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Are Monoterpene Emissions influenced by Humidity?

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Abstract. Monoterpene mixing ratios and fluxes were measured above a ponderosa pine plantation in the Sierra Nevada mountains from July to October 1998. Data were obtained during a variety of weather regimes including periods of extreme heat and dryness as well as during rain. Monoterpene emissions were highly elevated during and after the rain events, and the expected exponential increase of emissions with temperature did not occur during extremely hot and dry conditions, suggesting an influence of ambient humidity levels on monoterpene emissions. Therefore, we propose a modified emission algorithm based on responses to both temperature and humidity.

1. Introduction

Monoterpene emissions from coniferous trees can be significant contributors to both photochemical activity and secondary aerosol formation [*Chameides et al.*, 1988; *Andreae and Crutzen*, 1996]. At present, models of monoterpene emission rates from leaves presume emissions to be driven by ambient light and temperature [e.g. *Ciccioli et al.*, 1997], or by temperature only [e.g. *Tingey et al.*, 1980; *Guenther et al.*, 1993]. However, available flux data from several coniferous tree species show considerable scatter when the latter approach was used [e.g. *Juuti et al.*, 1991]. Wetting increases monoterpene emissions from plants, as recently reported for rain [*Janson*, 1992; *Helmig et al.*, 1998], fog [*Riemer et al.*, 1994], and dew [*Lamb et al.* 1985; *Street et al.*, 1998]. Some researches have claimed that relative humidity influences monoterpene emissions [e.g. *Dement et al.*, 1975], whereas others have disputed it [*Juuti et al.*, 1990; *Janson*, 1993]. The current monoterpene emission model does not include such dependencies [*Guenther et al.*, 1995].

We present new evidence that monoterpene emissions depend on ambient humidity levels.

2. Experimental

Hydrocarbon measurements were made continuously from July to October 1998 above a ponderosa pine (*Pinus ponderosa* L.) plantation at one-hour intervals. The measurements were part of a larger field experiment at the Blodgett Forest Research Station on the western slope of the Sierra Nevada mountains (38° 53' 42.9" N, 120° 37' 57.9" W, 1315 m elevation). The pine plantation (owned by Sierra Pacific Industries, SPI) consisted of even aged trees (6-8 years old) that were 3-5 meters tall. Among them were a few individuals of douglas fir (*Pseudotsuga menziesi*), white fir (*Abies concolor*), black oak (*Quercus kellogii*), and incense cedar (*Calocedrus decurrens*), and the understory was dominated by manzanita (*Arctostaphylos* spp.) and whitethorn (*Ceonotus cordulatus*). Approximately 30% of the fetch ground area was covered by the pine trees and 55% by shrubs. The site is characterized by a Mediterranean climate, with daytime winds typically upslope from the southwest, and nighttime winds downslope from the northeast.

VOCs containing up to 10 carbon atoms were quantified using a dual channel GC-FID with two identical polyethylene-glycol columns (DB-Wax©, 60 m, 0.32 mm ID, 0.5 μm film). Two samples (300 ml) were obtained simultaneously from approximately 2.5 and 4.5 m above the tree height and preconcentrated on Silcosteel© micro-traps filled sequentially with glass beads, Carbopack B, and Carbosieve SIII, at -25°C. Samples were rapidly desorbed (~15s) into the carrier gas by resistance heating (see *Lamanna and Goldstein* [1999] for details). A ppm-standard of α-pinene, Δ-3-carene and d-limonene in UHP N_2 (Scott-Marrin Inc., Riverside, CA) was diluted automatically into the sample stream at a controlled flow rate every 15 or 30 hours. In addition, we identified β–pinene using an uncalibrated standard, and an unknown monoterpene based on similarity of its behavior to the known monoterpenes. No significant differences could be noticed between standard additions done in front of the inlet filters or down the sampling line inside the temperature-controlled shed, that housed the instrument. The RSD of the calculated response factors was better than 5% for Δ-3-carene and α-pinene, and 5-10 % for d-limonene. Uniform FID responses were assumed for all monoterpenes.

We determined ecosystem scale emissions using the flux similarity approach [*Goldstein et al.*, 1998]: Fluxes were computed as the product of the vertical monoterpene gradient and the sensible heat flux (eddy covariance) divided by the vertical temperature gradient. Fluxes were only calculated when temperature gradients were larger than two standard deviations of their calibration agreement, and when sensible heat flux and temperature gradients had the same sign. Monoterpene gradients were corrected for differences between the measurement channels using samples taken from the same height every fifth measurement. Gradients >0.01 ppb could be distinguished at the 95% confidence level. The typical daytime accuracy of the reported fluxes is estimated to be ± 60% (see *Goldstein et al.* [1996] for details).

