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3 **The Variation on the Atmospheric Concentrations of Biogenic**
4 **Carbonyl Compounds and their Removal Processes in the**
5 **Northern Forest at Moshiri, Hokkaido Island in Japan**

6

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19

1 **Abstract**

2 Biogenic aldehydes, hydroxycarbonyls and dicarbonyls in gas and particle phases
3 were collected with an annular denuder sampling system (ADSS) in a *Quercus Crispula*
4 and *Picea Glehnii Mast* mixed forest. Eighty samples were collected from 22 to 29 August,
5 2002. The size distributions of aerosols were also observed concurrently with a scanning
6 mobility particle sizer (SMPS). The gaseous concentrations of these carbonyl compounds
7 ranged from the detection limit (approximately 1 pptv) to 154 pptv (630 ng m⁻³, 4-
8 oxopentanal), and the particulate concentrations ranged from the detection limit
9 (approximately 3 ng m⁻³) to 200 ng m⁻³ (4-oxopentanal). Although the production processes
10 of these compounds are different from each other, the temporal variations of the gaseous
11 concentrations were quite similar. In addition, the variation was also similar to that of the
12 ambient temperature. Furthermore, gas-to-particle conversion was suggested to be an
13 important removal process of these compounds. We could evaluate the importance of the
14 gas-to-particle conversion as a removal process of the gaseous species by an ADSS
15 measurement. In addition, the results of our experiment indicated that the conversion
16 includes two processes. The first is an adsorption onto the aerosols which have already
17 existed in the atmosphere. The next is dissolution into the water phases in the aerosols. The
18 latter process was particular to water soluble compounds. The measurement allowed us to
19 identify the most likely removal processes of biogenic semi-volatile organic compounds
20 (SOCs). In this paper, we discuss about these processes of semi-volatile and biogenic
21 carbonyls in the forest atmosphere.

22 **Index Terms:** annular denuder, adsorption, vaporization, semi-volatile, isoprene oxidation
23 products, gas-to-particle conversion

24

1 **1. Introduction**

2 Plants and microbes in the forest are known to produce many organic compounds,
3 and a part of them can be vaporized to the atmosphere. The compounds include isoprene,
4 monoterpenes, 2-methyl-3-buten-2-ol (232MBO) [*Hewitt and Street, 1992; Kesselmeier*
5 *and Staudt, 1999; Isebrands et al., 1999; Serca et al., 2001*]. These organics react with
6 oxidants such as OH, ozone and NO₃ in the air and/or on plant surfaces [*Atkinson et al.,*
7 *1989; Atkinson, 1990*]. However, we have so far little knowledge of emission and removal
8 processes of these organic compounds.

9 Most products of these atmospheric reactions contain oxygen atoms in their
10 molecule, and these oxygenated compounds often have lower vapor pressures than that of
11 their precursors. Organic compounds that have low vapor pressures tend to condense into
12 liquid or solid. This condensation includes gas-to-particle conversion of semi-volatile
13 organic compounds (SOCs) in the atmosphere. The gas-to-particle conversion of biogenic
14 SOCs produces new aerosols in the forest atmosphere [*Kavouras et al., 1998; Kavouras et*
15 *al., 1999*]. Furthermore, these biogenic SOCs can also grow the aerosols via their uptake
16 onto the aerosols that are already in the atmosphere [*Jang and Kamens, 2001; Matsunaga*
17 *et al., 2003; Jang et al., 2003; Matsunaga et al., accepted to Chemosphere*]. Because
18 aerosols reflect and scatter solar radiation, thus, they are known to have an important role
19 on the global climate [*Andreae and Crutzen, 1997*]. The optical properties of aerosols are
20 known to depend on their mass and composition. Thus, the gas-to-particle conversion of
21 gaseous SOCs is important not only as a removal process of gaseous SOCs but also as a
22 factor which changes the optical properties of the atmosphere.

1 There are a number of studies about emission processes and rates of biogenic
2 volatile organic compounds (BVOCs) [*Hewitt and Street, 1992; Yokouchi, 1994; Guenther*
3 *et al., 1995; Isebrands et al., 1999; Guenther, 1999; Serca et al., 2001*]. These studies have
4 led to the development of modeling studies. Owing to the studies, the emission rates and its
5 diurnal variation of major BVOCs such as isoprene, monoterpenes and 232MBO can now
6 be modeled well. In addition, there are also many studies on the degradation rates of
7 BVOCs as well [*Tuazon and Atkinson, 1989; Tuazon and Atkinson, 1990; Atkinson, 1989;*
8 *Ferronato et al., 1998*]. Thus, it seems to be possible to estimate the diurnal variations of
9 their oxidation products (mostly biogenic SOCs) from the emission rates and degradation
10 rates of their precursors. However, there are few studies that describe the diurnal variations
11 of the biogenic SOCs including the oxidation products of BVOCs. Thus, it is still unknown
12 whether the actual concentrations of the oxidation products of BVOCs are in agreement
13 with those estimated from emission rates and degradation rates of their precursors.

14 In the past two decades, the sampling methods for the SOCs in both gas and particle
15 phases have been advanced. In the beginning, they were mainly developed for assessment
16 of air pollution in urban areas. Because anthropogenic SOCs contain harmful compounds
17 such as polycyclic aromatic hydrocarbons (PAHs), they have been known as important air
18 pollutants [*Simoneit et al., 1991; Gundel et al., 1995*]. In addition, the anthropogenic SOCs
19 can be converted into fine particles whose diameter is less than 2.5 μm . These particles are
20 called as $\text{PM}_{2.5}$ and they can go into the inner part of the human lung, and cause more
21 serious injury than that of larger particles. Therefore, many sampling techniques for
22 anthropogenic SOCs have been developed. The annular denuder sampling system (ADSS)
23 is one of these techniques. Denuders were developed to remove the gaseous compounds in
24 the sample air, because gaseous compounds can act as a positive artifact of the aerosol
25 sampling. *Possanzini* and co-workers [1983] have developed a sampling system that is

1 based on denuder tubes. A similar system was also developed, the system can collect the
2 semi-volatile PAHs in both gas and particle phases [Gundel *et al.*, 1995]. A denuder tube
3 can selectively collect gaseous compounds in the sample air onto its inner walls, which are
4 coated with adsorbent or collection reagent, and particles can go through the denuder tube.
5 This is based on the difference of diffusion velocity between gases and particles, gases can
6 collide and be collected onto the inner walls within the time of passage, and however,
7 particles can not collide to the wall there is in the condition of a laminar flow. Particles that
8 have gone through the denuder tube are collected onto the filter that is connected at the
9 latter part of the tube. Thus, the ADSS can separately collect atmospheric SOCs in both gas
10 and particle phases.

11 In this study, we measured the concentrations of biogenic SOCs with the ADSS in
12 the northern forest in Hokkaido Island, Japan. Our sampling method is based on a
13 benzylhydroxyl oxime derivatization [Matsunaga and Kawamura, 2000], by which
14 atmospheric semi-volatile carbonyls can be measured with a high sensitivity. The SOCs
15 that we have measured include glycolaldehyde (GAL), hydroxyacetone (HAC),
16 methylglyoxal, n-nonanal, n-decanal, 4-oxopentanal (4-OPA) and other carbonyl
17 compounds. Although all of these compounds have high vapor pressures [Makar, 2001],
18 they abundantly exist in the aerosols [Matsunaga *et al.*, 2003; Matsunaga *et al.*, *accepted to*
19 *Chemosphere*]. Because there have been few reports that described diurnal variation of
20 these SOCs in the forest atmosphere, there is little information about the emission
21 processes of the biogenic SOCs and their removal processes. We will describe these
22 processes that are based on the results obtained from the observation using ADSS and
23 SMPS observations.

24

1 **2. Experimental**

2 *2.1 Sampling Site*

3 The sampling site is in the Uryu Experimental Forest of Hokkaido University (N
4 44° 21', E 142° 15', approximately 200 km north of Sapporo, rural area). Gas and aerosol
5 samples were collected from August 22nd to 29th, 2002. The experimental forest is a
6 mixed forest dominated by *Quercus Crispula* and *Picea Glehnii Mast.* The sampling site is
7 located approximately 1 km inside of the nearest forest boundary.

