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Ozone fluxes in a *Pinus ponderosa* ecosystem are dominated by non-stomatal processes: Evidence from long-term continuous measurements

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ABSTRACT

Ecosystems remove ozone from the troposphere through both stomatal and non-stomatal depositions. The portion of ozone taken up through stomata has an oxidative effect causing damage. We used a multi-year dataset to assess ozone deposition to a ponderosa pine plantation near Blodgett Forest, Georgetown, California. Environmental parameters, water and ozone concentrations and fluxes were measured continuously from January 2001 to December 2006. High levels of ozone concentrations (up to 100 ppb) were observed during the spring–summer period, with corresponding high levels of ozone fluxes (up to 30 μmol m^{-2} h^{-1}). During the summer season, we calculated that a large portion of the total ozone flux was due to non-stomatal processes, which is in agreement with previous studies suggesting that chemical reactions with BVOCs (biogenic volatile organic compounds) emitted by the ecosystem are mainly responsible for this ozone flux. We also report here the first direct measurement of BVOC + ozone oxidation products, confirming that ozone loss process is occurring below our flux measurement height. We analyzed the correlations of common ozone exposure metrics based on accumulation of concentrations (AOT40 and SUM0) with ozone fluxes (total, stomatal and non-stomatal). Stomatal flux, which is considered responsible for ozone damage, showed a weaker correlation with ozone concentrations than non-stomatal flux during summer and fall seasons. The non-stomatal flux is more strongly correlated with ozone concentration because BVOC emission and ozone concentration both increase with temperature. We suggest that AOT40 and SUM0 are poor predictors of stomatal ozone uptake, and that a physiologically based metric would be more effective.

1. Introduction

Ozone is considered one of the most dangerous oxidant molecules for plants (UNECE, 2004; EPA, 2007). Ozone concentration in the northern midlatitude atmosphere is increasing (Brasseur et al., 1998). It was estimated that by 2050 the average atmospheric concentration will exceed the 40 ppb threshold currently used for estimating oxidative damage to vegetation (Langner et al., 2005). Chronic stress by exposure to moderate ozone concentrations usually produces biochemical and physiological changes (Darrall, 1989; Sandermann et al., 1997; Zheng et al., 2002). The inhibition of carbon assimilation by photosynthesis and a decrease in plant growth is a common effect (Guderian et al., 1985), often associated with visible injuries (Bussotti et al., 2003; Vollenweider and Gunthardt-Goerg, 2005) under conditions of acute ozone concentrations in the atmosphere. Decline in stomatal conductance is a common effect of atmospheric ozone, so the capability of plants to exchange water and CO_2 will be negatively affected by rising ozone concentrations in the atmosphere (Wittig et al., 2007).

Plants act as a sink for ozone, through stomatal and non-stomatal processes. Stomatal conductance to ozone is the inverse of the sum of an array of resistances that ozone meets in specific locations along the path from outside the leaf to the reaction site inside the apoplast (Fares et al., 2008). Non-stomatal processes include ozone deposition to soil, stems, cuticles, and, in general, any external surface, along with gas-phase chemical losses involving reactions between ozone and BVOCs (biogenic volatile organic compounds) or nitric oxide (NO) emitted by the ecosystem (plants and soils) (Kurpius and Goldstein, 2003). In parallel with ozone formation, the emissions of some BVOCs increase with light (Niinemets et al., 2004) and exponentially with temperature (Tingey et al., 1991; Monson et al., 1992; Guenther et al., 1995), consequently producing higher emissions during spring–summer

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seasons (Holzinger et al., 2006) when ozone concentrations are highest.

At a regulatory level, identifying a reliable metric for ozone risk assessment is important. The metrics used for ecological ozone risk assessment are mostly based on the accumulated daytime ozone concentration. Typically, hourly O_3 concentrations from the NCLAN (National Crop Loss Assessment Network) program are used to calculate different means and cumulative statistics. Several metrics were developed using both threshold and functional concentration weighting and tested for best fit to NCLAN yield responses (Lefohn and Runneckles, 1987; Musselman et al., 1988; Rawlings et al., 1988) and described in EPA (US Environmental Protection Agency) directives (EPA, 1986, 1996). Concentration-based metrics calculated from 8 am to 8 pm were also used by EPA for generating a national exposure surface with the intent to analyze national ozone air quality, and develop maps of vegetation exposures and risk under different ozone level regimes and applied standards (EPA, 2007). These metrics are hourly averages of ozone concentration, SUM06 (sum of all ozone values greater than or equal to 0.06 parts per million) and W126 (a weighted sum of all ozone values).

The best representative metric in a ponderosa pine ecosystem in the Sierra Nevada mountains of California was found to be SUM0 (Panek et al., 2002; Kurpius and Goldstein, 2003), based on the sum of all daytime ozone concentrations. Therefore, we used the SUM0 metric in this study. The European directives (UNECE, 2004) suggest the use of the AOT40 (accumulated ozone over a threshold concentration of 40 ppb) for forest ecosystems, a metric which considers only daylight hours over a certain solar radiation intensity (Karenlampy and Skarby, 1996; Fuhrer et al., 1997). This second metric was also adopted in this study and compared to SUM0. Ozone concentration at the canopy-level is used to calculate these metrics.

Ozone concentration is not always correlated to ozone flux (Kurpius et al., 2002), and accumulated exposure to ozone does not take into account the physiology of plants nor the effective dose of ozone absorbed by plants via stomata (Panek et al., 2002). Drought stress in Mediterranean ecosystems induces stomatal closure, consequently limiting the ozone uptake by stomatal absorption even at high ozone concentrations (Emberson et al., 2007). This may result in much lower damage than predicted by the AOT40 index. In order to establish a cause–effect relationship considering only the effective concentration of ozone entering the leaf, a stomatal flux-based index has been considered (Karlsson et al., 2004; Simpson et al., 2007; Tuovinen et al., 2007; Tuovinen, 2009; Matyssek et al., 2007), and proposed for some tree species (Beech and Birch) in the risk assessment methodology adopted within the CLRTAP (Convention of Long-Range Transboundary Air Pollution) of UNECE (UNECE, 2004). Partitioning ozone flux between the stomatal and non-stomatal mechanisms is considered the best choice for ozone risk assessment (Emberson et al., 2000), although estimating the relative amount of the stomatal ozone flux depends on the ecophysiology of a specific ecosystem and requires more detailed information than is often available. Stomatal ozone uptake was found to be the major contributor to the total ozone flux at the whole plant and leaf level (Fredericksen et al., 1996; Fares et al., 2008), when adsorption sinks are limited and in dry conditions (Altimir et al., 2006). However, on wet plant surfaces and in presence of BVOC, considerable amounts of ozone can react with a multitude of waxes, salts, ions, and many other compounds leading the non-stomatal mechanisms to represent up to 30–70% of the total ozone flux in a *Pinus ponderosa* ecosystem (Kurpius and Goldstein, 2003; Goldstein et al., 2004), in a sitka spruce ecosystem (Coe et al., 1995), in a Mediterranean oak forest (Gerosa et al., 2005) in a northern mixed hardwood forest (Hogg et al., 2007) and in a sub-alpine ecosystem (Zeller and Nikolov, 2000).