3. Results and Discussion

Emission rates of the monoterpenes were correlated throughout the whole measurement period. Ambient mixing ratios of all five monoterpenes were highly correlated (Table 1) even though some variability was induced by atmospheric chemistry and dispersion. The pinenes and Δ-3-carene

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Table 1. Correlations and Slopes Between Δ-3-Carene Mixing Ratios and Fluxes and the Other Monoterpenes (Day- and Nighttime Data).

	Δ-3-carene			
	mixing ratio		emission flux	
	r^2	slope	r^2	slope
α-pinene	0.95	0.95	0.45	0.77
β-pinene	0.88	1.19	NA*	NA*
d-limonene	0.77	0.20	0.40	0.19
unknown	0.82	0.07	NA*	NA*

* not calculated due to uncertainties in resolving the vertical mixing ratio gradients for these compounds

dominated emissions. Whereas the β-pinene to Δ-3-carene emission ratio was similar to leaf level emission ratios reported for ponderosa pine [*Lerdau et al.*, 1994], the relative abundance of α–pinene was somewhat higher than previously reported. This implies either a different monoterpene emission spectrum of the ponderosa pine trees investigated due to age [*Latta and Linhart*, 1997] or regional differences [*Peloquin*, 1964; *Sturgeon and Mitton*, 1986], another α–pinene source, or a different monoterpene composition of non-leaf ecosystem monoterpene emissions [*Rhoades*, 1990; *Janson*, 1993; *Steinbrecher and Ziegler*, 1997]. We focus further discussion on Δ-3-carene mixing ratios and fluxes because they were the most precisely measured. Emission rates and mixing ratios can be estimated for other monoterpenes based on the correlations presented in Table 1. Figure 1 shows a plot of nighttime Δ-3-carene mixing ratios (at 6.7 m) versus air temperature and humidity data at tree height (4 m) for non-wet periods (excluding rainy times, and choosing a relative humidity, rH, under 90%). Ambient mixing ratios were highest at the highest temperatures and absolute humidities. The observed correlation between monoterpenes and humidity was in part due to their simultaneous buildup during stratified atmospheric conditions. Therefore, a simple covariation as suggested earlier [*Janson*, 1993] cannot be easily excluded.

Extreme changes in mixing ratios occurred during and after all three rainy periods, and are shown for one event in

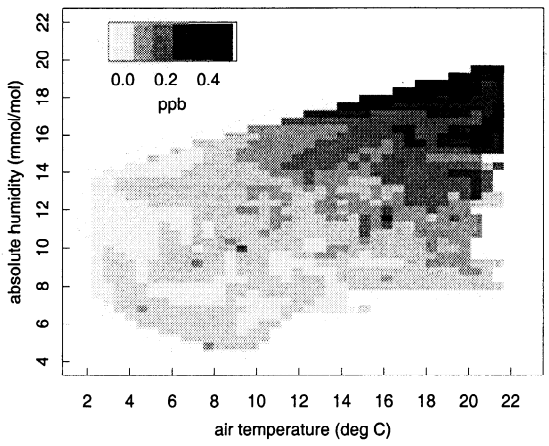

Figure 1. Variation of the nighttime (22-7h) Δ-3-carene mixing ratio with temperature and absolute humidity levels under non-wet conditions (see text).

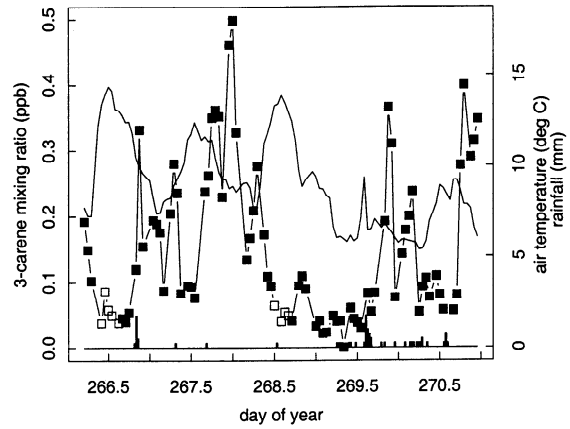

Figure 2. Δ-3-carene mixing ratio during a rain event (23-27 September)(solid symbols: rH > 80%, open symbols: rH < 80%). The upper line shows air temperature, the black bars represent rainfall.

