# Forest thinning experiment confirms ozone deposition to forest canopy is dominated by reaction with biogenic VOCs

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[1] Ecosystem ozone uptake can occur through stomatal and surface deposition and through gas phase chemical reactions. In a California pine forest, thinning dramatically enhanced both monoterpene emission and ozone uptake. These simultaneous enhancements provide strong evidence that ozone reactions with unmeasured biogenically emitted volatile organic compounds (BVOCs) dominate ozone uptake, and these unmeasured BVOC emissions are approximately 10 times the measured monoterpene flux. Branch enclosure measurements confirm more than 100 BVOCs are emitted but not typically observed above the forest. These BVOCs likely impact tropospheric composition as a previously unquantified source of secondary oxygenated VOCs, organic aerosols, and OH radicals. *INDEX TERMS:* 0315 Atmospheric Composition and Structure: Biosphere/atmosphere interactions; 0322 Atmospheric Composition and Structure: Constituent sources and sinks; 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; 1610 Global Change: Atmosphere (0315, 0325). **Citation:** Goldstein, A. H., M. McKay, M. R. Kurpius, G. W. Schade, A. Lee, R. Holzinger, and R. A. Rasmussen (2004), Forest thinning experiment confirms ozone deposition to forest canopy is dominated by reaction with biogenic VOCs, *Geophys. Res. Lett.*, *31*, L22106, doi:10.1029/2004GL021259.

## 1. Introduction

[2] Uptake of ozone ($O_3$) by ecosystems is measured to assess the negative impacts on plants and the implications for the tropospheric $O_3$ budget. Plant damage is thought to occur only if $O_3$ enters stomata. Several recent studies have found that 30–90% of total ecosystem $O_3$ uptake occurs through stomata [*Fowler et al.*, 2001; *Mikkelsen et al.*, 2000; *Kurpius and Goldstein*, 2003; *Cieslik*, 2004], and the remainder has typically been attributed to deposition on non-stomatal surfaces [e.g., *Fowler et al.*, 2001]. However, *Kurpius and Goldstein* [2003] recently showed that the non-stomatal flux increased exponentially as a function of temperature at a coniferous forest site. The exponential increase with temperature was consistent with the temperature dependence of monoterpene emissions from the same ecosystem, suggesting $O_3$ was lost via gas phase reactions with biogenically emitted terpenes before they could escape the forest canopy.

[3] Additional indirect evidence shows that a broad variety of trees emit reactive BVOCs that either do not escape the ecosystem canopy, or are not typically measured by current analytical techniques [*Ciccioli et al.*, 1999; *Faloona et al.*, 2001; *O'Dowd et al.*, 2002; *Di Carlo et al.*, 2004]. *Ciccioli et al.* [1999] observed emissions of sesquiterpenes in leaf enclosures in an orange orchard in Spain in 1995 and 1996 that were not observed in simultaneous above canopy measurements, and suggested they were oxidized before escaping the orchard canopy. *Faloona et al.* [2001] observed elevated OH concentrations at night correlated with $O_3$ mixing ratios in a northern Michigan forest, and suggested the OH was likely produced from reactions of $O_3$ with unmeasured terpenes. *Di Carlo et al.* [2004] showed total OH reactivity above the same forest exceeded that of known VOCs, that the excess increased exponentially with temperature, and inferred unknown biogenic terpenes were likely responsible. *O'Dowd et al.* [2002] suggested new particle growth measured in a boreal forest in Finland in 2000 occurred from condensation or coagulation of terpene oxidation products. Finally, *Mikkelsen et al.* [2004] reported an increase in non-stomatal flux related to temperature in a Norway spruce forest in Denmark, consistent with observations by *Kurpius and Goldstein* [2003] but in a very different ecosystem.

[4] *Schade and Goldstein* [2003] reported forest thinning dramatically enhanced monoterpene emissions. Here we show that $O_3$ uptake was similarly enhanced, providing strong evidence that gas phase chemical $O_3$ loss in the forest canopy is indeed occurring by reactions with unmeasured BVOCs. This observation also allows a quantitative accounting of these unmeasured BVOC emissions and places constraints on their chemical reactivity.

