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Monoterpene Emission Rate Measurements From a Monterey Pine

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The monoterpenes emitted from a Monterey pine (*Pinus radiata*) were investigated using a dynamic flow-through enclosure technique. The monoterpenes identified and quantified were α- and β-pinene, *d*-limonene + β-phellandrene, myrcene, camphene and Δ^3-carene, with α- and β-pinene accounting for over 80% of the total monoterpene emissions. The monoterpene emission rate increased with temperature, in good agreement with previous data for other coniferous species. The absence of added CO_2 to the synthetic air flow stream, exposure to elevated levels (300–500 ppb mixing ratio) of O_3 for 3–4 hours, and increased air movement within the enclosure had no observable effect on the monoterpene emission rate at a given temperature. In contrast, "rough handling" of the pine during the sampling protocol resulted in increases in the monoterpene emission rate by factors of 10–50. These results will be useful to those designing enclosure sampling protocols for the determination of the emission rates of biogenic organic compounds from vegetation.

INTRODUCTION

A variety of organic compounds, including isoprene (2-methyl-1,3-butadiene) and a series of monoterpenes, are emitted from vegetation (see, for example, *Rasmussen* [1970, 1972], *Graedel* [1979], *Zimmerman* [1979*a*, *b*], *Tingey et al.* [1979, 1980], *Lamb et al.* [1985, 1986], *Isidorov et al.* [1985]) and on regional or global scales these biogenic emissions may dominate over anthropogenic nonmethane organic emissions [*Zimmerman et al.*, 1978, 1988; *Lamb et al.*, 1987]. Recent computer modeling studies, using isoprene as a surrogate for all biogenic emissions, have shown that vegetative emissions may play important roles in the production of ozone in urban [*Chameides et al.*, 1988] and rural [*Trainer et al.*, 1987*a*] areas and in the chemistry of the lower troposphere [*Trainer et al.*, 1987*b*; *Jacob and Wofsy*, 1988].

The emission rate of isoprene from hardwood trees depends on light intensity [*Rasmussen*, 1972; *Tingey et al.*, 1979] and temperature [*Tingey et al.*, 1979; *Lamb et al.*, 1985, 1986]. *Tingey et al.* [1979] showed that the isoprene emission rate from a live oak (*Quercus virginia*) increased to an asymtotic value with increasing light intensity at a given temperature, and increased with temperature up to ~44°C. Monoterpene emission rates from coniferous species have also been reported to be temperature dependent, but independent of light intensity [*Rasmussen*, 1972; *Tingey et al.*, 1980; *Lamb et al.*, 1985]. The emission rate from a slash pine (*Pinus elliottii*) increased exponentially with temperature [*Tingey et al.*, 1980], showing an order of magnitude increase between 20° and 50°C.

The extensive studies of Lamb and coworkers showed that the emissions of isoprene from a deciduous forest and of α-pinene from Douglas fir made using an enclosure method were in reasonable agreement with micrometeorological gradient profile measurements [*Lamb et al.*, 1985] and that isoprene emission rates from oak (*Quercus garryane*) as measured by the enclosure method agreed very well with those derived from tracer measurements [*Lamb et al.*, 1986]. Enclosure methods of measuring emission rates [*Zimmerman*, 1979*a*, *b*; *Winer et al.*, 1983] have the obvious potential of disturbing the plant due to changing the microenvironment around the plant, through changes in humidity, temperature, CO_2 concentration, effective wind speed and mechanical motions, including damage to the plant from handling and/or from the enclosure itself. In this work, we have carried out a study of the effects of several of these variables on the emission rates of monoterpenes from a Monterey pine (*Pinus radiata*).

