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Importance of the wet precipitation as a removal and transport processes of atmospheric water soluble carbonyls such as isoprene oxidation products

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Key words; deposition rate, production rate, aerosol, cloud condensation nuclei

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, 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 in the beginning of the rain and decreased to relatively low level and became to be almost constant. This indicates the compounds were washed out from the atmosphere in the beginning and that these compounds also existed in the cloud condensation nuclei (CCN). Deposition rates of the carbonyl compounds due to rain fall were calculated for 9 samples collected during 20 hours. The deposition rates ranged from 0 (4-OPA) to 1.2×10^{-1} mgC m^{-2} hr^{-1} (MG) with the average of 2.9×10^{-2} mgC m^{-2} hr^{-1}. In addition, production rates of isoprene oxidation products (GA, HA and MG) in the area surrounding the sampling site were estimated with a chemical box model. Comparing between the deposition and production rates, the deposition rates exceeded the production rates in most samples. This indicates that the rain fall causes a large net deposition flux of the water soluble compounds from the atmosphere to the ground. On the other hand, insoluble carbonyl compounds such as n-nonanal and n-decanal were expected to be present in the atmosphere, but not detected in the rain during the sampling period. This suggests 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, 1986; Matsunaga et al., 1999; Matsunaga and Kawamura, 2000; Satsumabayashi et al., 2001). Wet precipitation samples contain almost all of the organic compounds which 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). A major part of the oxidation products of atmospheric hydrocarbons are water soluble carbonyls such as glyoxal (GO), methylglyoxal (MG), 4-oxopentanal (4-OPA), glycolaldehyde (GA) and hydroxyacetone (HA). These soluble compounds are abundant in rain and snow samples. 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). GO and 4-OPA are also oxidation products of atmospheric hydrocarbons. 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). 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 5 compounds exist in both gas and aerosol phases (Matsunaga et al, 2004b; Liggio et al., 2005).

In most previous studies, the target compounds which have been measured in wet precipitation samples were carboxylic acids, dicarboxylic acids, alkanes, low molecular weight and single function carbonyls. These compounds provide little or no information regarding their origin due to the simple structure. Satsumabayashi et al. (2001) has 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 the wet precipitation.

Deposition rates of the compounds in rain water can be obtained from the concentrations and precipitation rate. On the other hand, although GO and MG have multiple major sources, GA, HA and 4-OPA have only limited sources at the sampling site. Especially for GA and HA, isoprene is the most important precursor, and isoprene emission rate is predictable with an emission model. Chemical production rates of GA, HA and MG from isoprene can also be calculated with a box model. The flux of the compounds due to rain fall from atmosphere to ground can be evaluated by the comparison with their production rates. In this study, we present the importance of wet precipitation as a sink for the oxidation products of biogenic compounds.

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 for several 10 km. The sampling was started with the beginning of the rain and conducted from July 10th to 12th, 2002, and 12 rain samples were collected. Carbonyl analysis has been conducted for 9 samples collected from 16:30 (local time) July 10th to 14:30 July 11th. 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 hr^{-1} (average of 4.2 mm hr^{-1}). It was a continuous rain excluding the period between 22:30 on July 10th and 08:30 on 11th (average precipitation rate of 0.3 mm hr^{-1}).

2.2 Sample preparation and analysis

The rain samples were poisoned with 1 ml of chloroform to avoid microbial degradation and stored at a temperature of 4°C. Then, around 100 ml of sample was removed into a glass flask. Approximately 5 ml of derivatization reagent which is a 5% of *O*-benzylhydroxylammonium chloride (BHA) in methanol was added into the samples. The benzylhydroxyl oxime derivatization needed one night (at least 4 hours) 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. 2 μl of the derivative solution was injected into a GC/FID (Carlo Erba GC6000 with a flame ionization detector) which is 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. Details of this procedure is described in Matsunaga and Kawamura (2000).