Figure 2. During the first rain event, a warm summer shower, ambient mixing ratios increased by up to a factor of ten (data not shown) compared to mixing ratios at similar temperatures before the event. As a result, the potential for secondary aerosol formation increases substantially, because aerosol formation rates are dependent on the local monoterpene to NO_x ratio [*Zhang et al.*, 1992].

In Figure 3, the diurnal Δ-3-carene fluxes averaged over a four-day hot period at the beginning of August are compared to the fluxes measured under cooler conditions through the first rainy period in September. Average fluxes were comparable for these two periods; however, emissions during the rainy period occurred at 5-10 °C lower temperatures and were elevated during the actual rain events.

Fluxes measured under non-wet conditions revealed a covariance between ambient humidity and Δ-3-carene fluxes (Figure 4). During times when relative humidity dropped below 40%, the expected exponential increase in emissions with rising temperature did not occur. It thus appears that monoterpene emissions in this ecosystem were more strongly dependent on humidity than temperature under dry conditions. There are three possible explanations for the shown behavior: 1. Ambient humidity levels indeed

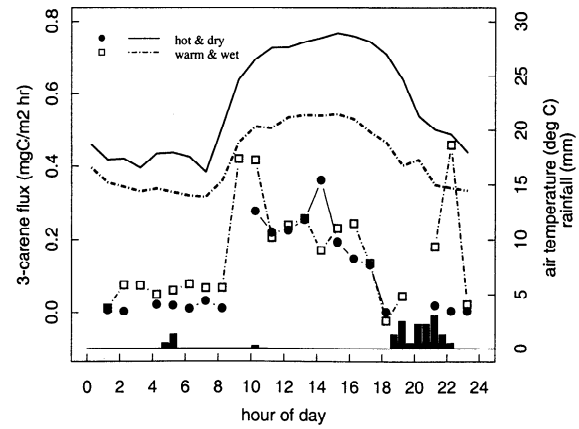

Figure 3. Diurnal mean Δ-3-carene flux during days 222-226 (hot & dry), and days 249-253 (warm & wet). The upper curves show average temperature for the same periods. Rainfall is indicated by bars at the bottom.

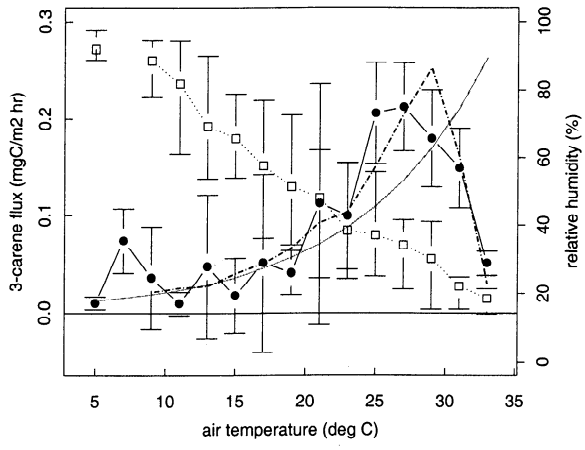

Figure 4. Two degree averaged Δ-3-carene flux (solid circles: mean with 90% confidence intervals) and relative humidity (squares: means with ranges) versus temperature, excluding all rainy periods. The gray, solid line represents the old model fitted to all data with $E_{m,r} = 0.063$ mgC m^{-2} hr^{-1} and $\beta = 0.11$. The black, broken line shows the new model with unchanged $E_{m,r}$, $c = 5$, and $\beta = 0.225$.

influence monoterpene emissions by a mechanism yet to be discussed; 2. Emissions are at least in part connected to stomatal opening and therefore plant transpiration as discussed for other conifers [e.g. *Steinbrecher and Ziegler*, 1997]; or 3. Emissions are lower due to the drought stress these ponderosa pine trees undergo during the summer. In view of the results presented by *Lerdau et al.* [1994], who found no connection between photosynthesis and monoterpene fluxes, we consider a connection between stomatal opening and monoterpene emissions unlikely for this ecosystem. Severe drought stress has been shown to ultimately decrease monoterpene emissions from mediterranean cypress approximately 50 days after the last watering [*Yani et al.*, 1993]. The authors attributed the change to either stomatal closure and/or metabolization of the monoterpenes reducing the pool size. However, the spring of 1998 was unusually wet in the Sierra Nevada, and drought stress effects did not appear before mid July. Though we cannot completely exclude a drought stress effect during the very hot days at the end of August, lack of a connection to stomatal closure and high fluxes during the following rain event suggest that this mechanism is unlikely.

