

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

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Abstract. Atmospheric oxidation of biogenic hydrocarbons, such as monoterpenes, is estimated to be a significant source of global aerosol. Whereas laboratory studies have established that photochemical oxidation of monoterpenes 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 two forest atmospheres, Kejimikujik National Park, Nova Scotia, Canada, and Big Bear, San Bernardino National Forest, California, U.S.A. The major identified aerosol products derived from α -pinene and β -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; Biesenhal *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, Kejimikujik National Park, Nova Scotia, Canada, and San Bernardino National Forest, California, U.S.A.

2. Ambient Sampling and Analysis

The measurement site in Kejimikujik 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 α -pinene and β -pinene were determined on-line using a Hewlett-Packard GC/MS [Biesenhal *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 m³, respectively. The diurnal temperature during the sampling period ranged from 11 to 21°C, and the relative humidity from 13% to 50% [Leaith *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, piñon 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 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

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Table 1. Monoterpene Oxidation Products Detected at Forest Sites

Name	Structure	note
C ₈ H ₁₂ O ₄ norpinic acid MW=172		a, b
C ₉ H ₁₄ O ₄ * pinic acid MW=186		c, d
C ₉ H ₁₄ O * nopinone MW=138		e, f
C ₉ H ₁₄ O ₂ hydroxy pina ketones MW=154		e, f
C ₉ H ₁₄ O ₃ norpinonic acid & its isomers MW=170		a, d
C ₁₀ H ₁₆ O ₃ * pinonic acid MW=184		g, d
C ₁₀ H ₁₆ O ₄ hydroxy pinonic acid MW=200		a, h
C ₉ H ₁₄ O ₂ norpinonaldehyde MW=154		g, f
C ₁₀ H ₁₆ O ₂ pinonaldehyde MW=168		g, d
C ₁₀ H ₁₆ O ₃ hydroxy pinonaldehydes MW=184		g, d
X ₁ MW=198	two carbonyl groups	g, d
X ₂ C ₉ H ₁₄ O ₄ MW=186	e.g.	i, d

* identification confirmed with an authentic standard.

^a known product of O₃ oxidation of α-pinene and β-pinene.

^b detected in Kejimikujik samples.

^c known product of O₃ oxidation of α-pinene, β-pinene, sabinene and Δ³-carene.

^d detected in Kejimikujik and Big Bear samples.

^e known product of O₃ oxidation of β-pinene.

^f detected in Big Bear denuder samples.

^g known product of O₂ oxidation of α-pinene.

^h detected in Big Bear denuder and filter samples.

ⁱ possible product of O₃ oxidation of limonene.

two denuders was used to quantify denuder collection efficiency. Samples were collected from 19:00 PDT Aug. 31 to 13:00 PDT Sep. 1, 1998 at a flow rate of 22 L min⁻¹. The back filter in the two-filter set-up was used for assessing filter adsorption of gaseous semivolatile organics. Ambient temperature during the sampling period varied from 18 to 32°C, and relative humidity ranged from 20% to 59%.

Denuder samples were extracted on-site, and all samples were stored at 0°C before analysis. The procedure for extraction, subsequent processing, and analysis of denuder and filter samples has been described elsewhere [Yu *et al.*, 1999]. The extracts of denuder and filter samples were derivatized by (2,3,4,5,6-pentafluorobenzyl) hydroxy amine (PFBHA) and N, O-bis (trimethylsilyl)-trifluoroacetamide. By this procedure, carbonyl functional groups of the oxidation products were converted into oximes, and carboxyl and hydroxyl function groups were converted into trimethylsilyl

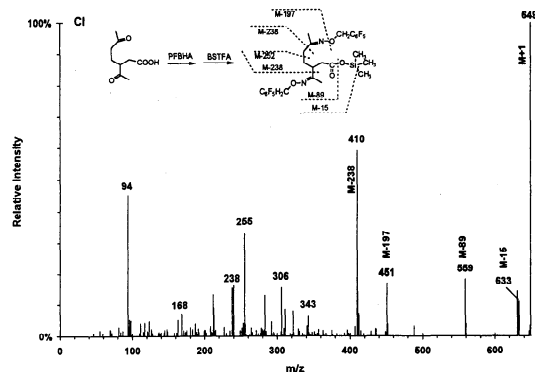


Figure 1. Chemical ionization mass spectrum for the derivative of a C₉ dioxo carboxylic acid compound detected in aerosol samples.