## 2. Methods

[5] The forest thinning and field measurements occurred in a ponderosa pine (*Pinus ponderosa* L.) plantation adjacent to Blodgett Forest Research Station in the Sierra Nevada Mountains, California (38°53′42.9″N, 120°37′57.9″W, 1315 m elevation) [*Schade and Goldstein*, 2001; *Goldstein et al.*, 2000; *Bauer et al.*, 2000]. The trees were planted in 1990 and had a dominant canopy height of ~6 m with ~1300 trees per hectare in Spring 2000. Thinning, a management procedure used routinely to reduce stand density, improve forest health, and optimize tree growth in plantations, was initiated on 11 May and continued through 15 June 2000. A masticator was used to

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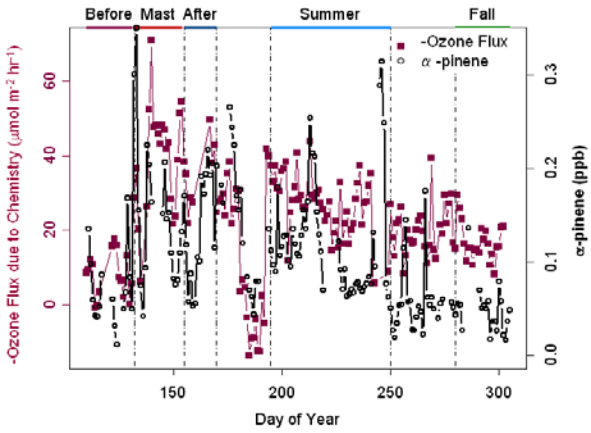


**Figure 1.** Timeline of daytime mean (0800–1800 PST) $O_3$ flux due to chemistry (filled squares, $O_3$ flux is into the forest) and α-pinene concentration (open circles). Bars across the top indicate the timing of thinning (mastication), and averaging periods used in later figures.

mechanically chew up smaller unwanted trees (~60%) from top-to-bottom, reducing green leaf biomass from ~320 g $m^{-2}$ to ~150 g $m^{-2}$ within the tower footprint. The branch and stem debris (400–500 g $m^{-2}$ dry weight) was left on site [*Schade and Goldstein*, 2003].

[6] Monoterpene mixing ratios and fluxes were measured hourly at 12 m with an automated in-situ Relaxed-Eddy-Accumulation (REA) GC-FID system [*Schade and Goldstein*, 2001; *Lamanna and Goldstein*, 1999], and were previously reported [*Schade and Goldstein*, 2003]. Ozone was measured with a closed-path fast-response chemiluminescent instrument (NOAA-ATDD) at 10 Hz and a UV photometric $O_3$ analyzer (Dasibi 1008-RS). Total ecosystem $O_3$ flux was determined by eddy covariance [*Bauer et al.*, 2000]. Total $O_3$ flux was partitioned to differentiate loss due to gas-phase chemistry from stomatal uptake and deposition to non-stomatal surfaces following *Kurpius and Goldstein* [2003].

## 3. Results

[7] Ozone flux due to chemistry and measured emissions of monoterpenes increased dramatically with the onset of thinning (mastication) (Figure 1). Maximum α-pinene mixing ratios and $O_3$ loss due to chemistry were observed when mastication was done in the tower footprint. During non-disturbed times fluxes were smaller and varied with temperature (Figure 2 for $O_3$ flux due to chemistry; *Schade and Goldstein* [2003] for monoterpene emissions). The temperature dependence is also evident in the lower values around day 185 when daytime temperatures dropped from ~25°C to 16°C for a week, then increased back to 23°C.

[8] Total $O_3$ flux, $O_3$ flux to stomatal and non-stomatal surfaces, $O_3$ loss to chemistry, and monoterpene flux (represented by α-pinene) all varied diurnally (Figures 3a–3d). The total $O_3$ flux, $O_3$ loss to chemistry, and monoterpene fluxes were all highest in the mastication and then the post-mastication periods. The $O_3$ flux to stomatal surfaces was highest during the premastication period, then decreased dramatically during mastication and post-mastication as the active leaf area of the plantation was decreased by 50% (Figure 3b). Stomatal and surface uptake increased slightly in the summer as new foliage developed, and then decreased again in the fall as the ecosystem became drought stressed and the plants decreased their stomatal conductance to conserve water. Total $O_3$ flux actually increased during mastication even though the stomatal uptake decreased (Figures 3a and 3b). The total $O_3$ flux decreased during the post-mastication period and again decreased even further during summer. Although the non-stomatal surface area increased as a result of leaving the mastication debris onsite, this can not account for the large enhancement of ozone flux during mastication because that surface area stayed the same during the post-mastication period when the ozone flux began to decrease. Instead, we infer that the massive increase of $O_3$ flux during and following mastication is driven by loss