3. Results and discussion

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

As shown in Figure 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. This clearly indicates that the sample collected at the beginning of the rain (No.1) contains a large amount of the compounds which 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; Matsunaga et al., 2005). It is very likely that the samples (No.2-No.9) could contain some compounds "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). This means that these water soluble carbonyls were transported to or produced in the cloud and acted as a component of CCN. In addition, 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

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 all of the data needed for the NMM calculation (e.g. hydrocarbon concentration) were not obtained in this experiment, we estimated the yield based on 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., in press), we found that the yields have a linear relationship with those concentrations. Therefore, the yields are empirically predictable using isoprene, NO_x and ozone concentration. Isoprene concentration was obtained as an output of a global model which is the Model for Ozone and Related chemical Tracers (MOZART; Horowitz et al., 2003). 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 within July 8th and 11th, 2002 were estimated to be 3.4%, 7.3% and 1.1%, respectively. Isoprene emission rate at the site is estimated to be 8.9×10^{-2} mgC m^{-2} hr^{-1} by the MOZART. A more recent isoprene emission model developed by Guenther et al. (2005) uses high resolution (<1km) land cover data and region specific emission factors predicts an isoprene emission of 3.6×10^{-1} mgC m^{-2} hr^{-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 estimations for isoprene emission rate, the estimated productions 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 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 other major precursors than isoprene, the ratio between the deposition and production rate (D/P) showed the highest value of the three compounds, indicating underestimation of the production rate. 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.

However, HA does not have any known major precursors or sources other than isoprene. Even in the case of HA, the deposition rate exceeded the production rate in most sampling periods. This means that wet precipitation is highly important as a removal process of the water soluble compounds from the atmosphere. It also suggests an accumulation and transport of the compounds by cloud development and precipitation processes, and the deposition flux of the compounds to the ground due to a wet precipitation exceeds the emission flux from the ground.

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; Matsunaga et al., 2003; Matsunaga et al., 2004). Atmospheric 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. (2004) reported that averaged nonanal concentration in northern Hokkaido Island in August was 18 pptv, and the aldehydes also exist in aerosol phase. These are 2-3 times smaller than those of GA, HA and MG, however, they are of the same order of magnitude. On the other hand, Henry’s law constants of

1-nonanal and 1-decanal are 0.70 (Yaws and Yang, 1992) and 0.62 (Zhou and Mopper, 1990) mol kg^{-1} atm^{-1}, respectively. These are more than 20000 times smaller than those of GA, HA and MG. Therefore, it is easily imagined that these insoluble compounds are difficult to dissolve 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 even if the aldehyde is insoluble.

Bowman et al., 2003 reported 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, because GA has been abundantly detected in the rain samples after the wash out. This suggests that nonanal and decanal do not exist with soluble carbonyls in aerosol and that an aerosol which contains non polar compounds such as nonanal and decanal does not effectively act as a CCN (external mixing of soluble and insoluble compounds in 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.

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References

Atkinson, R., 1989. Kinetics and mechanisms of the gas-phase reactions of the hydroxyl radical with organic compounds. J. Phys. Chem. Ref. Data 1, 1-246.

Atkinson, R., 1990. Gas-phase tropospheric chemistry of organic compounds: a review. Atmos. Environ. 24A, 1-41.

Aumont, B., Madronich, S., Bey, I., Tyndall, G. S., 2000. Contribution of secondary VOC to the composition of aqueous atmospheric particles: A model approach. J. Atmos. Chem. 35, 59-75.

Bacher, C., Tyndall, G. S., Orlando, J. J., 2001. The atmospheric chemistry of glycolaldehyde. J. Atmos. Chem. 39, 171-189.

Bey, I., Aumont, B., Toupance, G., 1997. The nighttime production of OH radicals in the continental troposphere. Geophys. Res. Lett. 24, 1067-1070.

Betterton, E. A., Hoffmann, M. R., 1988. Henry's law constants of some environmentally important aldehydes. Environ. Sci. Technol. 22, 1415-1418.

Bowman, J.-H., Barket, D. J. Jr., Shepson, P. B., 2003. Atmospheric chemistry of nonanal. Environ. Sci. Technol. 37, 2218-2225.

Ferronato, C., Orlando, J. J., Tyndall, G. S., 1998. Rate and mechanism of the reactions of OH and Cl with 2-methyl-3-buten-2-ol, J. Geophys. Res. 103, 25579-25586.

Fruekilde, P., Hjorth, J., Jensen, N. R., Kotzias, D., Larsen, B., 1998. Ozonolysis at vegetation surfaces: a source of acetone, 4-oxopentanal, 6-methyl-5-hepten-2-one and geranyl acetone in the troposphere. Atmos. Environ. 32, 1893-1902.

