Growth of organic aerosols by biogenic semi-volatile carbonyls in the forestal atmosphere

Sou Matsunaga\textsuperscript{a,b,}\textsuperscript{*}, Michihiro Mochida\textsuperscript{a}, Kimitaka Kawamura\textsuperscript{a}

\textsuperscript{a}Institute of Low Temperature Science, Hokkaido University, N19 W8, Kita-Ku, Sapporo 060-0819, Japan
\textsuperscript{b}Graduate School of Environmental Earth Science, Hokkaido University, N10 W5, Kita-Ku, Sapporo 060-0810, Japan

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Abstract

Gas and aerosol samples were collected from 13 to 15 August 2001 in \textit{Quercus} and \textit{Picea} mixed forest located at Uryu Experimental Forest of Hokkaido University using an annular denuder air sampling system. Gaseous concentrations of biogenic semi-volatile compounds (glycolaldehyde, hydroxyacetone, \textit{n}-nonanal and \textit{n}-decanal) showed a rapid increase in the morning and showed a maximum (61–105 pptv) around noontime. Then their concentrations significantly decreased in the evening, and showed a minimum at mid-night. On the other hand, these compounds in the particulate phase also showed a diurnal variation pattern similar to the gaseous compounds. However, the concentrations continued to increase until the evening and showed the maximum at nearly mid-night. The time lag of several hours in the peak of concentrations of these carbonyls in gas phase and particles indicates a gas-to-particle conversion probably through condensation and adsorption of gaseous compounds onto the pre-existing particles (growth of the aerosols). © 2003 Elsevier Science Ltd. All rights reserved.

Keywords: Oxidation products; Isoprene; Aldehydes; Condensation; Annular denuder; Benzyldihydroxyl oxime derivatization

1. Introduction

Atmospheric particles including organic aerosols play an important role in the radiation balance on the earth by scattering or absorbing light and acting as cloud condensation nuclei (Andreae and Crutzen, 1997; Matsunaga et al., 1999; Kawamura and Sagaguchi, 1999). Recent studies demonstrated that biogenic volatile organic compounds contribute to the formation and growth of aerosols through gas-to-particle conversion (Hatakeyama et al., 1989; Andreae and Crutzen, 1997; Kavouras et al., 1998, 1999; Guenther et al., 1995). Although monoterpenes are an important source of biogenic organic aerosols (Hatakeyama et al., 1989; Guenther et al., 1995; Kavouras et al., 1999; Hoppel et al., 2001), we still have missing sources that contributes to secondary organic aerosols of biological origin. In this study, we measured, in both gas and particle phases, glycolaldehyde and hydroxyacetone which are known as the oxidation products of isoprene (Tuazon and Atkinson, 1989, 1990; Atkinson, 1990), together with biogenic semi-volatile aldehydes (\textit{n}-nonanal and \textit{n}-decanal; Batten et al., 1995; Kesselmeier and Staudt, 1999). Here, we discovered a strong diurnal variation of these carbonyls with their particulate concentrations being comparative to the oxidation product of monoterpenes (pinonic acid). They are most likely produced in and/or emitted to the atmosphere as gases, and later converted to the particles. This study demonstrates that the semi-volatile carbonyls largely contribute to the formation and growth of aerosols in the forest and potentially play a significant role in the global budget of organic aerosols.
Aerosols are formed and grown by the materials that have relatively low vapor pressures such as sulfuric acid and the organic compounds called as semi-volatile organic compounds (SOCs, Andreae and Crutzen, 1997; Matsunaga et al., 1999; Kawamura and Sagaguchi, 1999). The SOCs are not only directly emitted from their sources but also formed from gaseous compounds by atmospheric oxidation (Hatakeyama et al., 1989; Kavouras et al., 1998, 1999). In addition, the emission rate of the biogenic SOCs on a global scale exceeds that of anthropogenic SOCs by the factors of ten or more (Andreae and Crutzen, 1997; Guenther et al., 1995). Oxidation products of monoterpenes have been regarded as one of the most important constituent of biogenic organic aerosols (Andreae and Crutzen, 1997; Guenther et al., 1995; Hoppel et al., 2001). However, biogenic SOCs still have uncertainties in their sources and components.