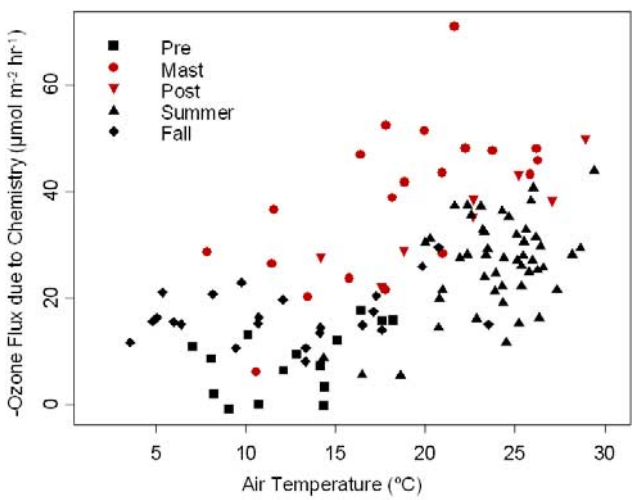


**Figure 2.** Daytime mean (800–1800 PST) $O_3$ flux due to chemistry versus air temperature, before, during, and after mastication, and in the following summer and fall.

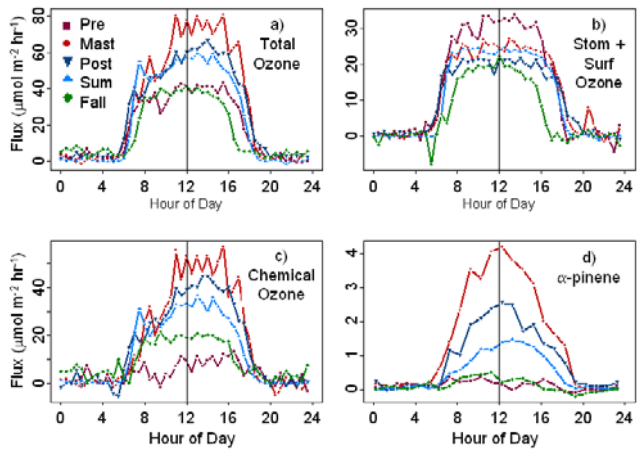


**Figure 3.** Mean diurnal cycles of a) total $O_3$ flux, b) stomatal and surface $O_3$ flux, c) gas phase chemical $O_3$ flux, and d) α-pinene flux, before, during, and after mastication, and in the following summer and fall ($O_3$ flux is into the forest, α-pinene flux is out of the forest).

of $O_3$ through chemical reactions with unmeasured terpenes or closely related BVOCs whose emissions were enhanced due to wounding.

## 4. Discussion and Conclusions

[9] Considered together, these observations provide a conclusive picture that the chemical loss of $O_3$ is due to reactions with BVOCs emitted in a similar manner as terpenes. The chemical $O_3$ loss scales with temperature just like monoterpene emissions during non-disturbed conditions [*Kurpius and Goldstein*, 2003]. In addition, the chemical $O_3$ loss and monoterpene emissions were both consistently higher during and post mastication than expected from their relationships to temperature during non-disturbed times. Both fluxes scaled with mechanical disturbance in a similar manner. We can conceive no other possible explanation for this behavior other than chemical $O_3$ destruction in and above the forest canopy by reactions with biogenically emitted VOCs.

[10] The observed $O_3$ flux due to chemistry is indicative of a large, previously unquantified source of reactive BVOCs (likely terpenoid compounds). We can determine the lower limit of these emissions lost by reaction with $O_3$ within 12 m of the forest floor by assuming a 1:1 stoichiometry for the reactions. This could be an overestimate if the reactive BVOCs had multiple double bonds and reacted with more than one ozone molecule before escaping the forest; however, we think this a minor complication because the residence time in the canopy is short (~90s) and the oxidation products would likely also follow other chemical degradation pathways or quickly partition into aerosols.

