Observation of gaseous and particulate products of monoterpene oxidation in forest atmospheres

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Abstract. Atmospheric oxidation of biogenic hydrocarbons, such as monoterpene, is estimated to be a significant source of global aerosol. Whereas laboratory studies have established that photochemical oxidation of monoterpene leads to aerosol formation, there are limited field studies detecting such oxidation products in ambient aerosols. Drawing on prior results of monoterpene product analysis under controlled smog chamber conditions, we have identified organic aerosol components attributable to monoterpene oxidation in forest atmospheres, Kejimkujik National Park, Nova Scotia, Canada, and Big Bear, San Bernardino National Forest, California, U.S.A. The major identified aerosol products derived from $\alpha$-pinene and $\beta$-pinene oxidation include pinic acid, pinonic acid, norpinonic acid and its isomers, hydroxy pinonaldehydes, and pinonaldehyde, concentrations of which in the aerosol phase are in the sub-ng m$^{-3}$ range. Identification of oxidation products in atmospheric aerosol samples serves as direct evidence for aerosol formation from monoterpenes under ambient conditions.

1. Introduction

The atmospheric aerosol-forming potential of biogenic hydrocarbons was noted as early as 1960 [Went, 1960], and laboratory studies have established that atmospheric oxidation of monoterpenes and sesquiterpenes leads to aerosol formation [Hoffmann et al., 1997; Griffin et al., 1999]. Production of biogenic secondary organic aerosols on a global basis is estimated to range between 30 and 270 Tg year$^{-1}$, a magnitude comparable to the production of biogenic and anthropogenic sulfate aerosols [Andreae and Crutzen, 1997].

Monoterpenes are important constituents of aerosol-forming biogenic compounds [Griffin et al., 1999]. Despite numerous field measurements of gas-phase monoterpenes [e.g., Roberts et al., 1983; Zimmerman et al., 1988; Clement et al., 1990; Biesenthal et al., 1998], there are few field studies in which their oxidation products have been measured. Recent advances in analytical methods have now made it possible to detect and identify such secondary organic aerosol components, which generally have multiple polar oxygenated functional groups [Yu et al., 1998; 1999]. Ambient measurements of biogenic hydrocarbon oxidation products in the atmospheric aerosol provide the link that establishes the importance of this source to global tropospheric aerosol. We present here measurements of monoterpene-derived aerosol components in two forest atmospheres, Kejimkujik National Park, Nova Scotia, Canada, and San Bernardino National Forest, California, U.S.A.

2. Ambient Sampling and Analysis

The measurement site in Kejimkujik National Park (44°26' N, 62°12' W) is situated in the Atlantic province of Nova Scotia. The park is in a forest consisting of a mixture of two-thirds coniferous and one-third deciduous trees [Bottenheim et al., 1994]. Ambient mixing ratios of $\alpha$-pinene and $\beta$-pinene were determined on-line using a Hewlett-Packard GC/MS [Biesenthal et al., 1998]. Aerosol samples were collected in July, 1996 over a period of 2 to 3 days at a flow rate of 10 L min$^{-1}$ on 47 mm quartz fiber filters. Since the aerosol samples were collected in a field campaign that did not include characterizing semivolatile organics as one of its goals, adequate sampling devices were not implemented to minimize sampling artifacts for semivolatiles. Collection of two filter samples analyzed in this work commenced on July 5 and July 8, based on a sampled air volume of 26.94 and 44.72 m$^{3}$, respectively. The diurnal temperature during the sampling period ranged from 11 to 21°C, and the relative humidity from 13% to 50% [Leaitch et al., 1999].

The measurement site in the San Bernardino National Forest is located in Big Bear Valley (34°13' N, 116°49' W), CA, at an elevation of 2150 meters. Lodgepole pines, pinion pines, oaks, and Douglas firs are major tree species in this area. Hourly measurements of gas-phase monoterpenes were achieved by collecting 300 L of air on Tenax tubes, and were then analyzed by a Hewlett-Packard GC/MS following thermal desorption using a Tekmar AeroTrap Desorber 6000. Two types of aerosol sampling devices were deployed, one consisting of one or two denuders followed by a glass fiber filter and the other one consisting of two 47 mm filters--a Teflon impregnated glass fiber filter and the other one consisting of two 47 mm filters--a Teflon impregnated glass fiber filter followed by a glass fiber filter. Two sampling trains were set up for each type of sampling device. The sampling train with
**Table 1. Monoterpene Oxidation Products Detected at Forest Sites**