2. Experimental

2.1. Sampling site

Gas and aerosol samples were collected from 13 to 15 August 2001 in Quercus and Picea mixed forest located at Uryu Experimental Forest of Hokkaido University (rural area, 200 km north of Sapporo) using an annular denuder air sampling system (Possanzini et al., 1983; Gundel et al., 1995; Eatough et al., 1999). The air sampling was conducted in the forest, whose canopy level was approximately 15 m high. The inlet of the sampler was set at 3.5 m above the ground level. Air sampling was conducted under a clean sky condition. Rain was not observed throughout the observation; however, fog emerged early in the morning. The wind speed at 3.5 m level was <0.01 m s\(^{-1}\), whereas at 10 m it ranged from 0.12 to 0.84 m s\(^{-1}\) (average, 0.42 m s\(^{-1}\)).

2.2. Sample collection and treatment

Carbonyl compounds were collected with annular denuder (URG-2000-30-3CSS; 242 mm length \(\times\) 30 mm i.d., distances of the inner walls are 1 mm and 1.5 mm) coated with \(O\)-benzylhydroxylammonium chloride, 47 mm quartz fiber filter that was impregnated by the same reagent as denuders, and back up denuder (Possanzini et al., 1983; Gundel et al., 1995; Eatough et al., 1999). A cyclone (50% cut-off diameter >2.5 \(\mu\)m) was set at the inlet of the sampling system. The front denuder collects gaseous compounds, whereas quartz fiber filter collects particulate compounds that have passed through the front denuder. The contamination of the front denuder by adsorbing of the particles is negligible. Finally, the back up denuder collects the compounds that evaporated from quartz fiber filter. The flow rate of air sampling was 41 min\(^{-1}\), and sampling time was 3.5 h. To exchange the denuder and filter, the pump was stopped for 30 min in between every sampling period (16:15–19:45, 20:15–23:45, 24:15–03:45, 04:15–07:45, 08:15–11:45 and 12:15–15:45 local time). In order to remove ozone and other oxidants, NO was mixed with the ambient air at the inlet of the cyclone, where the concentration and mixing flow rate of NO was controlled to be 0.5% and 1 ml/min, respectively.

Carbonyl compounds collected on the denuders and filters were in situ reacted with the reagent and derivatized to benzyl hydroxyl oximes (BH oximes) by the reagent. The collection efficiency of each gaseous compound described in this study was more than 90%. Formation of the particulate compounds on the filters was also checked, and the artifact on the filters was found to be negligible. Details of the sampling method and the results of more examinations for the sampling system are under preparation for a contribution by Matsunaga and co-workers. The BH oximes in denuders were extracted with ethyl acetate on the sampling site, and the extracts and filter samples were stored at \(-20^\circ\)C prior to the analysis. The extracts and filters were analyzed by GC/FID (Carlo Erba GC6000). Details of analytical procedure are described in Matsunaga and Kawamura (2000). Estimated errors in the determination of gaseous and particulate compounds were \(\sim \pm 10\%\) and \(\sim \pm 15\%\) at 10–50 pptv, respectively. The values which indicate the concentrations of the compounds in the manuscript have been already subtracted the blank values. Identification of the compounds measured in this study was conducted by comparison with authentic standards.