In this work, we illustrate the dynamics of stomatal and non-stomatal ozone fluxes measured from 2001 to 2006 in a ponderosa pine plantation located in the Sierra Nevada Mountains of California. The goal of this study was (1) to examine the longer term dataset for consistency with previous shorter term studies performed in the same forest ecosystem at an earlier stage of development which suggested that non-stomatal ozone fluxes were a dominant portion of the total ozone fluxes; (2) to determine whether plant physiology dominates both stomatal and non-stomatal ozone fluxes (3) to show how well ozone fluxes correlate with ozone concentrations during the four seasons, through the use of two common metrics (SUM0 and AOT40) correlated with the accumulated total, stomatal and non-stomatal ozone fluxes.

2. Material and methods

2.1. Site description

The Blodgett Ameriflux site (38°53′42.9″N, 120°37′57.9″W) is located at 1315 m above sea level in the Sierra Nevada Mountains of California, near Georgetown, adjacent to the UC Berkeley Blodgett Forest Research Station, on land owned by Sierra Pacific Industries. Trees were planted in 1990 at a density of ∼1300 trees/ha, and underwent a precommercial thinning in 2000, removing ∼60% of the trees and cutting back all the shrubs. The dominant tree species is ponderosa pine (*P. ponderosa* L.). The major understory shrubs are *Arctostaphylos manzanita* (Mazanita) and *Ceonothus cordulatus* (Ceanothus). The total LAI (leaf area index) increased from 1.2 in 2001 to 2.9 in 2006, with a mean height increasing from 4 m to 7.6 m during the same period. The soil has 60% sand and 29% loam with a pH of 5.5 ± 0.29 with approximately 6.9% organic matter and 0.17% nitrogen (details are given in Goldstein et al., 2000). The site is characterized by a Mediterranean climate, with warm dry summers and cold wet winters, and with a typical mountain wind regime bringing daytime air up the mountain slopes from the nearby Sacramento valley urban area, while at night a gentle downslope wind reverses the direction. Diurnally averaged daytime temperatures were rarely below 0 °C in the winter (days 0–80, 335–365 Fig. 1A), and maximum average summer temperatures (days 172–264) of 25 °C. Air temperature and vapour pressure deficit (VPD)

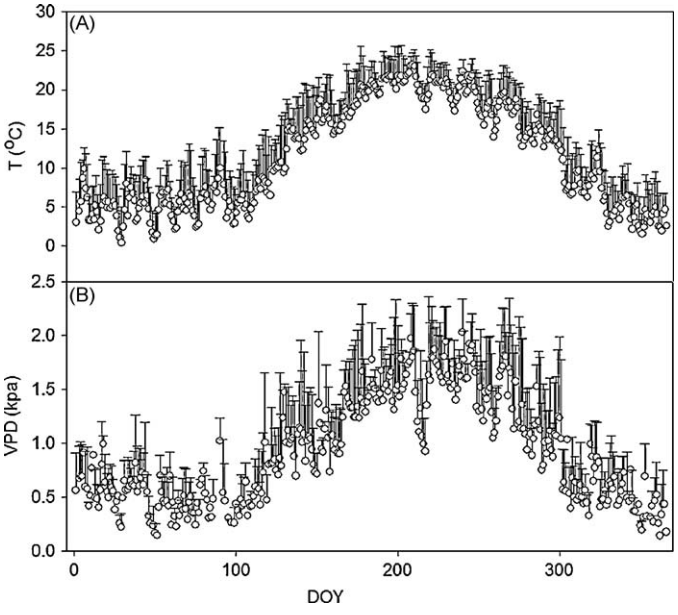

Fig. 1. Daily averages of temperature (panel A) and vapour pressure deficit (VPD; panel B), Standard deviation in each panel is based on the average values for the years 2001–2006.

Table 1
For each season of the years 2001–2006 we report: percentage of non-stomatal ozone flux over the total ozone flux, mean of temperature (T) and vapour pressure deficit (VPD) during the light hours (06:00–20:00), seasonally sum of rain, ozone fluxes, percentage of valid observations (N). Values ± standard errors ($n = 4$) are reported. For each year, the errors are calculated from the standard deviation of the mean of the four seasons.

Time period		NS O_3 flux (%)	T (°C)	VPD (kpa)	Rainfall (mm)	Ozone flux ($gO_3\,m^{-2}$)	N (%)
Year	Season						
2001	Spring	47.4	14.7	1.18	165	−2.36	84
	Summer	64.8	22.2	1.8	0	−2.61	89
	Fall	66.4	15.6	1.2	108	−1.27	90
	Winter	14.9	5.1	0.5	275	−0.72	64
	Mean ± se	48 ± 12	14.4 ± 3.5	1.17 ± 0.26			81 ± 6.0
	Total				548	−6.96	
2002	Spring	68.2	13.3	0.92	239	−1.98	76
	Summer	42.6	22.2	1.78	0	−2.27	96
	Fall	55	13.8	1.04	200	−1.11	82
	Winter	10.3	5.3	0.5	444	−0.51	84
	Mean ± se	44 ± 12.4	13.6 ± 3.5	1.06 ± 0.27			84 ± 4.0
	Total				883	−5.88	
2003	Spring	46.1	12.3	0.87	419	−2.37	84
	Summer	53.8	22.2	1.79	38	−2.61	91
	Fall	61.1	14.9	1.26	104	−1.37	95
	Winter	37.7	7.3	0.53	297	−1.01	75
	Mean ± se	50 ± 5	14.1 ± 3.1	1.11 ± 0.27			86 ± 4.3
	Total				858	−7.36	
2004	Spring	46.7	14.2	0.97	78	−2.71	46
	Summer	54.6	22.1	2.03	22	−2.12	92
	Fall	65.3	11.7	1.04	278	−1.49	57
	Winter	13.1	6.4	0.54	344	−0.86	76
	Mean ± se	44 ± 11	13.6 ± 3.2	1.14 ± 0.31			67 ± 10
	Total				722	−7.18	
2005	Spring	18.1	10.8	0.8	553	−2.07	57
	Summer	52.1	21.7	1.72	3	−2.97	57
	Fall	52.8	12.8	0.62	109	−1.42	87
	Winter	36.6	6.8	0.47	554	−0.83	77
	Mean ± se	40 ± 8.1	13 ± 3.1	0.9 ± 0.28			69 ± 7.5
	Total				1219	−7.29	
2006	Spring	34.9	12.4	0.87	588	−1.72	56
	Summer	43.5	22.2	1.92	2	−2.44	94
	Fall	46.1	12.9	0.97	159	−1.12	90
	Winter	7.02	4.3	0.54	242	−0.72	60
	Mean ± se	33 ± 9	13 ± 3.6	1 ± 0.29			75 ± 9.8
	Total				991	−6.00	
Mean ± se	Spring	43.6 ± 8.2	13.0 ± 0.7	0.9 ± 0.06	340 ± 105	−2.2 ± 0.14	67.2 ± 8.1
	Summer	51.9 ± 4.0	22.1 ± 0.1	1.8 ± 0.06	10.8 ± 7.8	−2.5 ± 0.12	86.5 ± 7.3
	Fall	57.8 ± 3.9	13.6 ± 0.7	1.0 ± 0.11	69.2 ± 35	−1.3 ± 0.06	83.5 ± 6.8
	Winter	13.6 ± 5.5	5.90 ± 0.6	0.5 ± 0.14	359 ± 59	−0.78 ± 0.07	72.7 ± 4.4
	Mean ± se	43.3 ± 6.8	13.6 ± 0.3	1.1 ± 0.04			77.5 ± 1.5
	Total ± se				870 ± 114	−6.7 ± 0.27	

