Gas-phase chemistry dominates O_3 loss to a forest, implying a source of aerosols and hydroxyl radicals to the atmosphere

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[1] Tropospheric ozone (O_3) effectively deposits to forested ecosystems but the fate of O_3 within the forest canopy is unresolved. We partitioned total measured ecosystem daytime O_3 deposition to a ponderosa pine (*Pinus ponderosa*) forest into its major loss pathways; stomatal uptake, non-stomatal surface deposition, and gas-phase chemistry. Total O_3 flux was dominated by gas-phase chemistry during the summer and by stomatal uptake during winter. O_3 loss due to gas-phase chemistry was exponentially dependent on temperature, with the same functionality as biogenic hydrocarbon emissions, implicating reactions with biogenic hydrocarbons as the likely gas-phase chemical O_3 loss process within the canopy. The reaction of O_3 with biogenically-emitted hydrocarbons leads to both hydroxyl radical formation and secondary aerosol growth with important effects on atmospheric chemistry and climate. *INDEX TERMS:* 0305 Atmospheric Composition and Structure: Aerosols and particles (0345, 4801); 0315 Atmospheric Composition and Structure: Biosphere/atmosphere interactions; 0322 Atmospheric Composition and Structure: Constituent sources and sinks; 0345 Atmospheric Composition and Structure: Pollution—urban and regional (0305); 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry. **Citation:** Kurpius, M. R., and A. H. Goldstein, Gas-phase chemistry dominates O_3 loss to a forest, implying a source of aerosols and hydroxyl radicals to the atmosphere, *Geophys. Res. Lett.*, *30*(7), 1371, doi:10.1029/2002GL016785, 2003.

1. Introduction

[2] Forests serve as a major sink for tropospheric ozone (O_3) [*Galbally and Roy*, 1980]. While total O_3 flux to ecosystems has been well quantified, the contributions of the loss processes within the canopy have been poorly defined. Within a forest canopy, O_3 can enter plants through open stomata but can also be deposited to non-stomatal surfaces or destroyed in chemical reactions. Stomatal uptake has long been considered the dominant pathway when the ecosystem is physiologically active while the non-stomatal pathways have been neglected. Recent studies suggest that the non-stomatal pathways can account for $10-70\%$ of total ecosystem flux [*Fowler et al.*, 2001; *Mikkelsen et al.*, 2000] but the fate of non-stomatally deposited ozone remains unknown. To examine this "missing sink" for O_3, we partitioned total daytime ecosystem O_3 flux into its major loss pathways. Here we provide the first evidence that the

dominant sink for O_3 loss in a ponderosa pine (*Pinus ponderosa*) ecosystem during summer months is gas phase chemical reactions. Within-canopy gas-phase reactions of O_3 with monoterpenes, sesquiterpenes, or other related compounds with short lifetimes would lead to secondary organic aerosol growth [*O'Dowd et al.*, 2002] and OH production [*Paulson et al.*, 1999], with important implications for tropospheric chemistry and climate.

2. Observations and Calculations

[3] From June 1, 2000 to May 31, 2001, we continuously measured total O_3 flux to a ponderosa pine plantation in the Sierra Nevada Mountains and partitioned it into three components: stomatal uptake, deposition to non-stomatal surfaces, and loss due to gas-phase chemistry. The ponderosa pine plantation is located $\sim$75 km downwind of Sacramento CA where it receives anthropogenically impacted air masses rising from the valley below during the day [*Bauer et al.*, 2000]. This work focused on daytime (0800–1800 PST) O_3 loss because the inability of sonic anemometers to resolve fine-scale eddies results in large uncertainties in total O_3 flux at night.

[4] Total O_3 flux (F_{O_3T}) was measured by the eddy covariance method at 12 m above the ground [*Bauer et al.*, 2000]. Wind speed was measured with a three-axis sonic anemometer (ATI Electronics, Inc.) at 10 Hz. Ozone was measured with a closed-path fast-response chemiluminscent instrument (NOAA-ATDD) [*Bauer et al.*, 2000] at 10 Hz and a slower-response UV photometric O_3 analyzer (Dasibi 1008-RS) was used as a stable reference.