8 *2.2 Annular Denuder Sampling System (ADSS)*

9 Atmospheric SOCs were collected with the ADSS. An outline of the system is
10 presented in Fig. 1. The ADSS consists of an air inlet, cyclone, reaction tube, 1st denuder
11 tube, filter pack, backup denuder tube and a diaphragm pump. The sample air is mixed with
12 NO at the air inlet, resulting in the concentration of NO in the sample air to be of 2 ppmv.
13 This procedure is to destroy the atmospheric oxidants in the sample air such as OH, ozone
14 and NO₃ [Mochida *et al.*, 2003]. The sample air goes through the cyclone (URG-2000-
15 30EH, URG Corp., Chapel Hill, NC, U.S.A.), where particles larger than about 4 - 5 μm are
16 removed at the flow rate of 10 L min⁻¹. The Teflon reaction tube provides time for
17 destroying the atmospheric oxidants. The 1st denuder tube (URG-2000-30×242-3CSS,
18 URG Corp.) is a multi channel annular denuder, and the distances between each inner wall
19 are 1 mm and 1.5 mm. Its inner diameter and length are 30 mm and 242 mm, respectively.

20 The denuder tube was coated with a purified *O*-benzylhydroxylammoniumchloride
21 (BHA, first grade, Wako, Osaka, Japan) in a methanol solution as a collection reagent. The
22 denuder tubes were dried with a purified air flow before the sampling. In order to enhance

1 the collection efficiency of samples, an adsorbent (XAD-7, SUPELCO, Bellefonte, PA,
2 U.S.A.) was mixed with the solution of BHA. The XAD-7 was pounded to a fine powder
3 and cleaned with water, methanol and dichloromethane prior to being mixed with the
4 solution. The concentrations of BHA and XAD-7 were 5% and 3% (w/w) in the solution,
5 respectively.

6 Gaseous carbonyls in the sample air are immediately derivatized to its
7 benzylhydroxyl oximes (BH oximes) on the inner walls of the 1st denuder tube, and
8 trapped. Particulate compounds go through the 1st denuder and are trapped on a 47 mm
9 quartz fiber filter installed in the Teflon filter pack (URG-2000-30FG, URG Corp.). Some
10 of the compounds trapped on the filter can re-evaporate, and they are trapped by a backup
11 denuder tube. The same collection reagent as the 1st denuder tube was used for the backup
12 denuder tube. In this study, the compounds collected in the 1st denuder tube are regarded as
13 gaseous compounds, and the sum of the compounds collected on the filter and backup
14 denuder are the amount of particulate compounds. NO_x contained in the exhaust is removed
15 by a NO_x trap cell that contains approximately 500 g of Purafill (Al₂O₃ pellets coated with
16 KMnO₄, Nitta, Osaka, Japan). The exhaust is released at approximately 10 m away from
17 the ADSS and other instruments.

18 *2.3 Diffusion Mobility Analyzer (SMPS) and Weather Conditions*

19 The number concentration and size distribution of the aerosols were determined
20 with the SMPS (TSI Model 3936, TSI Inc., Shoreview, MN, U.S.A.). The SMPS can
21 determine the size and number of the aerosols whose diameter are 10 - 400 nm. The time
22 resolution of SMPS analysis was approximately 280 seconds, and we used the 1 hour
23 average of the number concentration and size distribution of the aerosols. The SMPS
24 analysis was conducted from 25 to 29 of August

1 Temperature, relative humidity, wind speed and wind direction were measured at
2 1.5 m, 3.5 m and 10 m above the ground. Because the sensor for the ambient temperature at
3 3.5 m above the ground was close to the sampling apparatus and is possibly affected by the
4 heat from the instruments, the temperature measured at 1.5 m above the ground is presented
5 here. Global light intensity (~2880 nm) was also measured with MS-43F (EIKO, Japan).
6 The height of the canopy level was approximately 15 m at the sampling site.

7 2.4 Sampling Procedure of the ADSS

8 The ADSS was placed at approximately 3.5 m above the ground, and the sampling
9 was conducted from August 22 to 29. The flow rate of the sample air and sampling time
10 were 10 L min⁻¹ and 3.5 hours, respectively. We changed the denuders and filters every 4
11 hours. To avoid contamination, the ADSS was turned off automatically for 30 minutes.
12 Therefore, the air samples were collected at 00:15-03:45, 04:15-07:45, 08:15-11:45, 12:15-
13 15:45, 16:15-19:45 and 20:15-23:45 (local time). The compounds collected in the denuders
14 were immediately extracted with approximately 10 mL of methanol and stored in 10 mL
15 glass centrifuge tubes with Teflon lined caps. The quartz fiber filters with aerosol samples
16 were stored in 150 mL glass bottles. These extracts and filters were stored in a freezer at
17 approximately -20°C prior to analysis.

18 2.5 Sample Treatment for the Carbonyl Compounds Collected with the ADSS

19 To remove the adsorbent in the extracts from the denuder tubes, the extracts were
20 separated by a centrifuge separator and were filtered with cleaned quartz fiber wool, and
21 placed into 25 mL pear flasks. Approximately 3 mL of methanol was added to the
22 adsorbent that remained in the centrifuge tube, and the remaining adsorbent was extracted
23 by ultrasonication for 5 minutes. After the ultrasonication, the methanol was also placed

1 into the pear flasks. These procedures were repeated three times. Aerosol samples on the
2 quartz fiber filters were extracted with approximately 5 mL of methanol by the
3 ultrasonication. The extract was filtered and was combined with the extract from the
4 backup denuder of the same sample. The extraction for the filters was also repeated three
5 times. These extracts were stored at room temperature within 24 hours, which allowed the
6 carbonyl compounds collected on the filters to react with the excess BHA in the extracts
7 from the backup denuders.

8 The extracts in the pear flask were concentrated to approximately 0.5 mL using a
9 rotary evaporator, and 10 mL of ethyl acetate was added. A 7 mL of pure water purified
10 with Milli-Q SP TOC (Millipore Corp., Billerica, MA, U.S.A.) and a 1 mL of 8M
11 hydrochloric acid were added. The mixture was shaken for about 1 minute, and the water
12 phase with excess BHA was removed and purified water and the hydrochloric acid were
13 added to the ethyl acetate in the flask. This procedure was conducted once more, and to
14 remove hydrochloric acid in the ethyl acetate by adding purified water to the solution. After
15 the shacking, the water phase was removed from the mixture, and the ethyl acetate phase
16 was replaced into a 50 mL pear flask. The solution in the 50 mL pear flask was
17 concentrated to less than 0.5 mL and was placed into a 1.5 mL glass vial with a Teflon
18 lined cap. The ethyl acetate in the solution was vaporized nearly to dryness with a gentle
19 argon flow, and 30 μ L of *N,O*-bis(trimethylsilyl)-acetamide (BSTFA, SUPELCO) was
20 added to trimethylsilylation (TMS) of hydroxyl (-OH) functional group. The scheme of the
21 derivatization is shown in Fig. 2. The mixture of the solution and TMS reagent was stored
22 for more than 2 hours at 60°C. After the TMS reaction, the TMS reagent was also
23 vaporized nearly to dryness and 50 μ L of n-hexane was added to the remaining solution.
24 Finally, 2 μ L of the solution was injected into a GC/FID. The details of the sample
25 treatment for carbonyl compounds have been described in *Matsunaga and Kawamura*

1 [2000]. All of the glass ware used for sampling and analysis were baked for 3 hours at
2 450°C before use. All of the solvents used in the procedures were special grade and
3 purchased from Wako, and they were re-distilled before use.