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EXPERIMENTAL PROCEDURE

The emission rate measurements were performed with a Monterey pine over a 4 week period, using the dynamic flow-through enclosure technique described by *Winer et al.* [1983]. For the majority of the measurements, the pine tree (of height ~1 m and planted in a plastic pot) was enclosed in a Teflon chamber of circular cross-section (diameter, 1.1 m) and height ~1 m. The chamber was fitted around the top of the plant pot, resulting in an approximately conical shape of volume ~450 L. Cylinder synthetic air (99.6% stated purity, with no organic compounds being observed in the region of monoterpene elution by the GC-FID analyses described below) was passed through a humidifier unit and premixed with CO_2 to yield a CO_2 mixing ratio of 360 ppm, and was flowed through the enclosure at a flow rate of 45 L min^{-1}. This flow was maintained for 15 min prior to sampling. All flows were monitored with calibrated rotameters, and the relative humidity and temperature in the enclosure were monitored by a Vaisala model HMI 32 instrument. The enclosure was equipped with a stirring fan which caused a just noticeable movement of the pine needles close to the fan. The tree was removed from the chamber between measurements and stored outdoors. All measurements were made outdoors under ambient solar lighting conditions.

After flowing synthetic air through the chamber containing

the tree for 15 min, gas samples of 1.3–1.4 L volume were collected at a flow rate of ~0.8 L min^{-1} onto Tenax-GC solid adsorbent for analyses by gas chromatography with flame ionization detection (GC-FID) and, in selected cases, combined gas chromatography-mass spectrometry (GC-MS). For the GC-FID analyses, the samples were thermally desorbed at 225°C for 5 min onto the head of a 15-m megabore DB-5 fused silica column which was held at 0°C, and then temperature programmed at 8°C min^{-1} to 200°C. The GC-MS analyses involved the thermal desorption of the samples at 250°C onto the head of a 50-m HP-5 capillary column held at −25°C for 10 min and then temperature programmed at 6°C min^{-1}. The identifications of the monoterpenes emitted were based on GC retention time matching with authentic samples (initially 1,2,4-trimethylbenzene was added as a retention time marker) and were confirmed by retention time and mass spectral matching from the GC-MS analyses. Quantifications of the monoterpenes were based on GC-FID peak areas.

Additional emission rate measurements were carried out using a continuously-stirred tank reactor (CSTR) chamber located inside a greenhouse with charcoal-filtered air [*Temple and Taylor*, 1985]. The chamber surface was Teflon, and the volume was 2000 L, with an air exchange rate of ~0.3 min^{-1} (~600 L min^{-1}). Ozone was supplied to the chamber at the desired concentration from a computer controlled gas manifold system. The temperature and relative humidity in the CSTR chamber were monitored as described above. The sampling and analyses were also as described above, except that the sample volume was increased to 2.5–2.8 L.

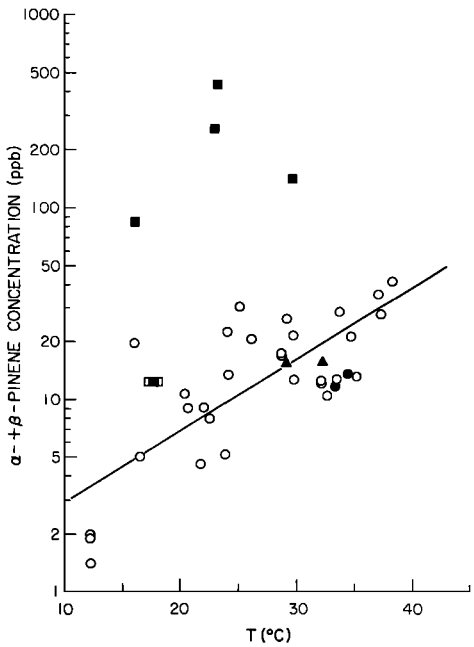

Fig. 1. Plot of the α- + β-pinene concentrations from a Monterey pine (*Pinus radiata*) measured in the Teflon enclosure as a function of temperature. Open circles, standard experiments (see text); solid triangles, carried out with no added CO_2; solid circles, carried out with increased air movement around the tree (see text); solid squares, immediately after rough handling (see text) of enclosed tree; square open on left side, 1 hour after rough handling experiment at ~16°C; and square open on right side, 2 hours after rough handling experiment at ~16°C; solid line, least squares fit to "standard" experiments shown.

Results and Discussion

GC-FID analyses of the gas samples collected from the enclosure containing the Monterey pine showed that the monoterpenes present were α- and β-pinene, d-limonene, myrcene, Δ^3-carene and camphene, with α- and β-pinene dominating. The GC-MS analyses showed the presence of a small amount, relative to d-limonene, of β-phellandrene which co-eluted with the d-limonene on the DB-5 column used for the GC-FID quantifications. Since these experiments were carried out as part of an on-going, long-term, study of the emissions of this tree, the biomass (or dry leaf weight) was not determined and the data are reported in terms of the concentrations (in ppb) of the monoterpenes in the enclosure used.