3. Results and discussion

3.1. Variations of concentrations of the SOCs

Figs. 1a–e present diurnal variations in the concentrations of both gaseous and particulate glycolaldehyde (GAL), hydroxyacetone (HAC), \(n\)-nonanal and \(n\)-decanal, and changes in light intensity, temperature and relative humidity at the sampling point. Gaseous concentrations of these compounds showed a rapid increase from 06:00 to 14:00 (local time). This diurnal pattern is consistent with the light intensity that showed a maximum around noontime (Figs. 1a–d). The gaseous concentrations became minimum early in the morning before the sunrise (02:00 to 06:00), and increased quickly showing a maximum around noontime. These variations suggested that the semi-volatile carbonyls were vigorously produced and/or released in the forestal atmosphere at daytime. However, their concentrations significantly decreased in the evening, and showed a minimum at mid-night.
Particulate GAL, HAC, nonanal and decanal were detected in the atmosphere. Their concentrations showed a diurnal variation pattern similar to the gaseous compounds. However, the concentrations continued to increase until the evening (18:00), when the relative humidity increased up to 80% (see Fig. 1a–e). The time lag of several hours in the peak of concentrations of these carbonyls in gas phase and particles indicates a gas-to-particle conversion probably through condensation and adsorption of gaseous compounds onto the pre-existing particles (growth of the aerosols). These processes should be accelerated in the afternoon when the ambient temperature decreased toward the evening. Interestingly, the gas/particle concentration ratios of GAL largely decreased from 14.8 to 0.79 at 24:00 14 August. Similar results were obtained for other three compounds. This shift of the gas/particle partitioning is involved with the formation and growth of aerosols that are accelerated in the afternoon/evening. The concentrations in particle phase decreased and showed a minimum from midnight to early in the morning. Such a decrease is probably caused by the deposition of aerosols within the forest and by the transport out of the area through vertical convection (Sillman et al., 2002).

3.2. Sources and fates of the SOCs

GAL and HAC are known as the oxidation products of isoprene (Tuazon and Atkinson, 1989, 1990; Atkinson, 1990). In addition, GAL is known as the oxidation products of 2-methyl-3-buten-2-ol (Ferronato et al., 1998) which is unsaturated alcohol emitted from Picea trees (Goldan et al., 1993). Nonanal and decanal are not likely produced in the atmosphere by the atmospheric chemical reactions. For nonanal, a production pathway is proposed (Simonet et al., 1988), that is, ozonolysis of unsaturated fatty acids containing a C\textsubscript{9} double bond at C-9 position (such as oleic acid), whereas it is not likely for decanal. However, the concentrations of nonanal and decanal are equivalent in both gas and particle phases (see Fig. 1), suggesting that the ozonolysis is not an important source of nonanal in the forestal atmosphere. If \( n \)-decanal could be produced by ozonolysis of its precursor, the precursor should have C\textsubscript{10} double bond at \( \Delta C_{10} \) position. The amount of aliphatic compound which have C\textsubscript{9} double bond on \( \Delta C_{9} \) position in the atmosphere and plant waxes are in general much smaller than the \( \Delta C_{10} \) double bonded compounds. Therefore, production of \( n \)-decanal by ozonolysis should be negligible. Recently, a significant emission of nonanal and decanal from vegetation has been suggested (Kesselmeier and Staudt, 1999). Thus, the direct emission of nonanal and decanal is the most likely source that controls their concentrations in the forestal atmosphere. The diurnal variation of the compounds was similar to that of ambient light intensity (see Figs. 1c and d), also suggesting a biogenic emission of these aldehydes.
Vapor pressures of oxygenated organic compounds, such as GAL and HAC, which are produced in the atmosphere by oxidative reactions, are generally lower than their precursors. These oxygenated compounds are sometimes semi-volatile and polar, and are likely dissolved in a water droplet such as fog and mist as well as the liquid phase in aerosols, which adsorb them. These SOCs can be present as gases in the beginning, but later converted to particles either by condensation or adsorption onto the pre-existing particles. The dissolution into the water droplets and/or the liquid phase in aerosols should accelerate gas-to-particle conversion of SOCs. The carbonyls tend to exist in gas phase at daytime under the conditions of higher ambient temperature and lower humidity, but are converted into particles in the evening by the mechanisms described above. Those condensation processes should be accelerated by an increase in numbers of aerosols (Kavouras et al., 1999) and a decrease in the ambient temperature (Kavouras et al., 1999) and an increase in the relative humidity from daytime to evening. Although a part of carbonyls in the particle phase would be vaporized from the aerosols when they are transported out of the canopy, some portion of them may stay in the aerosols. In addition, if the carbonyls would be further oxidized on the aerosols, the oxidation products are more polar and have lower vapor pressures than their precursors.