Guenther, A., Hewitt, C. N., Erickson, D., Fall, R., Geron, C., Graedel, T., Harley, P., Klinger, L., Lerdau, M., McKay, W. A., Pierce, T., Scholes, B., Steinbrecher, R., Tallamraju, R., Taylor, J., Zimmerman, P., 1995. A global model of natural volatile organic compound emissions. J. Geophys. Res. 100, 8873-8892.

Horowitz, L. W., Walters, S., Mauzerall, D. L., Emmons, L. K., Rasch, P. J., Granier, C., Tie, X., Lamarque, J.-F., Martin G. Schultz, M. G., Tyndall, G. S., Orlando, J. J., Brasseur, G. P., 2003. A global simulation of tropospheric ozone and related tracers: Description and evaluation of MOZART, version 2. J. Geophys. Res., 108, 4784, doi: 10.1029/2002JD002853.

Kawamura, K., Kaplan, I. R., 1986. Biogenic and anthropogenic organic compounds in rain and snow samples collected in Southern California. Atmos. Environ. 20, 115-124.

Liggio, J., Li, S.-M., McLaren, R., 2005. Heterogeneous reactions of glyoxal on particulate matter: identification of acetals and sulfate esters. Environ. Sci. Technol. 39, 1532-1541.

Matsunaga, S., Kawamura, K., Yamamoto, Y., Azuma, N., Fujii, Y., Motoyama, H., 1999. Seasonal changes of low molecular weight dicarboxylic acids in snow samples from Dome Fuji Station, Antarctica. Polar Meteorol. Glaciol. 13, 53-63.

Matsunaga, S., Kawamura, K., 2000. Determination of α- and β-Hydroxycarbonyls and Dicarbonyls in Snow and Rain Samples by GC/FID and GC/MS Employing Benzyl Hydroxyl Oxime Derivatization. Anal. Chem. 72(19), 4742-4746.

Matsunaga, S., Mochida, M., Kawamura, K., 2004a. High abundance of gaseous and particulate 4-oxopentanal in the forestal atmosphere. Chemosphere 55, 1143-1147.

Matsunaga, S., Mochida, M., Kawamura, K., 2004b. Variation on the atmospheric concentrations of biogenic carbonyl compounds and their removal processes in the northern forest at Moshiri, Hokkaido Island in Japan. J. Geophys. Res. 109, D04302, doi:10.1029/2003JD004100.

Matsunaga, S., Kato, S., Yoshino, A., Greenberg, J. P., Kajii, Y., Guenther, A. B., 2005. Gas-aerosol partitioning of semi volatile carbonyls in polluted atmosphere in Hachioji, Tokyo. Geophys. Res. Lett. 32, L11805, doi:10.1029/2004GL021893.

Matsunaga, S., Wiedinmyer, C., Guenther, A. B., Orlando, J. J., Karl, T., Toohey, D. W., Greenberg, J. P., Kajii, Y., Isoprene is a significant atmospheric aerosol component. Atmos. Chem. Phys. Discuss. in press.

Satsumabayashi, H., Nishizawa, H., Yokouchi, Y., Ueda, H., 2001. Pinonaldehyde and some other organics in rain and snow in central Japan. Chemosphere 45, 887-891.

Tuazon, E. C., Atkinson, R., Mac Leod, H., Biermann, H. W., Winer, A. M., Carter, W. P. L., Pitts Jr., J. N., 1984. Yields of glyoxal and methylglyoxal from NOx –Air photooxidation of toluene and m- and p- xylene. Environ. Sci. Technol. 18, 981-984.

Tuazon, E. C. and Atkinson, R., 1989. A Product Study of the Gas-Phase Reaction of Methyl Vinyl Ketone with the OH Radical in the Presence of NO_x. Int. J. Chem. Kinet. 21, 1141-1152.

Tuazon, E. C. and Atkinson, R., 1990. A Product Study of the Gas-Phase Reaction of methacrolein with the OH Radical in the Presence of NO_x. Int. J. Chem. Kinet. 22, 591-602.

Yaws, C. L., Yang, H.-C., 1992. Henry's law constant for compound in water in Thermodynamic and Physical Property Data, C. L. Yaws, ed(s)., Gulf Publishing Company, Houston, TX, 181-206 .