A theoretical explanation for a humidity dependence due to water adsorption on leaves has been discussed before [*Croteau*, 1977]. Water adsorbs to leaf surfaces in response to changing humidity levels [*Van Hove and Adema*, 1996]. Adsorbed water potentially increases the cuticular permeability, a mechanism still under debate (M. Riederer, University of Würzburg, Germany, *pers. comm.*). Whether monoterpene fluxes through the cuticle would increase as a result of water adsorption or monoterpenes would rather be physically displaced from the cuticle surface by the water is unclear. It is clear, however, that monoterpene emissions decreased dramatically as relative humidity, rH, decreased below ~40% (Figure 4), and can potentially be described by an adsorption-isotherm. We assumed a linear response of monoterpene flux to the relative amount of adsorbed water according to the BET isotherm, as commonly done in soil water adsorption studies. Figures 4 and 5 compare the old and new models, based on the following formula:

$$E_m = E_{m,r} \times \exp(\beta \times (T - T_r)) \quad \times \quad BET$$
$$BET = (c \times rH_n) / ((1 - rH_n) \times (1 + (c-1) \times rH_n)) \qquad (1).$$

The first term represents the temperature response ($E_{m,r}$ is the basal emission rate at 293 K). The second term introduces the new dependence on a normalized relative humidity (rH_n), and represents the BET isotherm. The parameter c, the BET constant, is sensitive to the bonding energy of the first water monolayer relative to the following layers. It should be smaller than for soils (~10), because leaves present a more hydrophobic surface. In order to fit the model to our data, rH was scaled to the lowest humidities we observed (~19%), by

$$rH_n = (rH - 18)/82 \qquad (2).$$

The model explained 82% of the variation of the mean fluxes, and identified the monolayer capacity of the leaves to be at 40-50% rH, which is consistent with total drying below these levels [*Klemm et al.*, 1999]. The new approach improves on the existing model by successfully capturing the prominent flux decrease at very low humidities (Figures 4 and 5). Separating the effect of rH from T was difficult due to the limited range of measured rH values associated with each T range, and the high variability of fluxes. Δ-3-carene fluxes were significantly correlated with relative humidity for temperatures of 30 ± 3 °C ($n = 46$, $r^2 = 0.16$, $p = 0.006$). This temperature range coincided with relative humidities below 40% where the BET model predicts a larger dependence.

4. Conclusions

Our data provide new evidence that ambient humidity can influence monoterpene fluxes. Whereas correlations between humidity and monoterpene concentrations could be biased by local atmospheric mixing, the flux data show increased monoterpene emissions at high humidities as well as during and after rain. This has probably not been reported in detail before due to limited use of whole ecosystem measurements compared to leaf and branch enclosure techniques. Enclosures typically expose the plant to high humidity levels, and whole ecosystem measurements have generally been carried out only over short periods, hardly allowing for

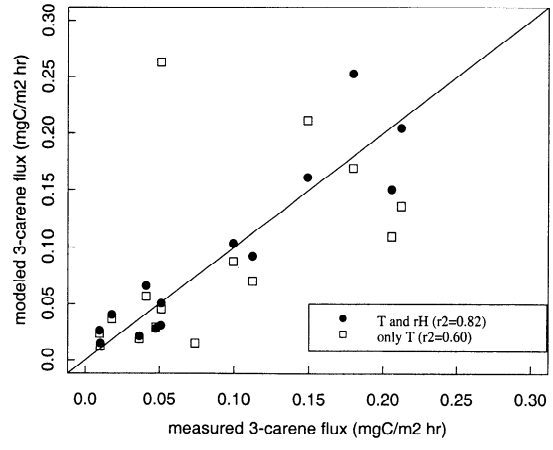

Figure 5. Comparison between the old and the new monoterpene emissions model with a 1:1 line.

observations during substantially different weather conditions. As the current modeling approach relies exclusively on the temperature response measured in enclosures, it probably overestimates monoterpene emissions in summer-dry mediterranean type ecosystems, and underestimates emissions under wet conditions. Based on our observation that ambient humidity levels can influence monoterpene emissions, we suggest implementing a humidity response in the current model algorithm based on water adsorption to surfaces modeled for example by the BET adsorption isotherm. We also suggest reevaluating existing field data and chamber measurements regarding this response. Controlled leaf level experiments should be carried out to evaluate the proposed model.

Furthermore, litter monoterpene levels remain substantial during decomposition [*White*, 1994; *Wood et al.*, 1995], and emissions from litter may also be stimulated under wet conditions. Our best-fit c-value of 5 might indicate that the forest floor contributes to whole ecosystem fluxes. Thus, we also suggest further investigation of those emissions.

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