followed similar annual patterns across the years, with the higher values during spring and summer, and large sub-weekly variation due to the passage of weather fronts as indicated with error bars in Fig. 1B. Annual precipitation during 2001–2006 was 870 ± 114 mm (Table 1), and concentrated almost exclusively in spring and winter (Table 1), with low precipitations in fall, and total absence of precipitation in summer except for 2003 and 2004 (38 mm and 22 mm, respectively). The highest precipitation occurred in 2005 (1219 mm), in 2006 there was less total annual precipitation (991 mm), but more concentrated in the spring, a more favourable period for plant growth. The precipitation relevant to a particular growing season is therefore better calculated from July to June (JJ) for this site, totaling 1197 mm in 2004–2005, and 1254 mm in 2005–2006.

2.2. Gas exchange measurements

The measurements were performed continuously from January 2001 to December 2006. Fast response measurements of ozone were made by chemiluminescence using Coumarin dye with an instrument custom developed by NOAA Research (Silver Spring, MD). The chemiluminescence detector was calibrated against 30 min average ozone concentrations from a UV ozone monitor (1008 DASIBI Environmental). The precision of this UV monitor is 1 ppb. CO_2 and water concentrations were measured with a closed path infrared gas analyzer (LI-6262, Lincoln, NE, USA). The raw analog data were recorded at 10 Hz for all gases. O_3 and water concentration were correlated with the vertical wind velocity according to the Eddy-Covariance technique extensively described in Goldstein et al. (2000) and Bauer et al. (2002). Fluxes of gases were calculated according to Eq. (1):

$$\Phi_c = \overline{w'c'} \quad (1)$$

where w is the vertical wind velocity and c the concentration of the gas at the measurement height (12.5 m). The prime indicates deviations from the 30 min means and the overbar indicates a time average. Wind velocity and sonic virtual temperature fluctuations were measured at 10 Hz with a three-dimensional sonic anemometer (Applied Technologies, Inc., Boulder, CO) mounted on a horizontal beam at 12.5 m above the ground.

Similarly, we calculated the fluxes of latent heat, according to Eq. (2):

$$\lambda E = \lambda \rho \overline{w'q'} \quad (2)$$

where ρ is the density of the dry air, λ is the vaporization heat of water, q is the specific air humidity.

In this work, we indicate negative fluxes when mass and energy transfer are from the atmosphere into the vegetation and soil. The sonic anemometer wind data was rotated to force the mean vertical wind speed to zero, and to align the horizontal wind speed onto a single horizontal axis. The time lag for sampling and instrument response was determined by maximizing the covariance between vertical wind velocity (w') and scalar (c') fluctuation. Errors due to sensor separation and damping of high frequency eddies were corrected using spectral analysis techniques as outlined by Rissmann and Tetzlaff (1994).

Environmental parameters were measured every 5 s and stored as 30 min averages on a CR10X datalogger (Campbell Scientific, Inc., Logan, UT). The parameters included air temperature and relative humidity in aspirated radiation shields at four heights, net radiation, photosynthetically active radiation, and atmospheric pressure. See Goldstein et al. (2000) for a more detailed description.

2.3. VOC measurements

Fluxes of monoterpenes and oxidation products were measured with a proton-transfer-reaction mass-spectrometer (PTR-MS) during four 2-week periods covering the period from mid-June to end of September 2005 (DOY 170–190, 199–213, 227–241, 253–270).

The setup was the same as described in Holzinger et al. (2006) and details about PTR-MS can be found in Lindinger et al. (1998). Briefly, the fluxes were calculated by Eddy-Covariance from fast measurements (5 Hz) of monoterpenes (mass/charge (m/z) ratio 137) and oxidation products (m/z 113) over a period of 30 min. The measurements of the 3D wind field (model *CSAT*-3 sonic anemometer, *Campbell* Scientific) and organic compounds were made above the canopy at a height of 12.5 m. The signal detected at m/z 113 is representative of a whole class of compounds which can be produced through the oxidation of mono- and sesquiterpenes (Lee et al., 2006a,b; Holzinger et al., 2005) which have so far only been identified by their mass to charge ratio. For these compounds, the concentration has been computed analytically (Lindinger et al., 1998). Gravimetrically mixed gas-standards of monoterpenes were automatically measured on a regular daily basis to calibrate the PTR-MS.

2.4. Partitioning between stomatal and non-stomatal ozone fluxes

The total ozone flux (F_{O_3}) is defined as the quantity of ozone molecules transferred from the air to the vegetative surface per unit time and area (Cieslik, 2009) and is partitioned in a stomatal and a non-stomatal component. F_{O_3} can be calculated by relating fluxes to concentrations through a series of resistances by analogy with an electric circuit obeying Ohm's law (Cieslik, 2004; Gerosa et al., 2005). If assuming a constant vertical flux between the measurement height and the top of canopy, and negligible intercellular ozone concentration (Laisk et al., 1989), the total ozone flux is expressed by:

$$F_{O_3} = F_{O_{3sto}} + F_{O_{3nsto}} = \frac{[O_3]_c}{R_{sto}} + \frac{[O_3]_c}{R_{nsto}} \quad (3)$$

where F_{O_3} is measured with the Eddy-Covariance technique and is equal to the sum of stomatal ($F_{O_{3sto}}$) and non-stomatal fluxes ($F_{O_{3nsto}}$); $[O_3]_c$ is the ozone concentration at the canopy-level derived from the ozone concentration at the measurement height after taking into account for the resistance terms (aerodynamic and boundary layers) as described by Gerosa et al. (2005), R_{sto} is the stomatal resistance to ozone flux and R_{nsto} is the non-stomatal resistance to ozone flux. The latter term includes all possible sinks which contribute to ozone removal besides the stomata. One class of non-stomatal sinks include chemical reactions in the gas phase between ozone and BVOC, NO_x, and radicals (Kurpius and Goldstein, 2003; Holzinger et al., 2005). Another class of non-stomatal sinks include ozone deposition into the soil and on plant surfaces (Altimir et al., 2006; Cape et al., 2009).