4 *2.6 GC analysis*

5 A capillary GC (Carlo Erba GC6000) equipped with a cold on-column injector,
6 fused silica DB-1701 capillary column (J&W Scientific, 0.32 mm i.d. × 60 m length, 0.25
7 µm film thickness) and an FID detector (280 °C) was used for the analysis of the
8 derivatives of the carbonyls. The column oven temperature was programmed from 70 °C to
9 75 °C at 40 °C min⁻¹, then to 150 °C at 15 °C min⁻¹, and to 280 °C at 5 °C min⁻¹ (the final
10 time was 15 min.). Peaks of the derivatives were identified by the comparison of the
11 retention time to that of the derivatives of authentic standards. The authentic standards were
12 purchased from Wako except for 4-OPA, which was synthesized by the ozonolysis of 6-
13 methyl-5-hepten-2-one (Tokyo Kasei, Tokyo, Japan) and evaluated with GC/MS. GAL,
14 HAC, nonanal, decanal, glyoxal and methylglyoxal and 4-OPA were quantified in this
15 study. Since the purity of the standard of 4-OPA is not known, the amount of 4-OPA was
16 calculated with the area of methylglyoxal, and was corrected with its carbon number. The
17 collection efficiency of each gaseous compound described in this study was more than
18 90%. Formation of the particulate compounds on the filters was also checked, and the
19 artifact on the filters was found to be negligible. Details of the sampling method and the
20 results of more examinations for the sampling system are under preparation for a
21 contribution by Matsunaga and co-workers. The detection limit of the ADSS sampling is 3-
22 5 ng m⁻³ (both gas and particle phases). Estimated errors in the determination of gaseous
23 and particulate compounds were ~±10% and ~±15% at 5-25 pptv, respectively. The

1 concentration values reported in the manuscript are the remainder after subtracting the
2 blank values.

3

4 **3. Results and Discussion**

5 *3.1 Variation of the concentrations of the Gaseous SOCs*

6 The first half of the experiment was mostly cloudy and partly rainy, the ambient
7 temperature was generally low (minimum: 8.6°C). The latter half was warmer than the first
8 half and had partly clear skies. August 26th and 27th were clear sky days, and a heavy rain
9 was observed on the 28th. Table 1 presents the maximum, minimum, average and median
10 of the gaseous concentrations of the compounds which have been collected in this
11 experiment. The concentrations of the gaseous SOCs varied more than a factor of 20 within
12 a day. Their concentrations were generally high at noontime and decreased at nighttime.
13 The SOCs discussed in this study are produced from several production processes, their
14 structure and production schemes are shown in Fig. 3. GAL, HAC and methylglyoxal are
15 oxidation products of isoprene [Tuazon and Atkinson, 1989; Tuazon and Atkinson, 1990;
16 Atkinson, 1989]. GAL is also an oxidation product of 232MBO [Ferronato et al., 1998].
17 Methylglyoxal may also have other sources. Nonanal and decanal are probably emitted
18 from vegetation and microbial processes [Kesselmeier and Staudt, 1999; Matsunaga et al.,
19 2003]. 4-OPA is known to be produced by a particular process. This is an oxidation product
20 of the organic compounds that exist on the surfaces of plants, such as squalene [Fruekilde
21 et al., 1998; Matsunaga et al., accepted to *Chemosphere*]. 4-OPA is also produced by the
22 oxidation of 6-methyl-5-hepten-2-one (6-MHO), which is directly vaporized from the
23 vegetation via the oxidation of its precursors on the vegetation surfaces [Fruekilde et al.,

1 1998]. Fig. 4 shows the variation of the gaseous concentrations of HAC, nonanal and 4-
2 OPA. Although their production processes are each differ, the temporal variations were
3 quite similar and correlated with that of the ambient temperature. This suggests at least two
4 possibilities. First, the increase of the gaseous concentrations of the SOCs is affected by
5 vaporization from their reservoir. Secondly, their emission and/or production rates are
6 controlled by the ambient temperature or a factor that has a similar variation to that of
7 correlated with temperature (e.g. light intensity).

8 Fig. 5a-c show the relationship between sum of the concentrations of these SOCs
9 (GAL, HAC, nonanal, decanal and 4-OPA) and the ambient temperature at the site. The
10 gaseous concentration increases with the increase in the ambient temperature (see Fig. 5a).
11 In the contrast, the particulate concentrations did not so increase with the temperature (see
12 Fig. 5b). The increase in the sum of the concentrations in both gaseous and particulate
13 phase with the temperature suggests rising a relationship with direct emission and/or
14 production (see Fig. 5c). Other SOCs measured in this study also has shown a similar
15 pattern. Although the possibility that the direct emission and/or photochemical production
16 rates of these SOCs correlate with the ambient temperature still remains, the differences of
17 the production processes of the SOCs suggest that the concentrations were not controlled
18 only by their source intensities.

19 There are several possibilities that can explain the rapid decrease in the
20 concentrations of the gaseous SOCs during afternoon. They are 1: Adsorption onto the
21 surfaces of plants and/or soil, 2: Gas-to-particle conversion, 3: Decrease of the source
22 emission from their sources and/or decrease of their production rate, 4: Precipitation
23 scavenging, 5: Degradation by the atmospheric oxidants and 6: Transportation out of the
24 forest. As seen in Fig. 4, several wet precipitation events were observed, but the gaseous

1 SOCs did not decrease at 12:00-16:00 of the 24th, 08:00-12:00 of the 25th and 04:00-08:00
2 of the 28th. Thus, wet precipitation scavenging (possibility 4) probably does not effectively
3 remove the gaseous SOCs. The atmospheric degradations of the SOCs (possibility 5) are
4 also not fast enough to explain the variations. For example, the degradation of GAL can
5 explain only less than 10% of the decrease in the concentration from 14:00 to 18:00 on
6 August 27th [Bacher *et al.*, 2001; Matsunaga *et al.*, 2003]. For the possibility 6, the
7 removal of the SOCs by vertical convection is not responsible for the diurnal variation
8 patterns of the gaseous SOCs, since the concentrations had a maximum during noontime
9 when the convection is greatest. If the vertical convection determines the variation patterns
10 of the SOCs, the maximum should be at nighttime. In addition, the variations of gaseous
11 SOCs did not agree with those of the particulate SOCs. If the variations of the SOCs were
12 controlled by the vertical convection, they should show same pattern. Therefore, it is most
13 likely that the diurnal variation patterns of the gaseous SOCs are controlled by their
14 emission intensities and removal processes except for 4, 5 and 6 mentioned above. We will
15 discuss about the possibilities 1 and 2 mentioned above as the controlling factors of the
16 variations of these SOCs. The possibility 3 still remains. Because, we did not measure the
17 emission rates of the SOCs and their precursors, we cannot identify the main removal
18 process of the gaseous SOCs. However, we can discuss about the important factors that are
19 effective to control the diurnal variation of the gaseous SOCs such as possibilities 1 and 2.

20 *3.2 Adsorption of the SOCs onto the Plant Surfaces*

21 As described above, we suggest that the vaporization to and removal from the
22 atmosphere is one of major controlling factors of the concentrations of the SOCs. The most
23 likely reservoir that can absorb and release the SOCs are the plant surfaces and/or soil
24 [Welke *et al.*, 1998]. Hornbuckle and Eisenreich [1996] have reported that the

1 concentrations of gaseous poly chlorinated biphenyls (PCBs) can be explained by the
2 ambient temperature from the results of the experiment at the forest. They suggested that
3 the concentrations of gaseous PCBs were controlled by the vaporization from the plant
4 surfaces (because the ground of their sampling site was covered with lichens, thus, there
5 was no exposed soil.) and the removal from the atmosphere. Because PCBs are fully
6 anthropogenic compounds, they could ignore the direct emissions of PCBs and obtain such
7 a simple conclusion. Our results also demonstrate some similarities with their results, and
8 the SOCs which we measured are also semi-volatile and sticky as PCBs. In addition,
9 because fogs were observed almost everyday in the forest, the lifetime of the aerosol
10 particles may be short (about one day). Thus, the aerosols are probably not an important
11 reservoir because of their short lifetime. However, the removal of the aerosols from the
12 atmosphere promotes the adsorption of the SOCs onto the surfaces such as plant and soil.
13 Although the possibility that all of the sources of the SOCs depend on the temperature still
14 remains, it is still more likely that the vaporization and removal control the gaseous
15 concentrations of the SOCs. To evaluate this hypothesis, we analyzed the extracts from
16 leaves of the predominant species (*Quercus Crispula* and *Picea Glehnii Mast*) in the forest,
17 and detected all of the SOCs, which were measured in this experiment, in the extracts.
18 Thus, the leaves of the predominant species may work as a reservoir for the SOCs, although
19 the possibility that the plants are the primary source of the SOCs can not be eliminated.