The flow rate was constant in each of the two enclosures, and hence for a given enclosure the monoterpene concentration was proportional to the emission rate. For the all-Teflon chamber volume and air flow used, after 15 min 1.5 air exchanges had occurred and the concentrations of the biogenic emissions are calculated to have been 22% below the steady state values. All emission measurements were taken 15 min after initiating the air flow, and uncertainties in the monoterpene concentrations due to variations in the approach to steady state are estimated to be less than ±20%. All measurements in the CSTR chamber were carried out under conditions such that the steady state concentrations were achieved.

Measurements as a Function of Temperature in the Teflon Enclosure

A series of measurements of the monoterpene concentrations in the enclosure were made over the period April 21 through May 12, 1989, under "standard" conditions, in which the CO_2 concentration was maintained at 360 ppm and the tree was handled as gently as possible. Thirty such measurements were carried out during 13 daytime periods, covering the times 0420–1540 hours. The temperature within the enclosure varied from 12°C to 39°C, and the relative humidity varied from 48 to 93%. The monoterpene concentrations showed no obvious dependence on the relative humidity, but increased with increasing temperature.

α- and β-pinene accounted for over 80% of the total monoterpene concentrations observed. The average percentage contributions of the individual monoterpenes to the total for these 30 measurements were: β-pinene, 48 ± 5%; α-pinene, 34 ± 5%; myrcene, ≤10%; *d*-limonene + β-phellandrene, 7 ± 2%; camphene, 0.6 ± 0.4%; and Δ^3-carene, 0.4 ± 0.6% (where the indicated errors are one standard deviation). Since there were indications that a small contribution of residual ambient air in the enclosure interferred with the myrcene measurements, the myrcene data are not discussed further. There was no evidence for any change in the monoterpene concentration distribution with temperature. Since α- and β-pinene were the major monoterpenes observed, their sum was used to examine the effects of temperature and other variables, as discussed below.

The measured α- + β-pinene concentrations in the enclosure are plotted against the temperature in Figure 1 (open circles). There is a clear increase in the emission rate with increasing temperature, and a least squares analysis of these

data obtained over the temperature range 12°–39°C leads to an exponent B in the assumed equation

$$\alpha\text{- + }\beta\text{-pinene concentration} = Ae^{BT}$$

of $B = 0.085 \pm 0.027$, where the indicated error is two least squares standard deviations. This temperature exponent is in excellent agreement with that of 0.074 determined by *Tingey et al.* [1980] for monoterpene emissions from slash pine over the temperature range of 20°–46°C.

The temperature dependence determined here for the emission of α- + β-pinene from a Monterey pine is very close to the temperature variation of the vapor pressures of these two monoterpenes, which corresponds to $B = 0.060$ over the temperature range ~0°–40°C (strictly, over extended temperature ranges the vapor pressures obey an equation of the form: vapor pressure = $Ce^{-D/T}$). Furthermore, the temperature dependencies of the vapor pressures of the monoterpenes are all very similar, and this is consistent with our observation that the monoterpene concentration distribution did not change with temperature and also with the data of *Tingey et al.* [1980] which showed essentially identical temperature dependencies of the emission rates from slash pine of the monoterpenes α- and β-pinene, myrcene, *d*-limonene and β-phellandrene.

The data shown in Figure 1 from this set of 30 experiments indicate that at any given temperature the scatter, or reproducibility, of the data for emissions from this one tree were ± a factor of ~2 around the mean. While one or two of the higher emission values may have been caused by unavoidable handling effects and some uncertainty (less than ±20%) existed because of the nonattainment of steady state conditions (see above), it appears that the majority of this ±2 factor in the emissions rate is due to fluctuations in the plant's emissions.

Effect of CO_2

Two experiments were carried out in which no CO_2 was added to the cylinder synthetic air. An identical, within the uncertainties, distribution of the monoterpenes was observed, and the measured α- + β-pinene concentrations are plotted in Figure 1 (solid triangles). These two data points are indistinguishable from the data obtained in the presence of tropospheric levels of CO_2, showing that, at least for the time scales pertaining for each of these experiments (15 min), the absence of CO_2 has no obvious effect on the relative abundances of the monoterpenes emitted or on the monoterpene emission rate.