<table>
<thead>
<tr>
<th>Name</th>
<th>Structure</th>
<th>Note</th>
</tr>
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<td>C$<em>9$H$</em>{14}$O$_4$</td>
<td><img src="image1" alt="Structure" /></td>
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</tr>
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<td><img src="image3" alt="Structure" /></td>
<td>e, f</td>
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<tr>
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<td></td>
</tr>
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</tr>
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<td>a, h</td>
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<tr>
<td>MW=186</td>
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</tr>
</tbody>
</table>

* identification confirmed with an authentic standard.
* known product of O$_3$ oxidation of $\alpha$-pinene and $\beta$-pinene.
* detected in Kejimkujik samples.
* known product of O$_3$ oxidation of $\alpha$-pinene, $\beta$-pinene, sabine and A$\gamma$-carene.
* detected in Kejimkujik and Big Bear samples.
* known product of O$_3$ oxidation of $\beta$-pinene.
* detected in Big Bear denuder samples.
* known product of O$_3$ oxidation of $\alpha$-pinene.
* detected in Big Bear denuder and filter samples.
* possible product of O$_3$ oxidation of limonene.

**Figure 1. Chemical ionization mass spectrum for the derivative of a C$_9$ dioxo carboxylic acid compound detected in aerosol samples.**

**3. Results and Discussion**

**3.1 Identification of Monoterpene Oxidation Products**

Oxidation products of $\alpha$-pinene and $\beta$-pinene in the ambient samples were identified by comparing GC chromatograms and mass spectra of the ambient samples with those obtained from controlled chamber experiments. Table 1 lists the chemical structures of the monoterpene oxidation products observed. Established products from oxidation of $\alpha$-pinene and $\beta$-pinene include pinic acid, norpinic acid, pinionaldehyde, norpinonaldehyde, hydroxy pinononaldehydes, pinonic acid, norpinonic acid, hydroxy pinonic acid, hydroxy pina ketones, and norpinoine. An unidentified product (denoted X$_1$), having two carbonyl groups and a molecular weight of 198 as determined from its EI and CI mass spectra, is observed in both laboratory generated aerosol in the $\alpha$-pinene/O$_3$ system and ambient aerosols at both sites. Besides oxidation products derived from $\alpha$-pinene and $\beta$-pinene, a compound denoted X$_2$, detected in samples from both sites, is identified as a C$_9$ dioxo mono-carboxylic acid, having a molecular weight of 186. Fig. 1 displays the CI mass spectrum for the PFBHA and TMS derivative of this compound X$_2$. The molecular weight and some structural information can be determined from the mass spectrum [Yu et al., 1998]. Ozone oxidation of limonene could lead to the formation of a C$_9$ dioxo mono-carboxylic acid, 3-acetyl-6-oxo-heptanoic acid, as illustrated in Fig. 2 [Horie et al., 1994; Neeb et al., 1997]. The mass spectrum shown in Fig. 1 is consistent with that expected for this compound.

**3.2 Kejimkujik Samples**

Table 2 lists mixing ratios of three monoterpenes and concentrations of various monoterpene oxidation products in the aerosol phase in two filter samples collected in Kejimkujik National Park. All the identified oxidation products are detected at the sub-nanogram m$^3$ level. The presence of monoterpene oxidation products in filter samples correlates with the observation that aerosol volume increased.
with the decrease in α-pinene and β-pinene during the same sampling period at this same site [Leaitch et al., 1999].

3.3 Big Bear Samples

Table 3 lists the mixing ratios of six monoterpenes and the concentrations of various monoterpene oxidation products detected in both the gas and aerosol phases in the San Bernardino National Forest of California. The denuder/filter set-up at this site allowed simultaneous determination of semi-volatile compounds in both gas and particulate phases. Species collected by the denuder represent those in the gas phase. Denuder collection efficiencies for the products in Table 3 range from 0.88 to 1.0. Gas-phase concentrations as determined from denuder samples have been corrected for the semi-volatile compounds in both gas and particulate phases.