20 3.3 Gas-to-Particle Conversion of the SOCs

21 Table 2 shows the maximum, minimum, average and median of the particulate
22 concentrations and the partition ratios (particle / (gas + particle)). The concentrations of
23 particulate SOCs are comparable to those of gaseous SOCs. This indicates that the gas-to-
24 particle conversion is also an important removal process of the gaseous SOCs. There is a

1 difference in the gas-to-particle conversion between water soluble compounds and
2 insoluble compounds. Fig. 6a and b shows the partition ratios of the SOCs (GAL, HAC,
3 nonanal and decanal). Fig. 6c shows the relative humidity (3.5 m above the ground) and the
4 aerosol number concentration obtained with the SMPS (10~400 nm) at the sampling site. A
5 large increase in aerosol concentrations was observed during the term 1 in Fig. 6a-c
6 (shaded). In this term, the partition ratios of all of the SOCs rapidly increased. This
7 indicates that the SOCs were converted into aerosols by the uptake onto the aerosol
8 particles that had already been present in the atmosphere. In addition, the uptake onto small
9 particles (< 10 nm) leads to growth of the small particles to larger than 10 nm. Similar
10 phenomenon was also observed in the term 3 in Fig. 6a-c and a previous experiment on
11 August 14, 2001 [Matsunaga *et al.*, 2003]. Other SOCs also showed the increase with the
12 same timing as the SOCs mentioned above (data not shown). Therefore, the uptake onto the
13 aerosols is probably a common gas-to-particle conversion process for all SOCs.

14 On the other hand, the term 2 in Fig. 6a-c indicates the term when the relative
15 humidity raised to 100%. In this term, although the aerosol concentration did not increase,
16 the partition ratios of GAL and HAC increased. In contrast, nonanal and decanal did not
17 show an increase during the term 2. The Henry's Law constants of nonanal and decanal are
18 lower than 1 ($\text{mol kg}^{-1} \text{atm}^{-1}$). These increases were particular to water soluble compounds
19 whose Henry's Law constant are larger than 10000 ($\text{mol kg}^{-1} \text{atm}^{-1}$) such as GAL, HAC, 4-
20 oxopentanal, glyoxal and methylglyoxal. This suggests that the increase in the partition
21 ratio was induced by the dissolution of the water soluble SOCs into the water phase in the
22 aerosols. Therefore, the dissolution into the water phase in the aerosols is important as a
23 gas-to-particle conversion process only for the water soluble SOCs. The relative humidity
24 was also 100% from 18:00 of Aug. 28th to 12:00 of 29th, however, the partition ratio did
25 not increase. In this term, the horizontal wind speed was relatively high (the average and

1 median of the wind speed during the sampling except for this term were 0.06 m s^{-1} and 0 m
2 s^{-1} , respectively.). This may be possibly because to the high wind speed ($0.1\text{-}1.02 \text{ m s}^{-1}$,
3 average: 0.44 m s^{-1} , median: 0.45 m s^{-1}) and high relative humidity activated the adsorption
4 and deposition of the aerosols, and decreased the aerosols in the forest atmosphere.

5

6 **4. Conclusion**

7 Biogenic semi-volatile organic compounds (SOCs) such as glycolaldehyde,
8 hydroxyacetone, n-nonanal, n-decanal, 4-oxopentanal, glyoxal and methylglyoxal in both
9 gas and particle phases have been measured in northern forest on the Hokkaido Island in
10 Japan. Their gaseous concentrations on fine days showed a clear diurnal variation.
11 Although they have different production processes, all gaseous concentrations were
12 strongly correlated with the ambient temperature. This suggests that the gaseous
13 concentrations of the SOCs are not controlled only by their production rates. In addition,
14 we found that gas-to-particle conversion is important as a removal process of the gaseous
15 SOCs. Because we have measured the concentrations of the SOCs in both gaseous and
16 particulate phases, this study could make an evaluation of the importance of gas-to-particle
17 conversion as a removal process of the gaseous SOCs. We also found a difference in the
18 gas-to-particle conversion between water soluble compounds and insoluble compounds.
19 Water soluble compounds can be converted into aerosols not only by the uptake onto the
20 aerosols but also by the dissolution into the water phase in the aerosols. Because, there are
21 few reports described about these SOCs in both gaseous and particulate phases, the
22 measurement of the SOCs with the ADSS and aerosol analysis with the SMPS provided us
23 important information about the removal processes of biogenic SOCs. Furthermore, our
24 data indicate that plants and soils are likely to be reservoirs for these SOCs. They may be

1 stored on plants or soil. Depending on the actual temperature and their partition between air
2 and reservoirs, SOCs can be released or deposited. In order to evaluate the effect of the
3 plant surfaces as a reservoir of the biogenic SOCs, other experiments such as bag enclosure
4 measurements are needed in the future.

5

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- 1 Andreae, M. O. and Crutzen, P. J., Atmospheric aerosols: Biogeochemical sources and role
2 in atmospheric chemistry, *Science*, **276**, 1052-1058, 1997.
- 3 Atkinson, R. et al., Evaluated Kinetic and Photochemical Data for Atmospheric Chemistry.
4 Supplement III, *J. Phys. Chem. Ref. Data*, **18**, 881-1097, 1989.
- 5 Atkinson, R., Gas-Phase Tropospheric Chemistry of Organic Compounds: A Review,
6 *Atmos. Environ.* **24A**(1), 1-41, 1990.
- 7 Bacher, C., Tyndall, G. S. and Orlando, J. J., The Atmospheric Chemistry of
8 Glycolaldehyde. *J. Atmos. Chem.* **39**, 171-189, 2001.
- 9 Ferronato, C., Orlando, J. J. and Tyndall, G. S., Rate and Mechanism of the Reactions of
10 OH and Cl with 2-Methyl-3-buten-2-ol, *J. Geophys. Res.*, **103**, 25579-25586, 1998.
- 11 Fontaine, V., Cabane, M. and Dizengremel, P., Regulation of phosphoenolpyruvate
12 carboxylase in *Pinus halepensis* needles submitted to ozone and water stress,
13 *Physiologia Plantarum*, **117**(4), 445-452, 2003.
- 14 Fruekilde, P., Hjorth, J., Jensen, N. R., Kotzias, D. and Larsen, B., Ozonolysis at vegetation
15 surfaces: a source of acetone, 4-oxopentanal, 6-methyl-5-hepten-2-one and geranyl
16 acetone in the troposphere, *Atmos. Environ.*, **32**(11), 1893-1902, 1998.
- 17 Guenther, A. et al., A global model of natural volatile organic compound emissions, *J.*
18 *Geophys. Res.* **100**, 8873-8892, 1995.