[11] Daytime mean $\alpha$-pinene flux was 3.5 $\mu$mol $m^{-2}$ $hr^{-1}$ during mastication, 1.2 $\mu$mol $m^{-2}$ $hr^{-1}$ during summer, and 0.4 $\mu$mol $m^{-2}$ $hr^{-1}$ during fall. Daytime $O_3$ flux due to chemistry was 50 $\mu$mol $m^{-2}$ $hr^{-1}$, 30 $\mu$mol $m^{-2}$ $hr^{-1}$, and 20 $\mu$mol $m^{-2}$ $hr^{-1}$, during those same periods. These comparisons show the unidentified BVOC flux that reacted with $O_3$ was 15 times the $\alpha$-pinene flux during mastication, and 25–50 times the $\alpha$-pinene flux during summer and fall. Since $\alpha$-pinene accounts for approximately 25% of the monoterpenes we routinely measure with our automated in-situ GC instrumentation [*Schade et al.*, 1999], we conclude that emissions of highly reactive terpenoid compounds have been drastically under measured in previous field campaigns. Emissions of compounds that reacted with $O_3$ before escaping the canopy were approximately 4 times larger than emissions of total measured monoterpenes during mastication and approximately 10 (6–13) times measured monoterpenes during more typical summer and fall conditions.

[12] In order for chemical reactions of $O_3$ plus terpenes to occur in the forest canopy and thus be included in our measurement of chemical $O_3$ flux, the terpene lifetimes must be in the range of the average turnover time (or sweep time) of air. *Holzinger et al.* [2004] used high time resolution temperature data and a surface renewal model to calculate a mean sweep time of ~90 seconds during summer daytime. For terpenes to react with $O_3$ before leaving the forest canopy, their lifetimes must therefore be of order 90 seconds or less. At a typical summer daytime $O_3$ concentration of 65 ppb [*Bauer et al.*, 2000], this corresponds to a reaction rate constant of $k_{03} = 8 \times 10^{-15}$ $cm^3$ $molecule^{-1}$ $s^{-1}$.

**Table 1.** Rate Constants and Estimated Lifetimes With Respect to 65 ppb $O_3$ for a Subset of the More Than 150 BVOC Identified in Branch Enclosures at Blodgett Forest

| BVOC | $k_{O3}$[a] ($cm^3$ $molec^{-1}$ $s^{-1}$) | Lifetime (s) |
|---|---|---|
| (E) 4, 8-dimethyl-1, 3, 7-nonatriene | ? | ? |
| $\alpha$-farnesene | ? | ? |
| $\beta$-farnesene | ? | ? |
| $\alpha$-Terpinene | $2.11 \times 10^{-14}$ | 34 |
| $\alpha$-humulene | $1.17 \times 10^{-14}$ | 62 |
| $\beta$-caryophyllene | $1.16 \times 10^{-14}$ | 63 |
| $\alpha$-Phellandrene | $2.98 \times 10^{-15}$ | 247 |
| terpinolene | $1.88 \times 10^{-15}$ | 388 |
| myrcene | $4.9 \times 10^{-16}$ | 1490 |
| $\alpha$-pinene | $8.66 \times 10^{-17}$ | 8430 |

[a]Reaction rate constants from *Calogirou et al.* [1999, and references therein].

[13] Branch enclosures were used to collect emission samples from the major plant species present at Blodgett Forest, revealing more than 300 BVOCs that could be chromatographically separated. Approximately 150 of these were qualitatively identified by matching their mass spectra to a NIST database. The reaction rate with $O_3$ for the majority of these compounds is not known, but those for a small subset are listed in Table 1. Some of these reaction rates are fast enough to allow oxidation within the forest canopy, and thus could be responsible for the chemical $O_3$ loss. Many of the compounds whose $O_3$ rate constants are unknown should be very reactive, including (E) 4, 8-dimethyl-1, 3, 7-nonatriene (DMNT, an acyclic homoterpene with three double bonds), which was one of the dominant compounds emitted from Ceanothus (common shrub at Blodgett Forest), $\alpha$-farnesene (an acyclic sesquiterpene with four double bonds) which was identified as an emission from manzanita, white fir, Ceanothus, and ponderosa pine enclosures (common plants at Blodgett Forest), and $\beta$-farnesene (an acyclic sesquiterpene with four double bonds) whose emission was enhanced from cut and drying ponderosa pine branches. These three compounds are known to be prominently emitted from herbivore damaged plants including maize and cotton [*Pare and Tumlinson*, 1999], thus their emissions are not limited to the pine forest we studied. There may be significant additional BVOCs not measured by our currently available analytical methods which also participate in the inferred $O_3$ reactions within the forest.