[5] O_3 flux to stomata (F_{O_3stom}) was determined using sap flow measurements. Sap flow was monitored using the heat-ratio method [*Burgess et al.*, 2001]. Eight sensor sets were deployed, one on the east side and one on the west side, in each of four trees. Specific details on instrument setup, sampling, and corrections are provided in *Kurpius et al.* [2003]. Tree canopy conductance (G_t) from the sap velocity measurements was calculated as:

$$Gt = \frac{\gamma \times \lambda \times Et}{Cp \times \rho \times VPD} \qquad (1)$$

where γ is the psychrometric constant (0.65 kPa K^{-1}), λ is the latent heat of vaporization of air (2.459×10^6 J kg^{-1}), E_t is the transpiration rate (kg H_2O m^{-2} h^{-1}), C_p is the specific heat of air (1004.2 J kg^{-1} K^{-1}), ρ is density of dry air at 1300 m (1.066 kg m^{-3}), and VPD is the vapor pressure deficit of the canopy air (kPa). Stomatal O_3 flux was calculated by first correcting tree canopy conductance to account for the difference in diffusivity between O_3 and

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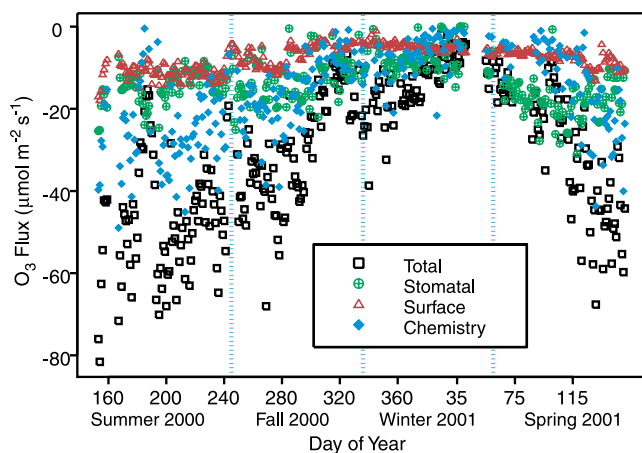
Figure 1. Daytime mean total O_3 flux partitioned into O_3 flux due to stomatal uptake, surface deposition, and chemistry. Uncertainty in the O_3 flux due to chemistry is estimated to be ±30%.

water vapor [*Massman*, 1998] and then multiplying conductance to O_3 by O_3 concentration.

[6] Hourly values of O_3 deposition to non-stomatal surfaces (F_{O_3surf}) were estimated using the FORFLUX model. FORFLUX is a multi-layer biogeochemical model designed to simulate diurnal and seasonal dynamics of carbon, water, and O_3 fluxes in forest ecosystems [*Zeller and Nikolov*, 2000].

[7] O_3 flux due to gas phase chemistry was calculated as the difference between total O_3 flux and stomatal and surface O_3 flux:

$$F_{O_3chem} = F_{O_3T} - F_{O_3stom} - F_{O_3surf} \pm \sigma_{FO_3chem} \quad (2)$$

F_{O_3T} was based on eddy covariance measurements, F_{O_3stom} was based on sap flow measurements, and F_{O_3surf} was estimated using FORFLUX. σ_{FO_3chem} is the random error associated with F_{O_3chem} and was calculated as:

$$\sigma_{FO_3chem} \left[\sigma_{FO_3T}^2 + \sigma_{FO_3stom}^2 + \sigma_{FO_3surf}^2 \right]^{1/2} \quad (3)$$

Under typical daytime summer conditions the standard deviation for O_3 flux due to chemistry (σ_{FO_3chem}) was 14.0 μmol m^{-2} h^{-1}.

[8] Systematic errors associated with $F_{O_3}T$ at this site have been previously examined [*Bauer et al.*, 2000]. The overall effect of the systematic errors involved in eddy covariance O_3 measurements would be to underestimate the flux, which would translate to an underestimation of the F_{O_3chem} term. Systematic errors associated with the sap flow measurements (F_{O_3stom}) have been previously assessed [*Burgess et al.*, 2001; *Kurpius et al.*, 2003]. The main systematic errors that cannot be corrected would result from radial heterogeneity and stand heterogeneity. Radial heterogeneity in sapwood flow was accounted for by measuring sap velocity of inner and outer wood. Core samples indicated that the wood was fairly uniform. Therefore, we expect errors associated with spatial heterogeneity of flow rates and wood properties to be small. Likewise, due to the

homogeneity of the plantation, we expect errors associated with scaling from tree to stand to be small: less than 5% difference in flow rates was observed in the sampled trees. Overall, while we cannot predict the direction of systematic errors that have not been fully accounted for, we expect them to be small.

[9] We calculated F_{O_3chem} by a second method, using an independent estimate of stomatal and surface deposition ($F_{O_3stom.surf}$) to help assess potential systematic errors. Canopy conductance was calculated from ecosystem scale H_2O flux, turbulence, and vapor pressure deficit measurements using an inverse Penman-Monteith equation, including corrections for boundary layer and aerodynamic resistances. $F_{O_3stom.surf}$ was then estimated by accounting for the difference in diffusivity between O_3 and H_2O [*Massman*, 1998] and multiplying conductance by O_3 concentration. In this alternative calculation O_3 flux due to chemistry was then calculated as:

$$F_{O_3chem} = F_{O_3T} - F_{O_3stom.surf} \pm F_{O_3error.} \quad (4)$$

We compared $F_{O_3stom} + F_{O_3surf}$ to $F_{O_3stom.surf}$ and found them to be closely correlated (intercept = 5.4, slope = 0.91, SE of the slope = 0.028, $r^2 = 0.78$). The near 1:1 slope of these two independent methods for determining the combined fluxes of stomata and non-stomatal surfaces suggest that neither method is significantly biased in either direction. The two methods of calculating O_3 flux due to chemistry (equations 3 and 4) were in excellent agreement (slope = 1.01, $r^2 = 0.88$).