- 1 Guenther, A., Modeling Biogenic Volatile Organic Compound Emissions to the
2 Atmosphere, *In: Nicholas, C. N. (Ed.), Reactive Hydrocarbons in the Atmosphere,*
3 Academic Press, San Diego, pp. 97-118, 1999.
- 4 Gundel, L. A., Lee, V. C., Mahanama, K. R. R., Stevens, R. K. and Daisey, J. M., Direct
5 determination of the phase distributions of semi-volatile polycyclic aromatic
6 hydrocarbons using annular denuders. *Atmos. Environ.* **29**(14), 1719-1733, 1995.
- 7 Hewitt, C. N. and Street, R. A., A Qualitative assessment of the emission of nonmethane
8 hydrocarbon compounds from the biosphere to the atmosphere in the UK – present
9 knowledge and uncertainties, *Atmos. Environ.*, **26**(17), 3069-3077, 1992.
- 10 Hornbuckle, K. C. and Eisenreich, S. J., Dynamics of gaseous semivolatile organic
11 compounds in a terrestrial ecosystem--effects of diurnal and seasonal climate
12 variations, *Atmos. Environ.*, **30**(23), 3935-3945, 1996.
- 13 Isebrands, J. G., Guenther, A. B., Harley, P., Helmig, D., Klinger, L., Vierling, L.,
14 Zimmerman, P. and Geron, C., Volatile organic compound emission rates from
15 mixed deciduous and coniferous in Northern Wisconsin, USA, *Atmos. Environ.*,
16 **33**(16), 2527-2536, 1999.
- 17 Jacob, D. J., Heterogeneous chemistry and tropospheric ozone, *Atmos. Environ.*, **34**(12-
18 14), 2131-2159, 2000.
- 19 Jang, M. and Kamens, R. M., Atmospheric secondary aerosol formation by heterogeneous
20 reactions of aldehydes in the presence of a sulfuric acid aerosol catalyst, *Environ. Sci.*
21 *Technol.*, **35**, 4758-4766, 2001.

- 1 Jang, M., Lee, S. and Kamens, R. M., Organic aerosol growth by acid-catalyzed
2 heterogeneous reactions of octanal in a flow reactor, *Atmos. Environ.*, **37**(15), 2125-
3 2138, 2003.
- 4 Kavouras, I. G., Mihalopoulos, N. and Stephanou, E. G., Formation of atmospheric
5 particles from organic acids produced by forests, *Nature*, **395**, 683-686, 1998.
- 6 Kavouras, I. G., Mihalopoulos, N. and Stephanou, E. G., Secondary organic aerosol
7 formation vs primary organic aerosol emission: in situ evidence for the chemical
8 coupling between monoterpene acidic photooxidation products and new particle
9 formation over forests, *Environ. Sci. Technol.*, **33**(7), 1028-1037, 1999.
- 10 Kesselmeier, J. and Staudt, M., Biogenic Volatile Organic Compounds (VOC): An
11 Overview on Emission, Physiology and Ecology, *J. Atmos. Chem.*, **33**, 23-88, 1999.
- 12 Lloyd, A. C., Atkinson, R., Lurmann, F. W. and Nitta, B., Modeling potential ozone
13 impacts from natural hydrocarbons – I. Development and testing of a chemical
14 mechanism for the NO_x – Air photooxidations of isoprene and α -pinene under
15 ambient conditions, *Atmos. Environ.*, **17**(10), 1931-1950, 1983.
- 16 Makar, P. A., The estimation of organic gas vapor pressure, *Atmos. Environ.*, **35**(5), 961-
17 974, 2001.
- 18 Matsunaga, S. and Kawamura, K., Determination of α - and β -hydroxycarbonyls and
19 dicarbonyls in snow and rain samples by GC/FID and GC/MS employing benzyl
20 hydroxyl oxime derivatization, *Anal. Chem.*, **72**(19), 4742-4746, 2000.

- 1 Matsunaga, S., Mochida, M. and Kawamura, K., Growth of organic aerosols by biogenic
2 semi-volatile carbonyls in the forestal atmosphere, *Atmos. Environ.*, **37**(15), 2045-
3 2050, 2003.
- 4 Matsunaga, S., Mochida, M. and Kawamura, K. High abundance of gaseous and particulate
5 4-oxopentanal in the forestal atmosphere, accepted to *Chemosphere*.
- 6 Mochida, M., Matsunaga, S. and Kawamura, K., A model evaluation of the NO titration
7 technique to remove atmospheric oxidants for the determination of atmospheric
8 organic compounds., *Environ. Sci. Technol.*, **37**, 1589-1597, 2003.
- 9 Possanzini, M., Febo, A. and Liberti, A., A new design of a high-performance denuder for
10 the sampling of atmospheric pollutants, *Atmos. Environ.*, **17**, 2605-2610.
- 11 Serca, D., Guenther, A., Klinger, L., Vierling, L., Harley, P., Druilhet, A., Greenberg, J.,
12 Baker, B., Baugh, W., Bouka-Biona, C. and Loemba-Ndembi, J., EXPRESSO flux
13 measurements at upland and lowland Congo tropical forest site, *Tellus B*, **53**(3), 220-
14 234, 2001.
- 15 Simoneit, B. R. T., Sheng, G. Y., Chen, X. J., Fu, J. M., Zhang, J. and Xu, Y. P., Molecular
16 marker study of extractable organic-matter in aerosols from urban areas of China,
17 *Atmos. Environ.*, **25**(10), 2111-2129, 1991.
- 18 Tuazon, E. C. and Atkinson, R., A Product Study of the Gas-Phase Reaction of Methyl
19 Vinyl Ketone with the OH Radical in the Presence of NO_x, *Int. J. Chem. Kinet.*, **21**,
20 1141-1152, 1989.

- 1 Tuazon, E. C. and Atkinson, R., A Product Study of the Gas-Phase Reaction of Methyl
2 Vinyl Ketone with the OH Radical in the Presence of NO_x, *Int. J. Chem. Kinet.*, **22**,
3 591-602, 1990.
- 4 Welke, B., Ettliger, K. and Riederer, M., Sorption of volatile organic chemicals in plant
5 surfaces., *Environ. Sci. Technol.*, **32**(8), 1099-1104, 1998
- 6 Yokouchi, Y., Seasonal and diurnal variation of isoprene and its reaction products in a
7 semi-rural area, *Atmos. Environ.*, **28**(16), 2651-2658, 1994.
- 8

1 Figure 1 The outline of the annular denuder sampling system (ADSS).

2 Figure 2 Schemes of the benzyhydroxyl oxime (BH oxime) derivatization. The details
3 of the analytical method are described in *Matsunaga and Kawamura* [2000].

4 Figure 3 The production processes of the semi-volatile organic compounds (SOCs) that
5 were measured in this study.

6 Figure 4 The concentrations of hydroxyacetone (blue circles), n-nonanal (red squares)
7 and 4-oxopentanal (green diamonds) in the gas phase. The ambient temperature (black
8 dashed line) and precipitation rate (sky blue solid line, 1 hour average) are also shown.

9 Figure 5 The relationship between the concentrations of the SOC (glycolaldehyde,
10 hydroxyacetone, n-nonanal, n-decanal and 4-oxopentanal) and the ambient temperature. (a)
11 Sum of the gaseous concentrations. (b) Sum of the particulate concentrations. (c) Sum of
12 the gaseous and particulate concentrations.

13 Figure 6 (a) The partition ratios (particle / (gas + particle)) of glycolaldehyde (blue
14 circles and solid line) and hydroxyacetone (red squares). (b) The partition ratios of n-
15 nonanal (blue circles) and n-decanal (red squares). (c) The relative humidity (blue dashed
16 line) and the aerosol number concentration (10-400 nm, gray solid line) at the sampling
17 site. The shaded term 1 indicates the term that the aerosol number concentration was
18 rapidly increased. The shaded term 2 indicates the term that the relative humidity was
19 reached to 100%. The shaded term 3 indicates the term that the phenomenon similar to the
20 term 1 was observed.

Figure 1 (Matsunaga et al.)