The gaseous SOCs also adsorb on the surfaces of plant stems, and leaves the ground, or are oxidized by atmospheric oxidants such as OH. As seen in Fig. 1a, the concentration of gaseous GAL decreased from 184 ng m\(^{-3}\) (14:00) to 23.2 ng m\(^{-3}\) (22:00) on 14 August (the concentration decreased by 161 ng m\(^{-3}\) in 8 h). The decrease due to the oxidation with OH in the 8 h was estimated to be only ~11.6 ng m\(^{-3}\) (~7.2% of decreased gaseous GAL), assuming that concentration of OH and rate constants of the reaction between GAL and OH are 1 \times 10^6 (molecules cm\(^{-3}\)) and 9.9 \times 10^{-12} (cm\(^3\) molecules s\(^{-1}\); Atkinson et al., 1989; Bacher et al., 2001), respectively. Thus, the decrease in the concentration of GAL cannot be explained by the removal with OH only. Furthermore, the oxidation of GAL by ozone and NO\(_3\), and the photolysis are not important (Atkinson et al., 1989; Bacher et al., 2001). Therefore, a part of the gaseous GAL should be removed from the atmosphere by dry deposition onto the existing aerosols and other surfaces such as plant stems and leaves and soils at the sampling site. In addition, gaseous GAL was also removed from the forest by a vertical convection and probably was oxidized to more polar compounds during a long-range transport. The loss process of gaseous HAC is probably same as that of gaseous GAL.

### 3.3. Comparison with the oxidation product of monoterpenes

Pinonic acid, an oxidation product of \(\alpha\)-pinene (Kavouras et al., 1998, 1999; Hoppel et al., 2001), was also detected in the gas phase and particles. Concentrations of particulate pinonic acid ranged 0–781 ng m\(^{-3}\). Table 1 presents concentrations of a series of compounds measured in this study. Pinonic acid has been considered as the most abundant organic species in the aerosols derived from the oxidation of monoterpenes (Kavouras et al., 1998, 1999). The concentrations of GAL and HAC, as well as nonanal and decanal, in particles are comparative to that of pinonic acid (Table 1), indicating that these carbonyls are also important constituents of aerosols in the forestal atmosphere. Although the vapor pressures of these compounds are estimated to be several orders of magnitude higher than that of pinonic acid (Makar, 2001), their gas/particle partitioning ratios were comparative to that of pinonic acid (see Table 1). One explanation is that hemi-acetal and/or acetal are formed from such carbonyl compounds by a reaction with alcohols which is abundant in the atmosphere (Jang and Kamens, 2001). Under the ambient conditions, the carbonyls should adsorb onto and/or dissolve into the pre-existing aerosols more efficiently. Under the condition of high humidity that was recorded in the evening to night, the aerosols at the nighttime may become a complex mixture of water, organics, and inorganics. Hence, the apparent gas/particle partitioning ratios in the forestal atmosphere

<table>
<thead>
<tr>
<th>Compound</th>
<th>Max. (ng m(^{-3}))</th>
<th>Min. (ng m(^{-3}))</th>
<th>Med. (ng m(^{-3}))</th>
<th>Ave. (ng m(^{-3}))</th>
<th>Max. (ng m(^{-3}))</th>
<th>Min. (ng m(^{-3}))</th>
<th>Med. (ng m(^{-3}))</th>
<th>Ave. (ng m(^{-3}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glycolaldehyde</td>
<td>184 (78)</td>
<td>23 (10)</td>
<td>58 (24)</td>
<td>86 (36)</td>
<td>156</td>
<td>1</td>
<td>11</td>
<td>46</td>
</tr>
<tr>
<td>Hydroxyacetone</td>
<td>180 (61)</td>
<td>—</td>
<td>78 (26)</td>
<td>94 (32)</td>
<td>593</td>
<td>—</td>
<td>31</td>
<td>95</td>
</tr>
<tr>
<td>(n)-Nonanal</td>
<td>241 (102)</td>
<td>3 (1)</td>
<td>102 (43)</td>
<td>108 (46)</td>
<td>262</td>
<td>—</td>
<td>76</td>
<td>91</td>
</tr>
<tr>
<td>(n)-Decanal</td>
<td>249 (105)</td>
<td>16 (7)</td>
<td>133 (56)</td>
<td>127 (54)</td>
<td>290</td>
<td>16</td>
<td>47</td>
<td>76</td>
</tr>
<tr>
<td>Pinonic acid</td>
<td>164 (22)</td>
<td>—</td>
<td>—</td>
<td>37 (5)</td>
<td>781</td>
<td>—</td>
<td>194</td>
<td>212</td>
</tr>
</tbody>
</table>

Detection limits were 1 ng m\(^{-3}\) in both gas phase and particles (for glycolaldehyde).
should be smaller than those estimated from their vapor pressures under laboratory conditions, as suggested by Jang and Kamens. In addition, there is a possibility that low volatility of the carbonyl compounds is due to the formation of gem-diol (Streiwieser Jr. and Heathcock, 1981).