3. Results and Discussion

[10] Within-canopy chemistry was the dominant daytime O_3 loss process accounting for 45–55% of the total, while stomatal uptake and non-stomatal deposition accounted for 25–35% and 20%, respectively in summer (Figure 1 and Figure 2). The role of chemistry was still large in fall (38% of total O_3 flux), minor in winter (15%), and moderate in spring (25%). The absolute amount of O_3 loss due to
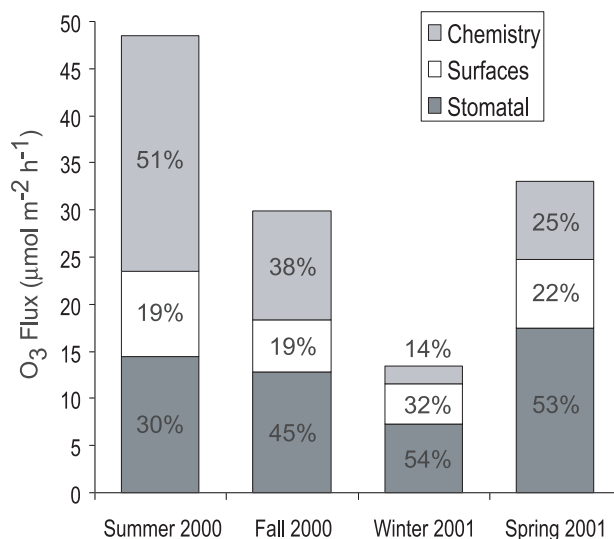

Figure 2. Seasonal contributions of daytime mean O_3 flux with percentages shown on bars.

chemistry showed an exponential dependence on temperature (Figure 3), consistent with the seasonal changes in the relative importance of this loss term, and consistent with observations over a Scottish moorland [*Fowler et al.*, 2001] for total non-stomatal O_3 deposition. *Fowler et al.* [2001] argued that this non-stomatal deposition was due to temperature dependent thermal decomposition on surfaces. We suggest a more likely mechanism is gas-phase reactions with biogenic hydrocarbons whose emission is exponentially dependent on temperature.

[11] Terpenes are biogenically-emitted hydrocarbons that are reactive with O_3, and their emission rates increase exponentially with temperature [*Schade et al.*, 1999]. The temperature dependent monoterpene emission rate observed at this site (sum of the main monoterpenes: α-pinene, β-pinene, d-3-carene, and d-limonene) [*Schade et al.*, 1999] is similar to the observed temperature dependence of O_3 flux due to chemistry (Figure 3) (r^2 = 0.60). However, the overall magnitude of O_3 flux due to chemistry was ~10 times higher than the observed emission rate of the monoterpenes above the forest canopy. Further, the lifetimes of the measured monoterpenes are sufficiently long (~11 to 190 min) to make these compounds unlikely candidates for reacting with substantial amounts of O_3 within the canopy [*Valentini et al.*, 1997]. We propose, rather, that a wider suite of hydrocarbons, including monoterpenes, sesquiterpenes, and related compounds with lifetimes with respect to reaction with O_3 less than ~10 min, could contribute significantly to gas-phase within-canopy O_3 loss. For example, *Ciccioli et al.* [1999b] found substantial within-canopy removal of the sesquiterpene β-caryophyllene, likely through reaction with O_3. Sesquiterpenes react with O_3 much faster than the monoterpenes [*Arey et al.*, 1991], and the temperature dependence of their emissions is similar [*Ciccioli et al.*, 1999b; *Winer et al.*, 1992]. Sesquiterpenes have been observed in a variety of plant species [*Arey et al.*, 1991; *Winer et al.*, 1992] and for some plants sesquiterpene emission rates exceed monoterpenes emission rates [*Winer et al.*, 1992]. However, due to measurement limitations there remains a high degree of uncertainty regarding the specific sesquiterpenes emitted from plants and the magnitude of the emissions [*Ciccioli et al.*, 1999a]. Depending on the magnitude of the within-canopy O_3-hydrocarbon chemistry, fluxes of hydrocarbons that react rapidly with O_3 could be significantly underestimated [*Makar et al.*, 1999] or not observed at all by above canopy flux measurement techniques [*Ciccioli et al.*, 1999b].