B+C = Particle Phase
A = Gas Phase

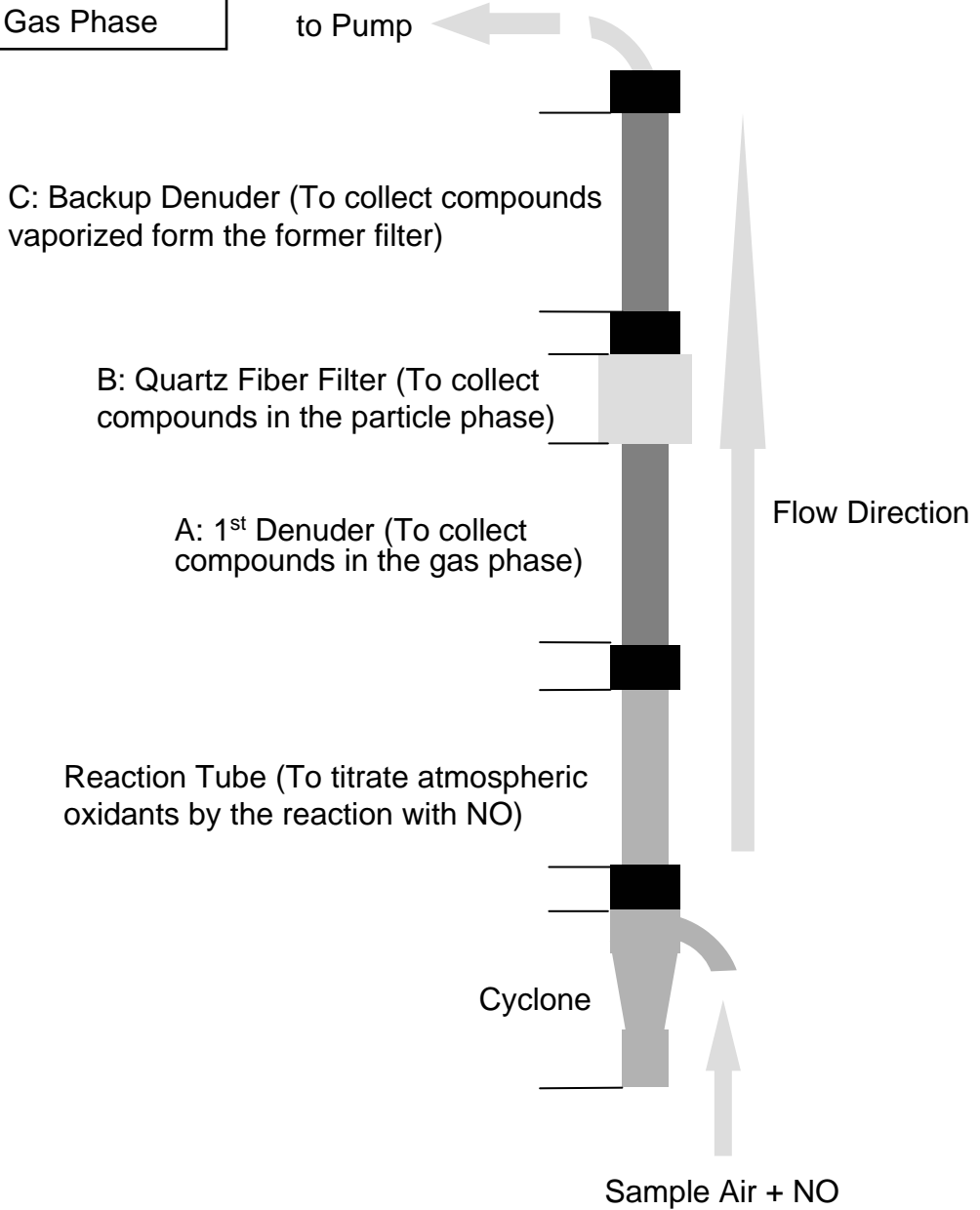


Figure 2 (Matsunaga et al.)

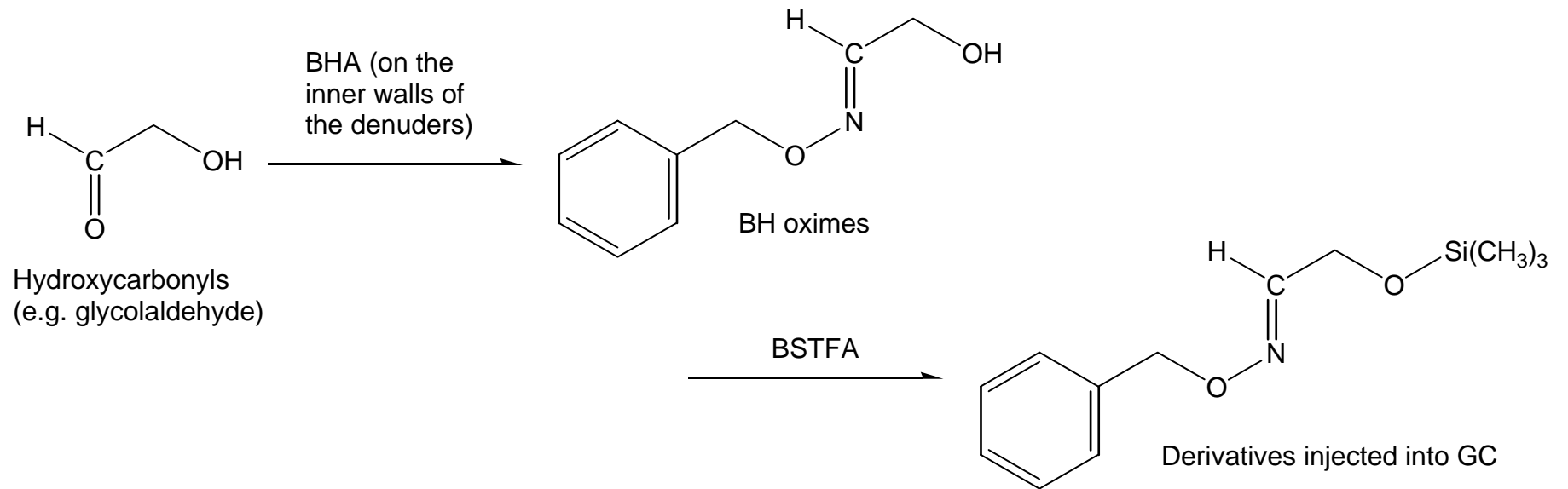
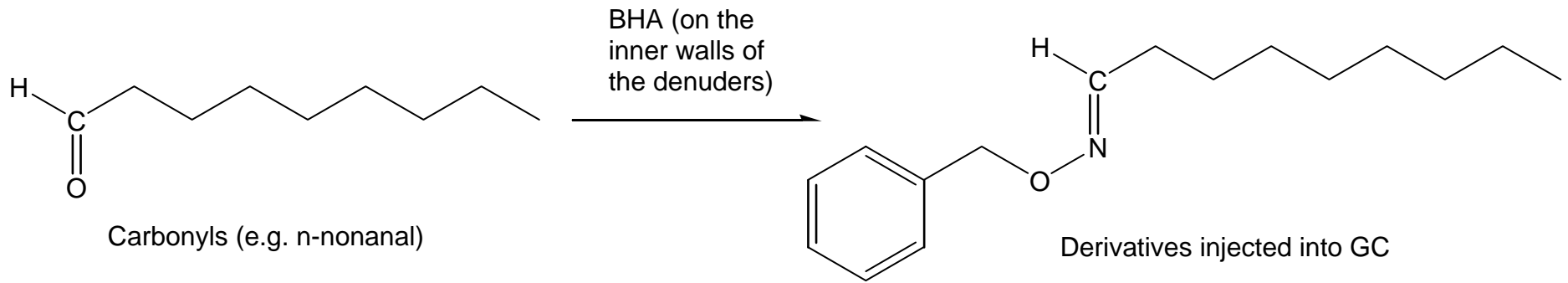
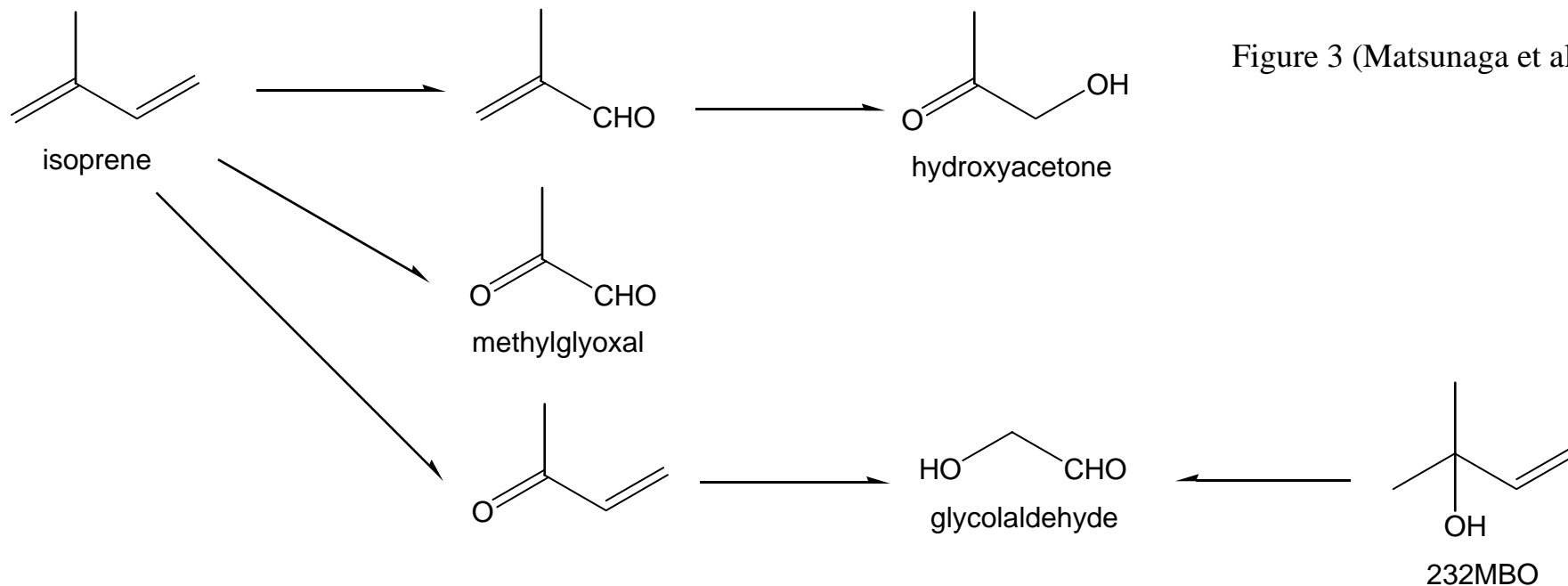
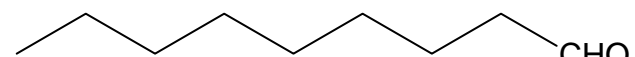