Comparison of filter samples in the presence and absence of a denuder in front of the sampling train indicates that the filter-only technique suffers a positive sampling artifact. Semivolatile products are also detected on the back filter in the filter-only set-up, which is evidence for filter adsorption of gaseous semivolatile organics. Concentrations obtained via the filter-only technique are 120%-137% higher than those obtained using the denuder/filter sampling device for sampling conditions employed at the Big Bear site. McDow and Huntzicker [1990] observed a significant increase of positive artifact with decreasing filter face velocity for a quartz fiber filter. They estimated that at low organic carbon concentrations, the correction factor due to adsorption could exceed 50% at a sampling face velocity of 40 cm s⁻¹. Considering the lower face velocity (~20 cm s⁻¹), the positive artifact observed at the Big Bear site is in general agreement with McDow and Huntzicker's results. Therefore, the filter-only technique is not adequate for measurements of biogenic oxidation products in the aerosol phase. Concentrations derived from the two Kejimkujik filter samples likely overestimate the actual aerosol concentrations for this reason.

4. Comparison with Prior Field Studies

Previous field measurements of particulate-phase terpene oxidation products have been limited to pinonaldehyde, pinonic acid, and nopinone. A recent study has also measured ambient concentrations of pinic acid and norpinonic acid [Kavouras et al., 1999]. Yokouchi and Ambe [1985] measured pinonaldehyde concentrations of 2-3 ng m⁻³ in aerosol samples collected in the cedar forest at Kiyosumi and in the pine forest at Tsukuba in Japan in summer time. Satsumabayashi et al. [1990] detected pinonaldehyde at 30 ng m⁻³, and hydroxy pinonic acid near Ispra, Italy at 90 ng m⁻³ using DNPH-coated cartridges. Since an ozone scavenger was used in this study, which also collected particles, this concentration reflects that in the gas-phase. Kavouras et al. [1998] reported aerosol concentrations for pinonic acid, nopinone, and pinonaldehyde ranging from 9-140, 0.3-13.2, and 0.17-32.1 ng m⁻³, respectively, at a forest site in Portugal. In the most recent study, Kavouras et al. [1999] deployed a denuder/filter sampling device to measure monoterpene oxidation products in both gas and aerosol phases in a conifer forest located in Pertouli in Central Greece. They reported diurnal particulate concentrations for pinic acid, pinonic acid, norpinonic acid, pinonaldehyde, and nopinone to be 1.0-25.7, 0.4-4.4, 0.2-5.4, 0.2-1.2, and 0-0.4 ng m⁻³, respectively. In this study, simultaneous measurements of Aitken nuclei also provided evidence that
the photooxidation products from biogenic precursors play a role in forming new particles.

Considering the many factors influencing concentrations of aerosol-phase monoterpene oxidation products, the wide variability of ambient concentrations among the six studies is not surprising. Pinonaldehyde, for example, was measured in all six studies with concentrations ranging from under detection limit to 100 ng m⁻³. Concentrations of precursor monoterpenes and atmospheric oxidants govern formation rate of the products. The higher mixing ratios of α-pinene (0-3.2 ppbv) and β-pinene (0-1.4 ppbv) may partly account for the more plentiful oxidation products in the aerosol phase in the study of Kavouras et al. [1999]. The aerosol-phase fraction of a semi-volatile organic compound, such as any of the monoterpane oxidation products, is known to be controlled by available organic aerosol mass and the compound's gas-aerosol partitioning coefficient, which, in turn, is a function of temperature and the overall aerosol chemical composition [Odum et al., 1996; Jang et al., 1997; Jang and Kamens, 1999; Yu et al., 1999]. Besides these factors intrinsic to aerosol formation, sampling artifacts can also introduce variability in the reported concentrations. For example, as noted earlier, the filter-only technique suffers a positive artifact from adsorption of gas-phase semi-volatiles onto the filter surface, whereas volatilization of aerosol-phase semi-volatiles introduces a negative artifact, which depends on sampling rate and filter area [McDow and Huntzicker, 1990]. In addition, a number of products (e.g. pinonaldehyde and norpinonic acid) do not have available commercial standards, and different surrogate compounds have been used to estimate their concentrations.

5. Conclusions

We have detected in two forest atmospheres a number of gas- and aerosol-phase products from oxidation of α-pinene and β-pinene, including pinic acid, norpinic acid, pinonic acid, norpinonic acid and its isomers, pinonaldehyde, Norpinonaldehyde, hydroxy pinonaldehydes, hydroxy pinonic acid, and norpinone. In addition, a C₁₀ dioxo carboxylic acid, detected at both sites, is postulated to be 3-acetyl-6-oxoheptanoic acid, a product expected from ozonolysis of limonene. Identification of monoterpenone oxidation products in aerosol samples serves as direct evidence for aerosol formation from monoterpenes under ambient conditions.

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References