3.4. Estimation of the global emission rate of four biogenic SOCs

Based on the present results, we estimate a potential contribution of GAL, HAC, nonanal and decanal to the global budget of organic aerosols. On a global scale, emission rates of monoterpenes have been estimated to be 127 Tg yr\(^{-1}\) (Guenther et al., 1995). The aerosol yields for monoterpenes were estimated to be 4.2–14.5\% (Griffin et al., 1999; Kanakidou and Tsagaridis, 2000). Pinonic acid accounts for ~28\% of the total oxidation products of monoterpenes (Kavouras et al., 1999) in particulate phase, thus the contribution of pinonic acid to the aerosols can be calculated to be 1.5–5.2 Tg yr\(^{-1}\).

On the other hand, the concentration ratios of these compounds to pinonic acid in the particles were calculated by using the data set obtained in this study (Table 2). The ratio of emission rate of isoprene to monoterpenes at our sampling site was estimated to be 7.4 (Kesselmeier and Staudt, 1999) with an assumption that population of Quercus and Picea are roughly equivalent in the experimental forest, whereas the ratio in a global scale was also estimated to be 3.9 (Guenther, 1999). Then, the ratios for GAL and HAC in Table 2 were multiplied by 0.53 (=3.9/7.4).

Based on these results and considering that the global emission rate of the biogenic organic aerosols is estimated to be 60 Tg yr\(^{-1}\) (Kiehl and Rodhe, 1995), we estimated the contributions of GAL and HAC to global aerosol formation and growth to be 0.19–0.68 Tg yr\(^{-1}\) (1.1–13\% of that of the oxidation products of monoterpenes (5.4–18 Tg yr\(^{-1}\))) and 0.29–1.1 Tg yr\(^{-1}\) (1.6–20\%), respectively. In a similar way, the global contributions of nonanal and decanal were estimated to be 0.69–2.6 (3.8–48\%) and 0.42–1.6 Tg yr\(^{-1}\) (2.3–30\%), respectively, with an assumption that the ratio of emission rate of these aldehydes to that of monoterpenes are roughly equal in the forests on a global scale. The range of total contribution of these compounds is 1.6–6.0 Tg yr\(^{-1}\) (8.9–110\%). This is obviously comparable to that of oxidation products of monoterpenes. Although some portions of the organic aerosols are deposited in the forest, the rest, as same as the case of gaseous compounds, should be transported out of the forest via the vertical convection. During the atmospheric transport, the organic species in the aerosols could be further converted to more oxygenated compounds whose vapor pressure should be lower than their precursors.

4. Conclusion

The concentrations of four biogenic semi-volatile carbonyl compounds in both gaseous and particulate phase were determined in the experimental forest. The diurnal variation of the concentrations indicated that they converted from gases to atmospheric particles. In addition, their concentrations in the particulate phase were comparable to that of oxidation product of monoterpenes. This demonstrates that the semi-volatile carbonyls that have not been regarded as the constituents of the aerosols, should be taken into account for the further consideration of the formation and growth of biogenic organic aerosols on a global scale.

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References


Table 2

<table>
<thead>
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<th>Ave.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glycolaldehyde</td>
<td>76</td>
<td>1</td>
<td>22</td>
</tr>
<tr>
<td>Hydroxyacetone</td>
<td>101</td>
<td>0</td>
<td>23</td>
</tr>
<tr>
<td>n-Nonanal</td>
<td>106</td>
<td>0</td>
<td>46</td>
</tr>
<tr>
<td>n-Decanal</td>
<td>229</td>
<td>15</td>
<td>49</td>
</tr>
</tbody>
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