[14] Terpene plus $O_3$ reactions typically create OH radicals [*Paulson et al.*, 1999] and thus are likely to have major impacts on OH concentrations within the canopy. Mean summer daytime $O_3$ flux due to chemistry is $-20$ $\mu$mol $m^{-2}$ $hr^{-1}$ at our site [*Kurpius and Goldstein*, 2003]. Assuming average OH yields of 0.5 to 1.0 from $O_3$ chemistry and a vertical depth of 12 m where the reactions occur, OH production of 1.5 to $3 \times 10^8$ molecules $cm^{-3}$ $s^{-1}$ would have to be present in and just above the forest. On a typical summer day with air temperature of 25°C the OH lifetime with respect to all the measured hydrocarbons at this site was 0.2 s [*Lamanna and Goldstein*, 1999]. The minimum OH lifetime observed above a Michigan forest at the same temperature using direct total OH reactivity measurements was of order 0.1 s, approximately 40% faster than the

lifetime calculated from all measured VOCs and other chemicals which react significantly with OH [*Di Carlo et al.*, 2004]. Assuming conservatively that other very reactive compounds we are not measuring at Blodgett Forest would decrease the OH lifetime by a factor of 2 to 4 compared to the measured compounds [*Lamanna and Goldstein*, 1999], OH lifetime is likely in the range 0.05 to 0.1 seconds. Based on this OH lifetime and the presumed OH production rate above, a steady state concentration of 0.8 to 3 $\times$ $10^7$ molecules $cm^{-3}$ (0.4 to 1.5 ppt) would be maintained by ozonolysis reactions alone; other sources of OH co-exist and would further enhance the OH levels. This analysis also suggests that $O_3$ chemistry within the canopy may significantly increase photochemical removal of compounds that react with OH. Compounds like isoprene, methylbutenol, $\alpha$-pinene, $\beta$-pinene and 3-carene should be reduced in and just above the canopy by 5–9% and 16–27% assuming OH levels of 1 $\times$ $10^7$ and 3.5 $\times$ $10^7$ molecules $cm^{-3}$, respectively.

[15] In order to provide insight regarding the relevance of our observations for the larger scale, we compare monoterpene emission capacities used in the most commonly accepted global and U.S. emission model to those we observed in the field. Leaf level monoterpene emission capacities used to represent emissions from conifer forests in the model are 2.3 $\mu g\ C\ g^{-1}\ hr^{-1}$ at 30°C [*Guenther et al.*, 1995]. Canopy scale $\alpha$-pinene emissions at Blodgett Forest, previously reported as a ground area based emission capacity of 0.19 mg C $m^{-2}$ $hr^{-1}$ at 30°C [*Schade and Goldstein*, 2001], when scaled for the foliar density of approximately 400 g $m^{-2}$ dry weight, are consistent with a leaf level $\alpha$-pinene emission capacity of 0.5 $\mu g\ C\ g^{-1}\ hr^{-1}$. Since $\alpha$-pinene emission is approximately 25% of the total above canopy monoterpene emission we observe, that scales to 2 $\mu g\ C\ g^{-1}\ hr^{-1}$ total monoterpene emission capacity above the canopy. This comparison makes clear that current models accurately represent the total monoterpene emissions we observed above the forest canopy, but they do not represent the emissions of the numerous highly reactive terpenes we infer are reacting with ozone before leaving the forest canopy.

[16] Globally, terpene emissions have been estimated to be approximately 25% of isoprene emissions on a mass basis [*Guenther et al.*, 1995]. If our findings are replicated by field measurements in additional ecosystems, our results suggest that total reactive terpene emissions might be roughly a factor of 10 higher than the typically measured and modeled monoterpene emissions, making them larger than isoprene emissions on a global scale. Our measurements also suggest that production of secondary organic aerosols and OVOCs from biogenic reactive terpene oxidation is likely a factor of 10 larger than previously assumed. The fate of these oxidation products and secondary aerosols also requires further study as they may not be dominantly transported away from forests; instead they could be oxidized or deposited within or near the forest canopy.

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