Figure 3 (Matsunaga et al.)

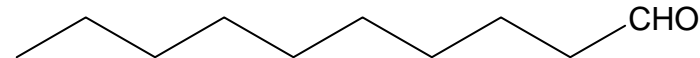


Vegetation etc.

Direct emission?

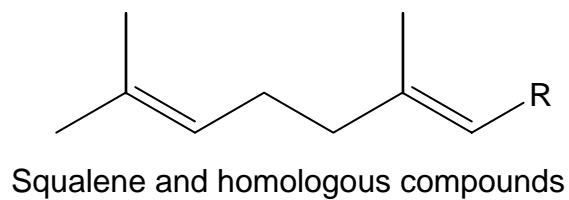


n-nonanal

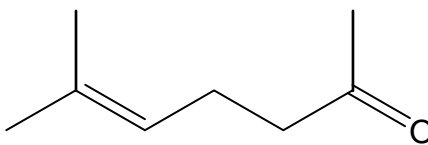


n-decanal

Vaporization
and/or Direct emission



Oxidation



Oxidation

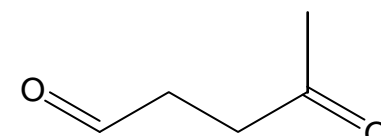


Figure 4 (Matsunaga et al.)

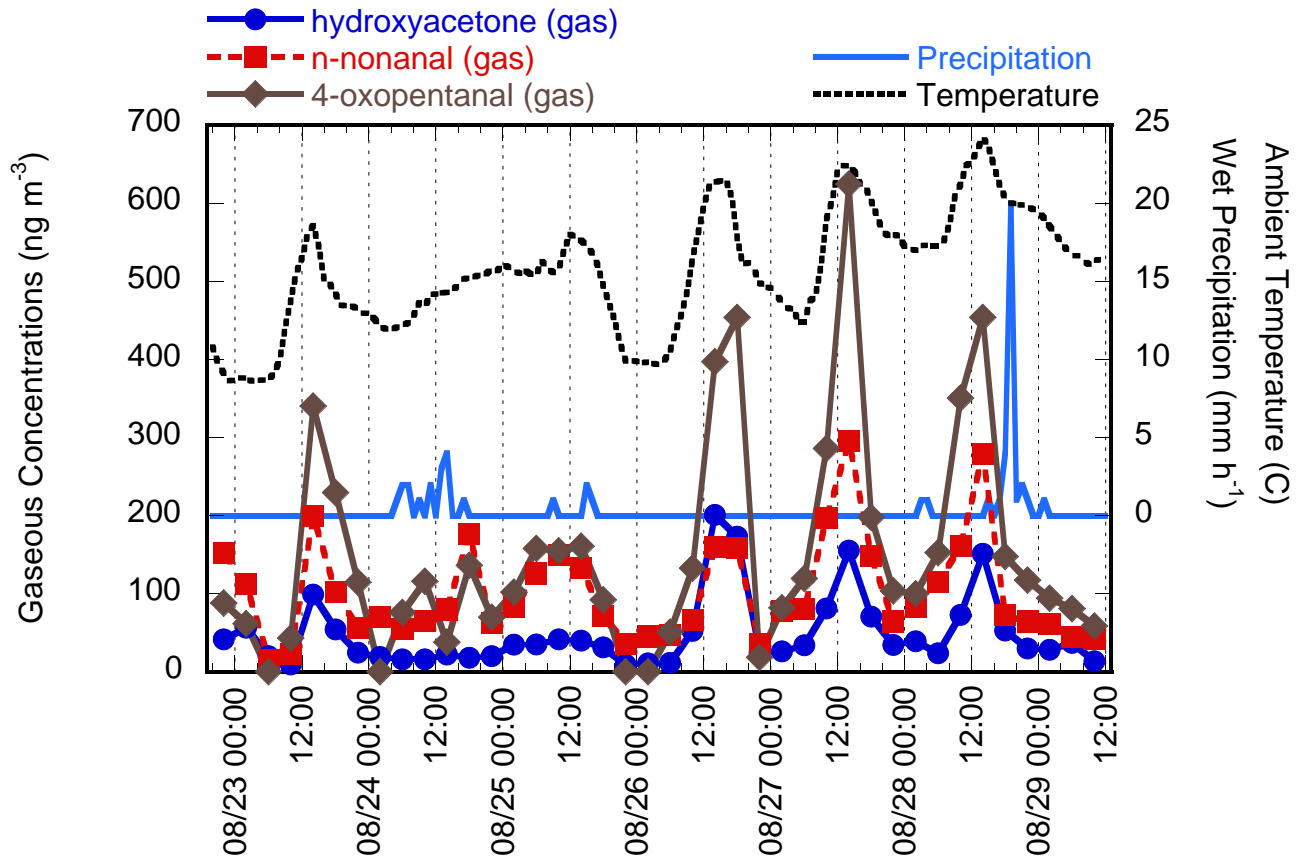


Figure 5 (Matsunaga et al.)