Using measurements of the latent heat flux (λE) we can calculate R_{sto} for water (Monteith, 1981; Kurpius and Goldstein, 2003; Cieslik, 2004; Gerosa et al., 2005):

$$\lambda E = \frac{\rho c_p [e_s(T_0) - e(z_m)]}{\gamma (R_a + R_b + R_{sto})} \quad (4)$$

where ρ is the air density, c_p is the air heat capacity, $e_s(T_0)$ is the water vapour pressure at the evaporating surface, $e(z_m)$ is the water vapour pressure at measurement height z_m, γ is a psychrometric constant, R_a is the aerodynamic resistance calculated according to Eq. (5):

$$R_a = \int_{d+z_0}^{z_m} \frac{dz}{K(z)} \quad (5)$$

where z_m is the measurement height, d is the displacement height (approximated to 2/3 of z_m), z_0 is the roughness height (approximated to 1/10 of z_m). $K(z)$ is the vertical turbulence diffusion coefficient derived from the Monin-Obukhov similarity function (Monin and Obukhov, 1954; Dyer, 1974). The term R_b in Eq. (4) is the canopy boundary layer resistance as proposed by Hicks et al. (1987):

$$R_b = \frac{2(Sc/Pr)^{2/3}}{ku*} \quad (6)$$

where Sc is the Schmidt number and Pr is the Prandtl number (1.07 and 0.72 for ozone, respectively), k is the dimensionless von Karman constant (0.43), u^* is the friction velocity calculated from measurements of horizontal and vertical wind directions. R_{sto} was the main resistance, with ($R_a + R_b$) rarely exceeding 5% of R_{sto}.

In order to exclude evaporative sources (from soil and leaf surfaces) the days including rain-events and the following 2 days were excluded from the calculation of water fluxes. In addition, four surface wetness sensors (Model 237, Campbell Scientific, Inc., Logan, UT) were installed on branches as described by Misson et al. (2005a). Data were filtered for points showing low resistances due to total water condensation on the surfaces.

To obtain the stomatal resistance for ozone, we multiply the R_{sto} for water by the ratio of the molecular diffusion coefficients for water vapour and ozone in the air (1.65; Marrero and Mason, 1972).

Once we calculate the stomatal ozone flux using the stomatal resistance for ozone, we define the remaining residual term of ozone flux to be the non-stomatal flux, ie $F_{O_{3nsto}} = F_{O_3} - F_{O_{3sto}}$.

The ozone deposition velocity was obtained dividing the total ozone flux by the ozone concentration.

2.5. Ozone metrics

Two metrics based on accumulated exposures were calculated: SUM0 and AOT40, expressed in units of ppb h. The first metric is one of several indices used by the USDA Forest Inventory and Analysis Ozone Biomonitoring Program to quantify ambient ozone concentrations in terms of seasonal ozone exposures of forests (USDA Forest Service, 2004). SUM0 is defined as the sum of average hourly ozone concentrations for all daylight hours (06:00–20:00)

during the year or a selected season (USDA Forest Service, 2004, Eq. (7)). This index has been evaluated as a good metric for ozone-sensitive plants by correlations with ozone damage (Salardino and Carroll, 1998).

$$\mathrm{SUM0} = \sum_{[06::00-20:00]} [\mathrm{O_3}]\Delta t \quad (7)$$

The second metric used, AOT40 (accumulated exposure over a threshold of 40 ppb), is the sum of average hourly ozone concentrations exceeding 40 ppb during the daylight (06:00–20:00) in which the global radiation is equal or above 50 W m^{-2} (European Environment Agency, 2004, Eq. (8)).

$$\mathrm{AOT40} = \sum_{\substack{[\mathrm{O_3}] > 40 \\ \mathrm{Rad.} > 50\,\mathrm{W\,m^{-2}}}} [[\mathrm{O_3}] - 40]\Delta t \quad (8)$$

This index excludes the low ozone levels, and is currently suggested for ozone risk assessment for European forests (UNECE, 2004; Karenlampy and Skarby, 1996; Fuhrer et al., 1997).

The most suitable metric of ozone risk to vegetation is the real accumulated ozone flux entering stomata (Emberson et al., 2000, 2007; Panek et al., 2002; Karlsson et al., 2004). In order to compare the SUM0 and AOT40 metrics with the actual flux, we calculated three metrics based on accumulated ozone fluxes. The first flux-based metric is SUMFLUX, expressed in μmol m^{-2} per each season of the years 2001–2006, calculated as the sum of the ozone flux during daylight hours in a similar manner as SUM0. The second flux-based metric is SUMFLUX$_{sto}$, similar to the previous metric but only accounting for stomatal ozone flux. SUMFLUX$_{sto}$ returns a similar indication as AF$_{st}$Y but calculated for the four seasons. AF$_{st}$Y is the accumulated stomatal flux above a threshold Y (Karlsson et al., 2004; Simpson et al., 2009; Tuovinen et al., 2007; Tuovinen, 2009), in this study considered = 0 because a phytotoxic threshold has not been identified yet for the observed ecosystems. The third flux-based metric is SUMFLUX$_{nsto}$, the sum of the non-stomatal ozone fluxes during light hours. SUM0 and AOT40 were tested to determine how well they correlate with these flux-based metrics. SUM0 has been calculated hourly for the four seasons and statistically correlated with hourly accumulated fluxes, while AOT40 was calculated for the entire growing season and correlated for the years 2001–2006 with the equivalent cumulative fluxes.

3. Results

3.1. Meteorology and ecosystem response

From 2001 to 2006 we observed only a limited effect of drought stress during the dry season in terms of decreased levels of stomatal conductance and water evapotranspiration during the hottest summer days (Fig. 3C). On a diurnal averaged basis, no observable mid-day depression in latent heat flux and water evapotraspiration occurred (Fig. 2D and E). For certain years (2002, 2005, 2006) relatively higher levels of temperature and precipitation during the day period 305–340 led to an increase of the interannual average of stomatal conductance (Fig. 3C). During winter, air temperatures (daily average of 5.6 ± 0.6 °C) were not so low to represent a limiting factor for growth at this altitude (1315 m) of the Sierra Nevada. The highest levels of latent heat and evapotranspiration were recorded in mid-day (Fig. 3D and E) and corresponded to higher values of photosynthetically active radiation, temperature, and VPD (Fig. 3A–C), with a moderate interannual variability especially for the summer season.