Yokouchi, Y., Ambe, Y., 1985. Aerosols formed from the chemical reaction of monoterpenes and ozone. Atmos. Environ. 19, 1271-1276.

Yokouchi, Y., Mukai, H., Nakajima, K., Ambe, Y., 1990. Semi-volatile aldehydes as predominant organic gases in remote areas. Atmos. Environ. 24A, 439-442.

Zhou, X., Mopper, K., 1990. Apparent partition coefficients of 15 carbonyl compounds between air and seawater and between air and freshwater; Implications for air-sea exchange, Environ. Sci. Technol. 24, 1864-1869.

Figure 1 Concentrations of water soluble carbonyl compounds detected in temporal rain samples.

Figure 1 Matsunaga et al.

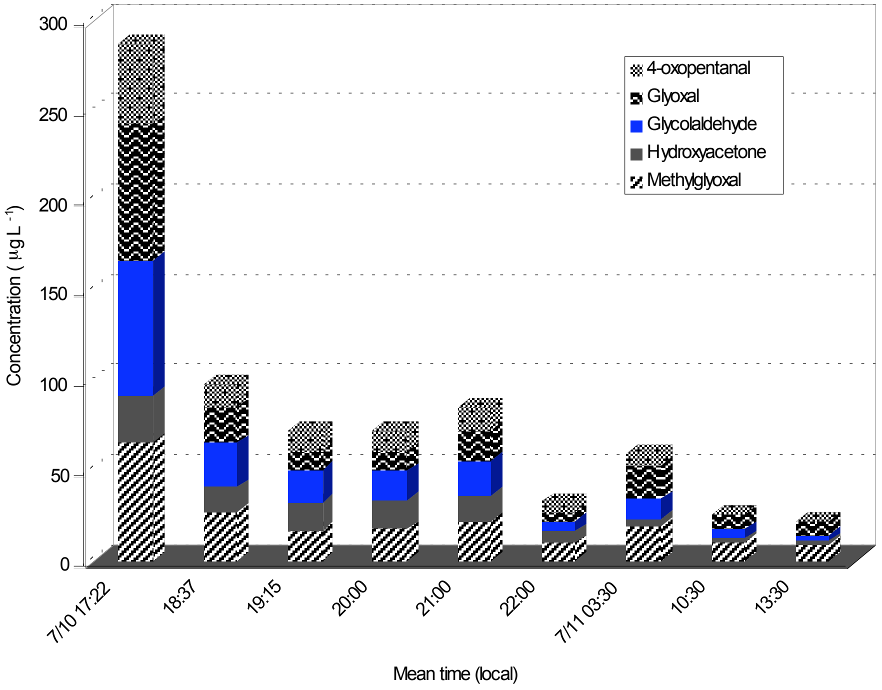

Table 1 Concentrations and deposition rate of the carbonyls in rain samples.

	Sampling			**GO**	**MG**	**4-OPA**	**GA**	**HA**	**GO**	**MG**	**4-OPA**	**GA**	**HA**	**Precipitation**
No.	Start	End	Time	Concentrations					Deposition rates					
	Local time		*hr*	$\mu g\ l^{-1}$					$mgC\ m^{-2}\ hr^{-1}$					$mm\ hr^{-1}$
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 (No.2-No.9)	12	16	10	13	9	1.8E-02	3.0E-02	2.4E-02	1.9E-02	1.8E-02	
			No.1-Ave.(No.2-No.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* $^{-1}$		365000^{a}	32000^{a}		41500^{b}	20000^{c}						

GO: glyoxal, MG: methylglyoxal, 4-OPA: 4-oxopentanal, GA: glycolaldehyde, HA: hydroxyacetone, Detection limit was approximately 0.3 µg l^{-1}, however, it varies with sample volume and compound. a: Zhou and Mopper, 1990, b: Betterton and Hoffmann, 1988, c: Zhou and Lee, unpublished data.

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

				GA		**HA**		**MG**	
Yield				0.034		0.073		0.011	
				MOZART	MEGAN	MOZART	MEGAN	MOZART	MEGAN
Production rate	$mgC\ m^{-2}\ hr^{-1}$			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 mgC m^{-2} hr^{-1}. D/P: ratios between the deposition and production rates.