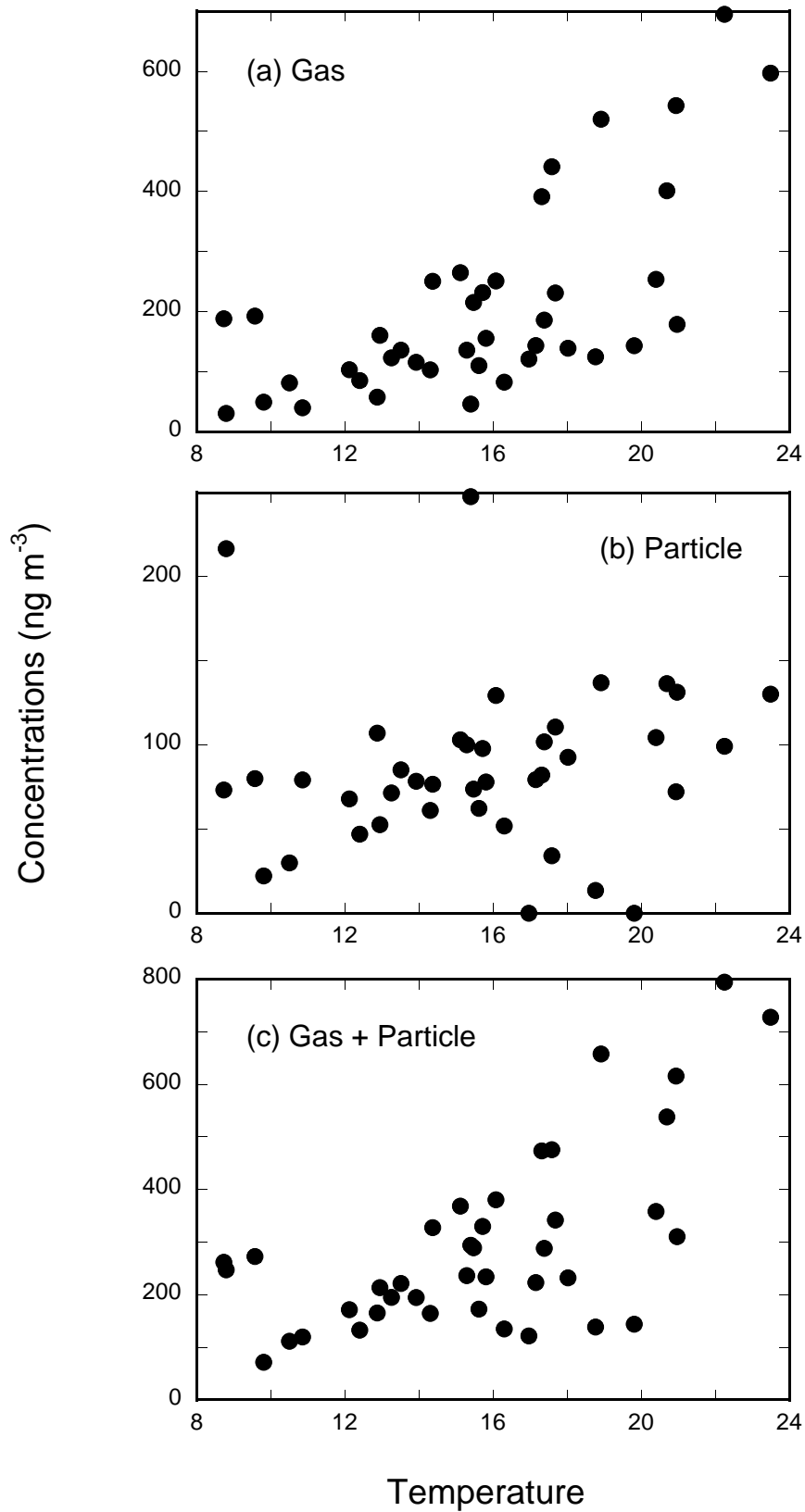


Figure 6 (Matsunaga et al.)

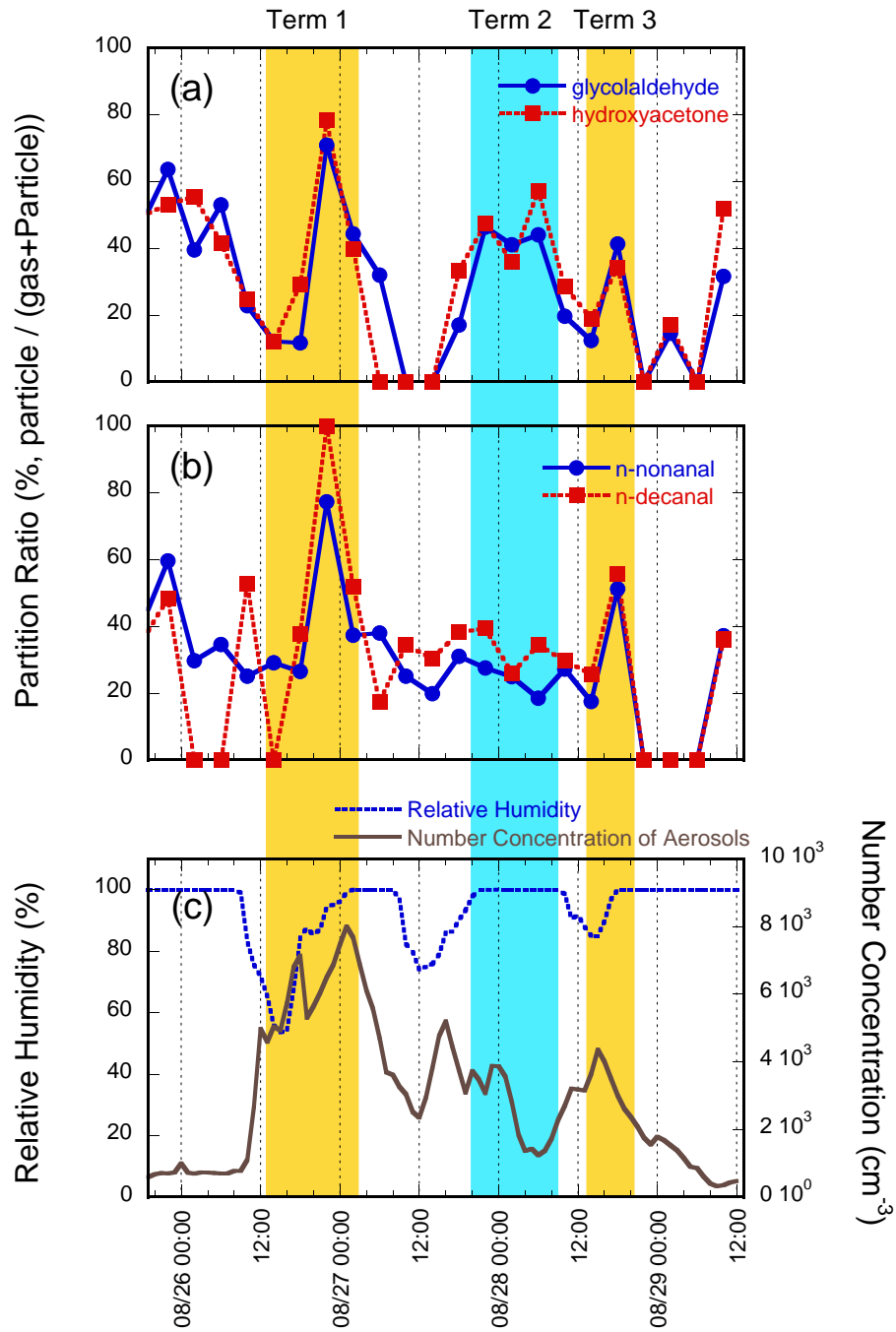


Table 1 The maximum, minimum, average and median of the gaseous concentrations of the SOCs

	Maximum ng m ⁻³	(pptv)	Minimum	Average	Median
glycolaldehyde	283	(116)	10	72	40
hydroxyacetone	201	(67)	9	48	34
n-nonanal	295	(51)	15	102	79
n-decanal	163	(26)	*	44	41
glyoxal	154	(65)	*	42	32
methylglyoxal	257	(88)	12	83	66
4-oxopentanal	625	(153)	*	150	109

*: Below the detection limit (3~5 ng m⁻³)

Table 2 The maximum, minimum, average and median of the particulate concentrations and the gas-particle partition ratios (particle / (gas + particle)).

	Particulate concentrations (ng m ⁻³)			Partition ratios (P/(G+P)%)		
	Maximum	Minimum	Median	Maximum	Minimum	Median
glycolaldehyde	76	*	28	33	75	40
hydroxyacetone	89	*	22	20	78	36
n-nonanal	119	*	43	46	86	28
n-decanal	81	*	21	21	100	30
glyoxal	91	*	31	32	100	46
methylglyoxal	188	*	43	40	94	35
4-oxopentanal	196	*	57	53	100	30

*: The particulate concentration was below the detection limit (3~5 ng m⁻³)