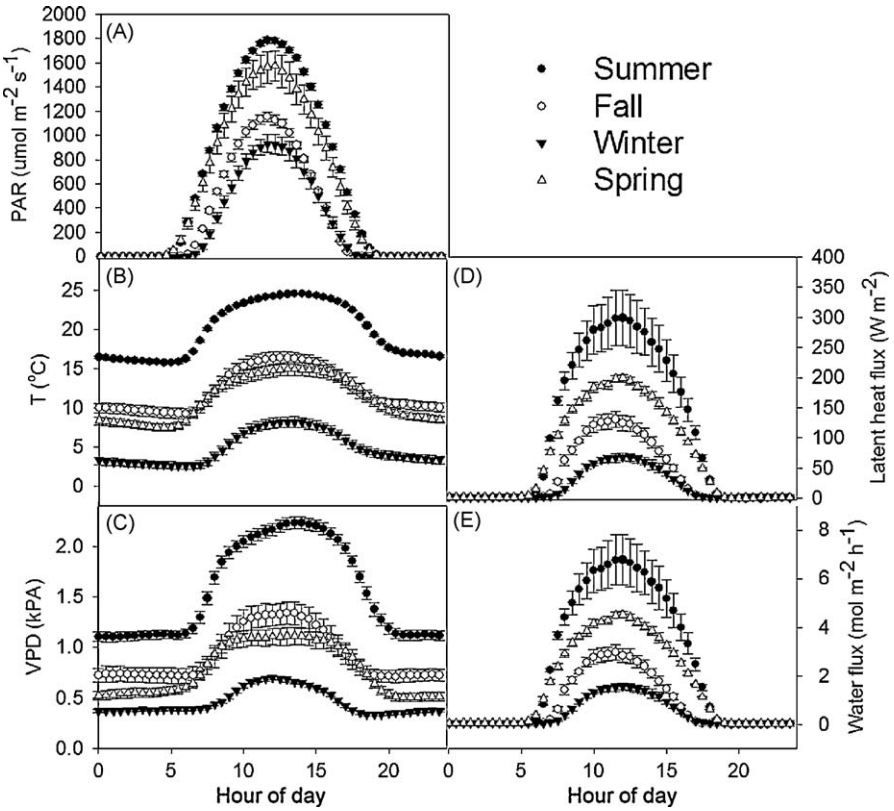

Fig. 2. Photosynthetically active radiation (PAR; panel A), temperatures (panel B), vapour pressure deficit (VPD: panel C), latent heat flux (panel D), water fluxes (panel E), shown as hourly means averaged for the years 2001–2006. Standard errors are also reported (n = 6). The different symbols represents the four seasons: summer (DOY 172–264, ●), spring (DOY 81–171, △), fall (DOY 265–355, ○), winter (DOY 356–380, ▼).

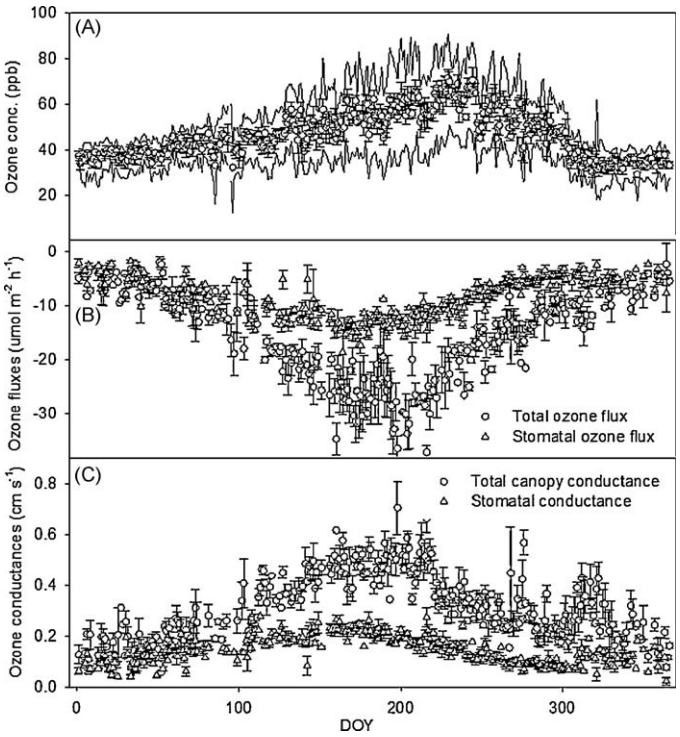

Fig. 3. Panel A: daily averages of ozone concentration (the continuous lines describe the minimum and maximum daily concentrations averaged for the 6 years of observations). Panel B: daily averages of total and stomatal ozone fluxes. Panel C: daily averages of total and stomatal ozone conductance. Standard errors ($n = 6$) represent from the average values for the years 2001–2006 are reported.

3.2. Ozone concentrations and fluxes

Daily ozone concentrations frequently exceed 60 ppb during the summer (days 172–264, Fig. 3A), and are rarely below 25 ppb during the cold season (days 0–100, 335–365). The annual cumulative ozone flux ranged between a minimum value of -5.88 g m^{-2} in 2002 and a maximum value of -7.36 g m^{-2} in 2003, with an average value over the 2001–2006 period of -6.7 ± 0.27 g m^{-2} yr^{-1} (Table 1). Averaging accumulated ozone flux by season shows that spring (32.5%) and summer (36.9%), dominate over fall (19.1%) and winter (11.5%) in their contributions to total annual ozone deposition.

Each year from 2001 to 2006 showed this clear trend with highest ozone fluxes (up to -40 μmol m^{-2} h^{-1}) in the spring–summer period, reaching the maximum levels in mid-July (≈day 200, Fig. 3B). The total measured ozone fluxes were best correlated with temperature (Fig. 4) and VPD, with R^2 of 0.62 and 0.85, respectively. Ozone stomatal flux (Fig. 3B) accounted for 56.7% of the total annual ozone flux (Table 1). Stomata were the main contributor to ozone fluxes during the winter period (average of 86.4%), while non-stomatal ozone fluxes were much higher in the summer-fall period (around 55% of the total ozone flux), and were more related to temperatures ($R^2 = 0.54$) than the stomatal ozone fluxes ($R^2 = 0.30$).

On a multi-year basis, the partitioning between stomatal and non-stomatal ozone fluxes showed a predominance of the non-stomatal component in the dayhours, especially in summer and fall, accounting for up to 65% of the total ozone flux (Fig. 5). BVOC may contribute to non-stomatal ozone uptake, and for this reason we report here the first measurements of BVOC oxidation product fluxes detected at a molecular weight of 113 Da. The flux of the mass 113 oxidation products was 12% of the total monoterpenes emission (Fig. 6A) with a diurnal cycle matching a combination of monoterpene emission and non-stomatal ozone fluxes (Fig. 6B).