Effect of Simulated Wind Speed

As discussed above, for the "standard" set of measurements the enclosure was equipped with a small fan which led to a just observable needle movement close to the fan. In order to investigate the effect of air perturbation, a household 3-speed fan was installed in the enclosure and operated at medium speed for one experiment and then at high speed for a further experiment, both leading to pronounced needle movement. The data obtained (not differentiated for fan speed) are plotted as the solid circles in Figure 1. In addition to the monoterpenes, a series of other organic compounds were emitted from the fan lubrication system (as shown by an experiment without the tree present in the enclosure), including 1,2,4-trimethylbenzene which co-eluted with myrcene on the DB-5 column. The relative abundances of α-pinene, β-pinene, Δ^3-carene, camphene and d-limonene (+ β-phellandrene) were unchanged from the "standard" experiments, and the α- + β-pinene concentrations were within the scatter of the "standard" data set (Figure 1). These observations imply that air movement has no marked effect on the monoterpene emission rates, at least under the experimental conditions used in this study.

Effect of Rough Handling

Four experiments were carried out in which the pine tree was roughly handled while in the enclosure prior to sampling. This was achieved by manually compressing, and then releasing, the enclosure around the tree in a repetitive manner during the 15 min flush of the chamber preceeding sampling. The tree was hence in repeated contact with the Teflon enclosure, although no obvious damage (for example, broken needles) occurred. While the relative abundances of the individual monoterpenes were essentially identical to those in the "standard" measurements, the emissions were greatly increased. As shown in Figure 1, the α- + β-pinene concentrations for the "roughed up" tree experiments (solid squares) were factors of 10–50 higher than those in the "standard" experiments conducted at the same temperature, far outside of the reproducibility of the individual experiments. These data show that rough handling markedly increases the monoterpene emission rates for this Monterey pine. Similar effects have recently been observed for citrus and other broad-leaved plants (J. Arey et al., The emission of *cis*-3-hexen-1-ol and *cis*-3-hexenylacetate from agricultural species, submitted to *Atmospheric Environment*, 1990).

For the rough handling experiment conducted at 16–17°C, emission rate measurements were also made at intervals following the initial experiment to determine the time needed for the vastly increased emission rate to return to "normal." As shown in Figure 1 the measurement 1 hr after the rough handling appears to have been within the normal emission range, as was the replicate 2 hrs after the rough handling.

Effects of Exposure to Elevated O_3 Concentrations

As discussed above, these measurements were carried out in a CSTR chamber. Measurements of the concentrations of the monoterpenes were carried out prior to and immediately after the Monterey pine had been exposed to O_3 concentrations of 300 ppb for 3 hours and 500 ppb for 4 hours. Because of the higher flow rate in the CSTR chamber than in the Teflon enclosure (~600 L min^{-1} versus 45 L min^{-1}), the monoterpene concentrations in the CSTR chamber were significantly lower (by an average factor of 24, which can be compared to the factor of ~10–11 expected from the flow rates and residence times in the two chambers), and only α- and β-pinene could be analyzed accurately. Two sets of experiments were carried out. In the first, three measurements were taken prior to the addition of O_3 at a mixing ratio of 300 ppb (for 3 hours) to the CSTR chamber, and measurements were taken immediately after the O_3 supply was turned off, and at 40 min and 80 min after. In the second experiment, measurements were taken prior to O_3 addition (500 ppb for a 4 hour period), immediately after turning off the O_3 supply and 65 min and 165 min later.