[12] The inferred magnitude of O_3-hydrocarbon reactions in the forest canopy has important implications for secondary organic aerosol growth [*Andreae and Crutzen*, 1997; *Zhang et al.*, 1992] and possibly for hydroxyl radical formation [*Atkinson and Aschmann*, 1993; *Paulson et al.*, 1999]. Atmospheric aerosols contribute to the radiative forcing of climate, contribute to haze [*Fehsenfield et al.*, 1992], and provide cloud condensation nuclei [*Andreae and Crutzen*, 1997; *Novakov and Penner*, 1993]. The aerosol-forming potential of terpenes was recognized as early as 1960 [*Went*, 1960] and these compounds are now believed to contribute significantly to secondary organic aerosol growth [*Zhang et al.*, 1992]. It has recently been reported [*O'Dowd et al.*, 2002] that aerosol particles produced over forests are composed primarily of organic species derived
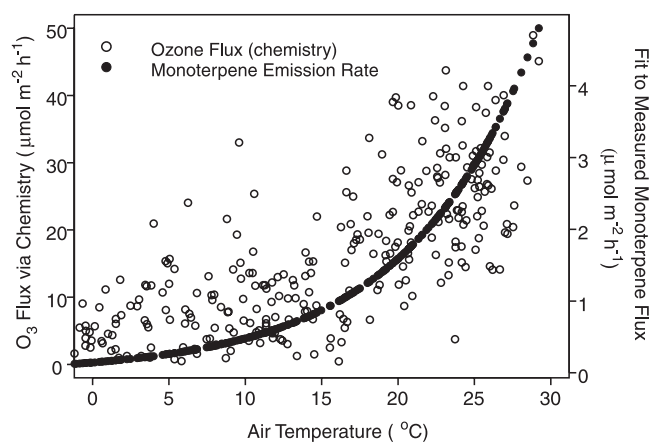

Figure 3. Daytime mean O_3 flux due to chemistry versus daytime mean air temperature. A fit to the measured emission rate of monoterpenes from ecosystem is overlaid as black filled circle [*Schade et al.*, 1999].

from oxidation of biogenically emitted terpenes. Yields of organic aerosols from photooxidation of terpenes range from 5 to 100% with the highest values observed for sesquiterpenes [*Andreae and Crutzen*, 1997]. The yield of hydroxyl radical from reactions of O_3 with terpenes range from 0.1 to 1.0 [*Paulson et al.*, 1999]. Therefore, quantifying O_3 loss in forest canopies due to reaction with biogenic hydrocarbons is of great importance for understanding the natural background of secondary organic aerosols and possible hydroxyl radical formation.

[13] NO emissions from soil have a strong dependence on temperature with a Q_{10} of approximately 2 [*Williams et al.*, 1992]. The expected relative increase in NO emission rate with temperature is similar to the increase in O_3 flux due to chemistry (r^2 = 0.63). Typical NO fluxes from soils in California are $2-20$ ng m^{-2} s^{-1} [*Anderson and Poth*, 1989; *Davidson et al.*, 1993]. Upon release from the soil, NO rapidly reacts with O_3 and forms NO_2 (lifetime of NO with 50 ppb O_3 < 1 min). In the presence of sunlight NO_2 is photolyzed back to NO, and the resulting atomic oxygen reacts with O_2 to regenerate O_3 (NO_2 lifetime is ~2 minutes during summer at this latitude). The ratio of NO to NO_2 is 1:4 at steady state during summer daytime [*Dillon et al.*, 2002] so 0.8 O_3 are effectively removed for every NO emitted. Therefore, reaction with NO could account for ~0.2 to 2 μmol m^{-2} h^{-1} (1–8% of O_3 flux due to chemistry during the summer). A potential additional source of NO at this site is emissions from plants and could be of equal magnitude to emission from soils [*Wildt et al.*, 1997]. The residence time of air within the canopy is on the order of ~10 minutes. This would allow a small fraction of NO to escape from the canopy before reaction and result in a slightly smaller contribution of NO to O_3 loss due to chemistry. We therefore estimate a highly uncertain range of O_3 flux attributed to NO_x chemistry to be $0.4-4$ μmol m^{-2} h^{-1} with a likely quantity of $1-3$ μmol m^{-2} h^{-1} during the summer.

4. Conclusions

[14] O_3 flux due to gas phase chemistry was the dominant O_3 sink to the forest when air temperature was

high, suggesting a large unrecognized source of reactive compounds in forested environments. New measurements of highly reactive mono- and sesquiterpene emissions are needed in order to quantify the importance of their oxidation products to secondary aerosol loading in the atmosphere, and their potential impacts on atmospheric chemistry and climate.

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