Table 2 reports the correlations of a metric based on accumulated ozone concentrations (SUM0) with metrics based on accumulated total, stomatal and non-stomatal ozone fluxes. While the average summer correlation of SUM0 with SUMFLUX was 0.33, SUM0 correlated more strongly with the non-stomatal flux ($SUMFLUX_{nsto}$, 0.47). During this same period, the correlations of SUM0 with accumulated stomatal ozone flux ($SUMFLUX_{sto}$) were still lower (average = 0.38) because high temperatures and

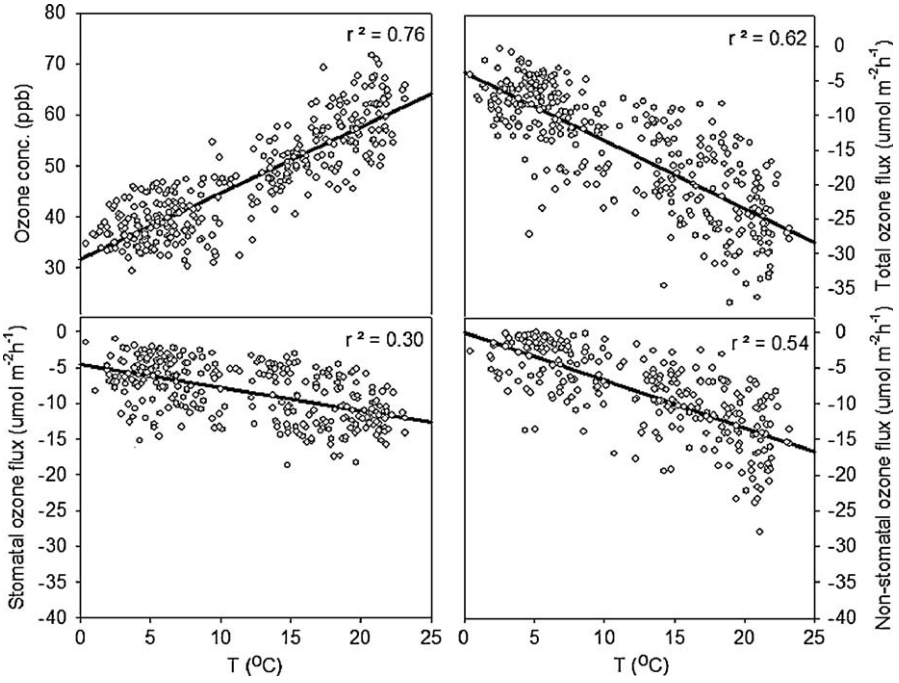

Fig. 4. Correlation of ozone concentration, total ozone fluxes, stomatal ozone fluxes and non-stomatal ozone fluxes with temperature. Data are reported as daily average of the 2001–2006 period.

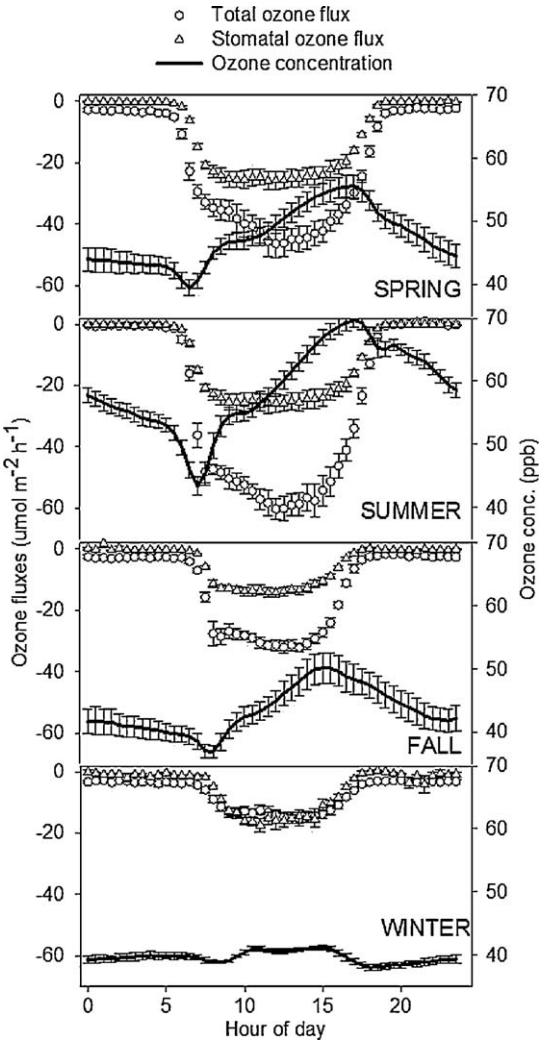

Fig. 5. Ozone concentration, total ozone flux and stomatal ozone flux reported for the four seasons and shown as hourly means and averaged for the years 2001–2006. Standard error is also reported ($n = 6$).

VPD induced stomatal closure during this period of higher atmospheric ozone concentration. In spring, SUM0 correlated better with $SUMFLUX_{sto}$ than $SUMFLUX_{nsto}$ ($r = 0.61$ and 0.52, respectively). During fall, the best correlation of SUM0 was with SUMFLUX and $SUMFLUX_{nsto}$ ($r = 0.48$). During winter, the correlations between SUM0 and both stomatal and non-stomatal fluxes were poor ($r = 0.38$ with $SUMFLUX_{sto}$ and 0.34 with $SUMFLUX_{nsto}$).

AOT40 was the second metric based on accumulated ozone concentration used in this study. The best interannual correlation between AOT40 calculated for the growing season and the equivalent accumulated fluxes was with $SUMFLUX_{sto}$ ($r = 0.35$), but still was not statistically significant ($P = 0.49$). Similar results were observed using the same correlation exercise in spring and summer. For these seasons the correlation between AOT40 and $SUMFLUX_{sto}$ were the highest ($r = 39$ and 0.62, respectively) but still statistically non-significant ($P = 0.44$ and 0.16, respectively).

4. Discussion

4.1. Stomatal and non-stomatal ozone sinks

Stomatal conductance and water evapotranspiration during the hottest summer days were not significantly depressed (Fig. 2D and E, Fig. 3C). This ecosystem's general tolerance to drought stress during summer periods was explained by Panek (2004) and Misson et al. (2005b) by the ability to conserve water through an increase in water use efficiency. The scarcity of summer rainfall events reduces the contribution of water soil evaporation to the total evaporated measured water flux so that the observed transpiration can be attributed mainly to the plants. Previous studies demonstrated that forest floor evapotranspiration typically contributes less than 10% of total latent heat flux during most of the growing season (Kelliher et al., 1992; Wilson et al., 2001).