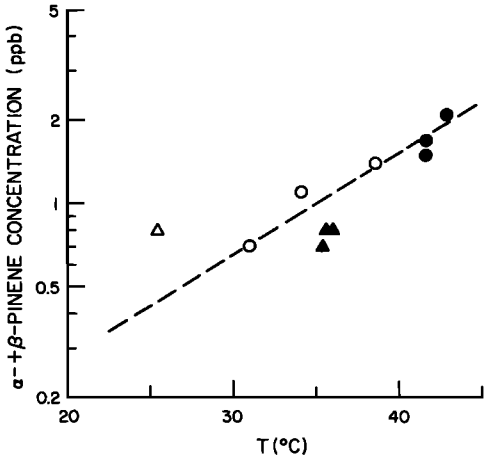

Fig. 2. Plot of the α- + β-pinene concentrations from a Monterey pine measured in the CSTR chamber as a function of temperature. Open circles and triangle, prior to addition of O_3 to the CSTR chamber; solid circles, after cessation of O_3 exposure at 300 ppb for 3 hours; solid triangles, after cessation of O_3 exposure at 500 ppb for 4 hours; dashed line, temperature dependence obtained from Teflon enclosure "standard" experiment measurements shown in Figure 1.

Since the temperatures within the CSTR chamber increased throughout each experiment, the temperature dependence of the α- + β-pinene emission rate determined in the all-Teflon chamber was assumed to allow comparison of the data taken before and after the exposures to O_3. The α- + β-pinene concentrations measured during these experiments are plotted in Figure 2, with the dashed line being the temperature dependence obtained from the Teflon enclosure "standard" experiments shown in Figure 1. When the temperature dependence of the monoterpene emission rate is taken into account, the α- + β-pinene concentrations measured prior to and after exposure of the pine to 300 ppb of O_3 for 3 hours were indistinguishable. For the exposure to O_3 at 500 ppb for 4 hours the measured α- + β-pinene concentrations before and after the O_3 exposure were essentially constant. These concentrations were within a factor of 2 of those expected based on the temperature (see Figure 2), with the pre-exposure data point for this 500 ppb O_3 exposure appearing to be somewhat high. These data then indicate that, within the expected reproducibility of ± a factor of ~2, the monoterpene emissions were not affected to any significant extent by these 3–4 hour exposures to elevated O_3 at levels which were at or above those observed in polluted urban areas in the United States.

The small data set for these O_3 exposures requires cautious interpretation of the data. The Monterey pine was growing in ambient Riverside air and, therefore, exposed to levels of O_3 occasionally reaching ~200 ppb. The data do suggest, however, that sudden high levels of O_3 will not result in a marked increase (or decrease) of monoterpene emissions.

Conclusions

Our experimental data on the temperature dependence of α- + β-pinene emissions from a Monterey pine are in agreement with the earlier results of *Tingey et al.* [1980] for a slash pine, showing a monoterpene emission rate increase of an order of magnitude for an ~30°C temperature increase. As also discussed by *Tingey et al.* [1980], this temperature dependence of monoterpene emission rates is very similar to the temperature dependence of the monoterpene vapor pressures.

The experimental variables investigated in this study have implications for the design and use of enclosure methods for the direct determination under field conditions of biogenic emission rates from vegetation. The data obtained in this study indicate that the emission rates are not affected, outside of the ± a factor of ~2 repeatability, by neglecting to add CO_2 at ambient levels to the pure air flow or by use of a fan to ensure mixing within the enclosure. However, mechanical agitation of the plant through touching of the needles with the Teflon film markedly increased the emissions rates. Clearly, extreme care must be taken in fitting the enclosure over the plant or portion of the plant for which emissions are to be measured.

To date, two enclosure methods have primarily been used for direct field measurements, these being the semi-static enclosure technique developed and used by *Zimmerman* [1979*a*, *b*] and the dynamic flow technique of *Winer et al.* [1983] used in this study. The semi-static enclosure technique involves enclosing the branch in a Teflon chamber, partially evacuating this chamber and taking a background sample, and then filling the chamber with pure air and again sampling. While the semi-static enclosure method would appear to be prone to high emission rates caused by touching of the leaf surfaces with the enclosure during evacuation, the general agreement between the data reported from such studies and from micrometeorological and tracer flux measurements [*Lamb et al.*, 1985, 1986] suggests this is not the case, in part perhaps due to correction from the background sample for excess emissions [*Zimmerman*, 1979*b*].

The micrometeorological and tracer flux approaches have stringent requirements involving large areas of similar vegetation with long fetch and cannot be readily used in many areas. Enclosure techniques for emission rate measurements under field conditions are therefore necessary. It appears that if care is taken, reliable measurements can be obtained from enclosure experiments.

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