(TMS) groups. The resulting derivatives were then analyzed by GC/MS, using both electronic ionization (EI) and chemical ionization (CI) modes for identification and quantification. Blank filters in both studies were treated and analyzed following the same procedures applied to the sample filters. Quantification of products for which authentic standards do not exist was achieved by using surrogate compounds that have the same functional groups and approximate carbon numbers [Yu *et al.*, 1999].

3. Results and Discussion

3.1 Identification of Monoterpene Oxidation Products

Oxidation products of α-pinene and β-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 α-pinene and β-pinene include pinic acid, norpinic acid, pinonaldehyde, norpinonaldehyde, hydroxy pinonaldehydes, pinonic acid, norpinonic acid, hydroxy pinonic acid, hydroxy pina ketones, and nopinone. An unidentified product (denoted X₁), 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 α-pinene/O₃ system and ambient aerosols at both sites. Besides oxidation products derived from α-pinene and β-pinene, a compound denoted X₂, detected in samples from both sites, is identified as a C₉ 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 X₂. 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 C₉ 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 Kejimikujik 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 Kejimikujik 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

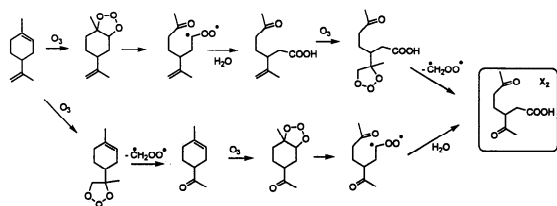


Figure 2. Formation pathways for a C₉ dioxo carboxylic acid product from oxidation of limonene.

with the decrease in α -pinene and β -pinene during the same sampling period at this same site [Leitch *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 denuder collection efficiency for each product. As evident in Table 3, the monoterpene oxidation products at this site predominately exist in the gas phase. A number of oxidation products were detected solely in the gas phase due to either their high volatility (e.g. nopinone, hydroxy pina ketones, and norpinonaldehyde) or to such a low concentration in the air that the amount partitioned to the aerosol phase is below detection limit (e.g. norpinonic acid and hydroxy pinonic acid).

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

Table 2. Monoterpene Oxidation Products in Filter Samples Collected in Kejimikujik National Park, Nova Scotia

monoterpene	mixing ratio (pptv)		Product	Conc. (ng m ⁻³)	
	960705 ^a	960708 ^a		960705 ^a	960708 ^a
α -pinene	88-283	147-642	norpinic acid ^b	0.34	0.34
β -pinene	69-401	209-864	pinic acid	0.48	0.59
camphene	60-442	156-561	norpinonic acid & its isomers ^c	0.24	0.04
			pinonic acid	0.39	0.13
			pinonaldehyde ^d	0.19	0.08
			hydroxy pinonaldehydes ^c	0.12	ND ^e
			X ₁ ^d	0.12	0.13
			X ₂ ^c	0.19	0.13

^a Dates when aerosol samples commenced

^b Quantified using the calibration factor and recovery for pinic acid.

^c Quantified using the calibration factor and recovery for pinonic acid.

^d Quantified using the calibration factor and recovery for 5-methylcyclohexane-1,3-dione.

^e Not detectable.

Table 3. Gaseous and Particulate Monoterpene Oxidation Products in Samples Collected in San Bernardino National Forest, California

Monoterpene	mixing ratio (pptv)		Product	conc. (ng m ⁻³) ^a	
	Range	Avg.		gas	aerosol
α -pinene	22-119	63	pinic acid	11.5	0.5
β -pinene	16-111	50	norpinonic acid & its isomers	12.3	ND ^b
limonene	13-63	27	pinonic acid	202.4	0.8
camphene	7-76	36	norpinonaldehyde	4.7	ND
Δ^3 -carene	2-21	10	pinonaldehyde	280	1.0
junipene	0-8	5	hydroxy pinonaldehydes	16.8	0.5
			X ₁	3.3	0.2
			X ₂	17.8	0.8
			hydroxy pinonic acid	9.0	ND
			hydroxy pina ketones	18.0	ND
			nopinone & isomers ^c	132.9	ND

^a average values of two samples.

^b Not detectable.

^c Possible isomers include primary carbonyl products from ozone oxidation at the external C=C bond in limonene and camphene.

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 Kejimikujik 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 100 ng m⁻³ at two mountainous sites in central Japan. Calogirou *et al.* [1997] observed pinonaldehyde 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 pinonic acid, pinic 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 monoterpene 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 nopinone. In addition, a C₉ dioxo carboxylic acid, detected at both sites, is postulated to be 3-acetyl-6-oxoheptanoic acid, a product expected from ozone oxidation of limonene. Identification of monoterpene oxidation products in aerosol samples serves as direct evidence for aerosol formation from monoterpenes under ambient conditions.

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