1})					
1	07/10 16:30	07/10 18:15	1.75	76	66	45	75	26	1.1E-01	1.2E-01	9.6E-02	1.1E-01	4.5E-02	3.6
2	18:15	19:00	0.75	20	27	13	25	14	3.0E-02	4.8E-02	2.9E-02	3.5E-02	2.5E-02	3.6
3	19:00	19:30	0.5	11	17	12	17	15	1.6E-02	3.1E-02	2.5E-02	2.5E-02	2.7E-02	3.6
4	19:30	20:30	1	11	17	11	16	16	2.3E-02	4.1E-02	3.2E-02	3.1E-02	3.7E-02	4.8
5	20:30	21:30	1	16	22	14	20	14	3.2E-02	5.2E-02	3.9E-02	3.8E-02	3.2E-02	4.8
6	21:30	22:30	1	5.1	9.5	5.9	5.6	6.5	1.0E-02	2.3E-02	1.7E-02	1.1E-02	1.5E-02	4.8
7	22:30	07/11 08:30	16	18	20	6.3	11	3.7	2.0E-03	2.6E-03	9.9E-04	1.1E-03	4.7E-04	0.3
8	07/11 08:30	12:30	4	8.3	9.8	—	5.1	2.4	9.8E-03	1.4E-02	—	5.8E-03	3.3E-03	2.9
9	12:30	14:30	2	7.8	8.9	—	3.4	1.8	1.8E-02	2.6E-02	—	7.9E-03	5.0E-03	5.7
Maximum				76	66	45	75	26	1.1E-01	1.2E-01	9.6E-02	1.1E-01	4.5E-02	
Minimum				5.1	8.9	—	3.4	1.8	2.0E-03	2.6E-03	—	1.1E-03	4.7E-04	
Median				11	17	11	16	14	1.8E-02	3.1E-02	2.5E-02	2.5E-02	2.5E-02	
Average				19	22	12	20	11	2.8E-02	3.9E-02	2.7E-02	2.9E-02	2.1E-02	
Average (Nos. 2–9)				12	16	10	13	9	1.8E-02	3.0E-02	2.4E-02	1.9E-02	1.8E-02	
No. 1—average (Nos. 2–9)				64	49	34	62	17	9.6E-02	8.9E-02	7.3E-02	8.8E-02	2.7E-02	
	Henry's constant	mol kg^{-1} atm^{-1}	365 000[a]	32 000[b]		41 500[c]	20 000[d]							

GO: glyoxal, MG: methylglyoxal, 4-OPA: 4-oxopentanal, GA: glycolaldehyde, HA: hydroxyacetone. Detection limit was approximately 0.3 mg l^{-1}, however, it varies with sample volume and compound.

[a] In local time.
[b] Zhou and Mopper (1990).
[c] Betterton and Hoffmann (1988).
[d] Zhou and Lee (unpublished data).

Table 2
Comparison between the estimated production rate of the compounds and observed deposition rate due to the precipitation

Yield			GA 0.034		HA 0.073		MG 0.011	
			MOZART	MEGAN	MOZART	MEGAN	MOZART	MEGAN
Production rate		$mg\,C\,m^{-2}\,h^{-1}$	3.0E-03	1.2E-02	6.5E-03	2.6E-02	9.5E-04	3.8E-03
D/P	1	07/10 16:30	07/10 18:15	36	9.0	6.9	1.8	120	31
	2	18:15	19:00	12	3.0	3.8	1.0	50	13
	3	19:00	19:30	8.3	2.1	4.2	1.1	32	8.1
	4	19:30	20:30	10	2.6	5.7	1.4	43	11
	5	20:30	21:30	13	3.2	5.0	1.3	55	14
	6	21:30	22:30	3.6	9.0E-01	2.3	5.9E-01	24	6.0
	7	22:30	07/11 08:30	3.8E-01	9.6E-02	7.3E-02	1.8E-02	2.7	6.8E-01
	8	07/11 08:30	12:30	1.9	4.9E-01	5.1E-01	1.3E-01	15	3.7
	9	12:30	14:30	2.6	6.6E-01	7.6E-01	1.9E-01	27	6.8

Production rate of the compound is in $mg\,C\,m^{-2}\,h^{-1}$. D/P: ratios between the deposition and production rates.

3.4. Insoluble aldehydes such as 1-nonanal and 1-decanal

Aliphatic aldehydes such as 1-nonanal and 1-decanal were not detected in the rain samples, although these compounds are commonly identified in the atmosphere. Yokouchi et al. (1990) have reported gaseous nonanal and decanal in the atmosphere. These aldehydes were detected also in aerosol phase (Matsunaga et al., 2004b, 2005). Atmospheric gaseous mixing ratios of nonanal and decanal in northern Japan in summer season are observed to be several tens of parts per trillion (ppt). For example, Matsunaga et al. (2004b) reported that the average nonanal concentration in northern Hokkaido Island in August was 18 pptv, and the aldehydes also exist in aerosol phase. The concentrations of these compounds are 2–3 times smaller than the concentrations of GA, HA and MG; however, they are of the same order of magnitude. Henry's law constants of 1-nonanal and 1-decanal are 0.70 (Yaws and Yang, 1992) and $0.62\,mol\,kg^{-1}\,atm^{-1}$(Zhou and Mopper, 1990), respectively. These values are more than 20,000 times smaller than those of GA, HA and MG. Therefore, it is easily imagined that these insoluble compounds do not dissolve easily into rain drops. However, these aldehydes are likely to be detected in rain samples if they are a component of the aerosol that acted as a CCN.

Bowman et al. (2003) reported a reaction rate constant of 1-nonanal with OH to be $3.6\pm0.7\times10^{-11}\,cm^3\,molecule^{-1}\,s^{-1}$. This is similar to that of GA ($1.1\pm0.3\times10^{-11}\,cm^3\,molecule^{-1}\,s^{-1}$; Bacher et al., 2001). Therefore, it is most likely that nonanal and decanal have a long enough lifetime to be transported into mid- and/or upper troposphere. The GA has been abundantly detected in the rain samples after the washout. This indicates that GA exists in aerosols in clouds. The reaction rate of nonanal suggests that nonanal and decanal can exist in aerosols in clouds as same as GA. However, as mentioned above, these insoluble aldehydes were not detected in rain samples. The hypothesis that insoluble aldehydes do not act as a component of the CCN effectively can be supported by a result from an experiment that focused on gas–aerosol partitioning of water soluble and polar carbonyls such as GA, HA and MG. Increase of anthropogenic and non-polar compounds was found to move the gas–aerosol equilibrium of polar carbonyls to gas phase (Matsunaga et al., 2005). This indicates polar carbonyls are difficult to exist together with non-polar compounds in the aerosols. This result can support the external mixing of water soluble and insoluble carbonyls in the aerosols.

4. Conclusion

A comparison between the deposition and estimated production rates of water soluble carbonyls has revealed that wet precipitation is an important removal process of soluble compounds from the atmosphere. In addition, insoluble carbonyls were not detected in the rain samples, although they are expected to exist in aerosol in the clouds. These

results suggested that soluble and insoluble compounds in aerosols are externally mixed and that an aerosol which contains insoluble compounds does not effectively act as a CCN.

Acknowledgments

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