High ozone concentrations occur at this site due to daytime upslope transport of polluted air from the Sacramento valley below and the interaction of NO_x in the polluted air with biogenic volatile organic compounds (mainly isoprene) emitted by the ecosystems between Sacramento and Blodgett Forest (Dillon et al., 2002; Dreyfus et al., 2002; Steiner et al., 2007). Daily ozone concentrations were above 60 ppb during the summer in response to high levels of light and temperature (days 172–264, Fig. 3A). The positive correlation ($R^2 = 0.76$) between temperature and ozone concentration (Fig. 4) is typical for this region (Day et al., 2007).

The average annual cumulative ozone flux over the 2001–2006 period was -6.7 ± 0.27 g m^{-2} yr^{-1} (Table 1). For 1999 Kurpius et al. (2002) reported a value of -6.1 g m^{-2} yr^{-1} which is well within the boundaries of our study period. The evidence that ozone stomatal flux (Fig. 3B) accounted for 56.7% of the total annual ozone flux (Table 1), but also that stomata were the main contributor to ozone fluxes during the winter period (average of 86.4%) suggests that during winter certain non-stomatal sinks were depressed (e.g. reactive BVOC emissions: monoterpenes, sesquiterpenes). The result that ozone deposition to non-stomatal surfaces is very limited (~23% during the year) agrees with previous research carried out by Kurpius and Goldstein (2003), in which stomatal fluxes were calculated from sap flow measurements. Non-stomatal ozone fluxes were much higher in the summer-fall period (around 55% of the total ozone flux), and were more related to temperatures ($R^2 = 0.54$) than the stomatal ozone fluxes ($R^2 = 0.30$). In the same ecosystem but at a younger developmental stage, Kurpius and Goldstein (2003) reported even higher values, ~64%. Similarly, Hogg et al. (2007) in a northern mixed hardwood forest found non-stomatal ozone fluxes responsible for 63% of the total fluxes. Even higher values (68.5%) were calculated by Gerosa et al. (2005) in a Mediterranean oak forest. In a sub-alpine forest ecosystem, Zeller and Nikolov (2000) calculated the non-stomatal ozone deposition to be 41% of the total flux over a whole year, and the non-stomatal uptake from scots pine shoots was found to be ~50% of the total ozone deposition by Altimir et al. (2004). These high levels of non-stomatal ozone fluxes during spring and summer suggest a strong influence of the temperature most likely through reactions of BVOCs with ozone in the gas phase. On the other hand, the ozone deposition on the leaf surfaces is also temperature-dependent. Cape et al. (2009) measured ozone uptake on different surfaces and consistently found an activation energy of ~30 kJ/mol. Using an Arrhenius-type equation with this activation energy a factor of 2.3 between winter and summer surface uptake should be expected (3 °C and 22 °C mean temperature were used respectively, Fig. 1A). However, we observed a much larger difference in non-stomatal ozone fluxes (factor of 3.8) between the two seasons (data not shown) which suggests that surface deposition is not the major contribution to the non-stomatal ozone flux.

During the year, ozone fluxes peaked at ≈day 200 (Fig. 3B), in contrast with the highest daily ozone concentrations recorded in August between days 210 and 240 (Fig. 3A). This difference in time between the peak in ozone flux and the maximum ozone concentration is likely due to a depressed stomatal conductance (Fig. 3C) in response to drought and moderately high temperatures (Fig. 1A) leading to high VPD (Fig. 1B). As mentioned above, certain years higher levels of precipitation and temperature occurred approximately in the month of November, thus leading to the increased average of conductance shown in Fig. 3C.

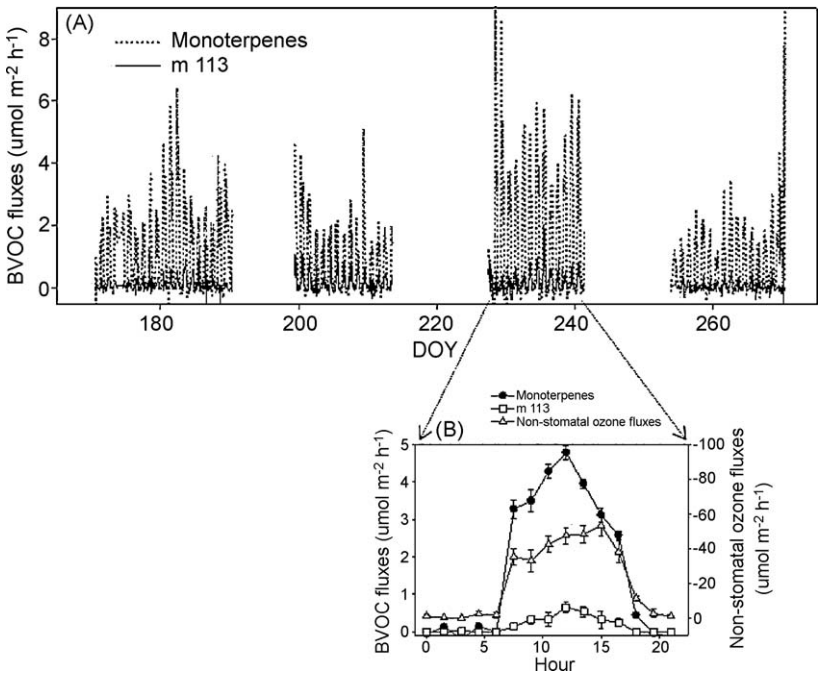

Fig. 6. Daily dynamics of monoterpene and oxidation product fluxes during four two-week periods (DOY 170–190, 199–213, 227–241, 253–270) in 2005 (panel A). Average of monoterpene fluxes, oxidation product fluxes detected on mass 113, and non-stomatal ozone fluxes during a 2-week period in summer 2005 (panel B). Standard error is also reported (n = 14).

Table 2
For each season of the years 2001–2006 we report: Pearson's correlation index (r), and P-value for the linear regression of SUM0 with accumulated total ozone flux (SUMFlux), accumulated stomatal ozone flux ($SUMFLUX_{sto}$) and accumulated non-stomatal ozone flux ($SUMFLUX_{nsto}$) based on hourly values.

Time period		SUM0 vs					
Season	Year	SUMFlux		$SUMFlux_{sto}$		$SUMFlux_{nsto}$	
		r	P-value	r	P-value	r	P-value
Spring	2001	0.69	***	0.67	***	0.7	***
	2002	0.64	***	0.67	***	0.32	**
	2003	0.56	***	0.71	***	0.51	***
	2004	0.43	***	0.28	*	0.64	***
	2005	0.68	***	0.76	***	0.49	***
	2006	0.49	***	0.58	***	0.48	***
	Mean	0.58 ± 0.04		0.61 ± 0.07		0.52 ± 0.04	
Summer	2001	0.18	*	0.29	**	0.49	***
	2002	0.23	*	0.5	***	0.36	**
	2003	0.38	**	n.s.	n.s.	0.7	***
	2004	0.44	***	0.16	n.s.	0.71	***
	2005	0.33	**	0.7	***	0.27	*
	2006	0.44	***	0.24	*	0.33	**
	Mean	0.33 ± 0.04		0.38 ± 0.08		0.47 ± 0.08	
Fall	2001	n.s	n.s.	n.s.	n.s.	n.s.	n.s.
	2002	0.54	***	0.46	***	0.42	******
	2003	0.49	***	0.24	*	0.52	***
	2004	0.33	**	n.s.	n.s.	0.41	***
	2005	0.56	***	0.44	**	0.59	***
	2006	n.s	n.s.	0.18	n.s.	n.s.	n.s.
	Mean	0.48 ± 0.04		0.38 ± 0.05		0.48 ± 0.03	
Winter	2001	0.25	**	n.s.	n.s.	n.s.	n.s.
	2002	0.33	**	0.21	*	0.33	**
	2003	0.41	***	0.37	**	0.37	**
	2004	0.47	***	0.38	****	0.53	***
	2005	0.41	***	0.7	***	0.23	*
	2006	0.17	n.s.	0.27	n.s.	0.26	*
	Mean	0.34 ± 0.04		0.38 ± 0.08		0.34 ± 0.04	

n.s. = not significant value where P-value >0.1. The correlations are based on the hourly values for which SUM0 was calculated. Values ± standard errors are shown.
* P-value <0.1.
** P-value <0.01.
*** P-value <0.001.

On a daily basis, the highest levels of ozone fluxes and the highest levels of ozone concentrations (Fig. 5) did not coincide: ozone fluxes peaked in the middle of the day, while ozone concentrations reached the highest levels in the late afternoon. For most summer days, the favourable period for plant physiology and stomatal aperture occurred before the maximum ozone concentrations, thus limiting the maximal potential ozone uptake by the plants but also avoiding the maximal potential detrimental effect of ozone. Similar dynamics were reported by Kurpius et al. (2002) in this ponderosa pine forest and by Mikkelsen et al. (2004) in a Norway spruce forest. This behaviour was similar in all seasons, but most pronounced in summer.

A drop in ozone concentration with a concurrent increase of ozone flux occurred in the early daylight hours. This "morning dip" effect could be attributed to the immediate light-induced stomatal opening. A factor contributing to the early morning ozone removal is that the air in the first morning hours is stably stratified (data not shown), and little vertical mixing occurs. In this regime of low turbulence, ozone is rapidly scavenged by the newly opened stomata which react to light and allow ozone entry and scavenging in the intercellular spaces. Additionally, fast ozone removal may have been caused by the reaction of ozone with NO produced by soils (Farmer and Cohen, 2008) over the night and accumulated under the canopy. Upon the initiation of turbulence ozone may enter the canopy oxidizing NO to NO_2 (Duyzer et al., 2004; Neyrinc et al., 2006). A third factor contributing to early morning ozone removal was a gas-phase reaction between BVOC and ozone in the shallow and stratified layer activated by the turbulence. Some BVOCs, sesquiterpenes in particular, have a fast reaction time with ozone (Atkinson, 1997), thus making possible ozone destruction on the order of few minutes after sunrise. In the early morning a high amount of BVOCs are available due to a nocturnal accumulation of BVOC in the stable below-canopy air layer (Holzinger et al., 2005), and emission of BVOC driven by light and temperature also becomes rapidly available (Lichtenthaler et al., 1997; Kesselmeier and Staudt, 1999). The ozone concentration returns to values exceeding the nocturnal concentrations in less than two hours after the "morning dip" (Fig. 5). As the day progresses, ozone concentrations continue to rise until reaching a maximum value around 4 pm.

On a multi-year basis, the partitioning between stomatal and non-stomatal ozone fluxes showed a predominance of the non-stomatal component in the dayhours, accounting for up to 65% of the total ozone flux (Fig. 5). This was reported by previous shorter term studies in the same ecosystem (Kurpius and Goldstein, 2003), in a Mediterranean oak ecosystem (Gerosa et al., 2005) and in a mixed hardwood forest (Hogg et al., 2007). *P. ponderosa* was recently shown to be a strong monoterpene and sesquiterpene emitter (Bouvier-Brown et al., 2007), and these BVOC emissions were found to be significantly dependent upon temperature and have short reaction time with ozone (from seconds to few minutes) likely contributing to ozone removal (Schade et al., 1999; Holzinger et al., 2007; Bouvier-Brown et al., 2009a). Our study is in agreement with previous studies at the same field site (Kurpius and Goldstein, 2003; Goldstein et al., 2004) in which BVOC emissions were found to be the main contributor to the non-stomatal sink of ozone through reactions in the gas-phase chemistry. The most recent studies (Bouvier-Brown et al., 2009b) carried out in the same pine ecosystem with a plant enclosure highlighted that a wide range of reactive sesquiterpenes (about 50% of the total BVOCs) are emitted and react with ozone before excaping the canopy, and the amount of ozone scavenged inside the canopy was quantified to be close to that calculated by Kurpius and Goldstein (2003). These studies support the idea that ozone is scavenged through reactions in the gas phase.

Holzinger et al. (2005) detected oxidation products in and above the canopy that were proposed to have been produced from BVOC plus ozone chemistry in the surface layer. In agreement with Holzinger's study, the flux of the mass 113 oxidation products was 12% of the total monoterpenes emission (Fig. 6A) with a diurnal cycle matching a combination of monoterpene emission and non-stomatal ozone fluxes (Fig. 6B). Oxidation products that are detected on other masses (not shown) could contribute significantly to the total emission. This data support our hypothesis of gas-phase reactions of ozone with organic compounds as the most plausible explanation for non-stomatal ozone loss at our site.

The emission of BVOC, differently from photosynthesis, is not inhibited under a moderate drought stress (Brilli et al., 2007), thus high rates of emission occur during partial stomatal closure as a response to dry conditions, and increase exponentially with temperature above the optimum for photosynthesis (Loreto and Sharkey, 1990). Heat and drought stress were found to depress the photosynthetic activity and increase BVOC emission in Mediterranean ecosystems (Rennenberg et al., 2006). These findings support our results showing that the non-stomatal ozone flux, which we mainly attribute to gas-phase reactions between ozone and BVOCs, was higher than the stomatal flux during the dry summer season. Our results may seem in contrast to the evidence that fall months were almost 10 °C colder than the summer months (Table 1), but with the highest non-stomatal contribution to the total ozone flux (Fig. 5). In the fall season however, the stomatal conductance was reduced due to limited water availability while BVOC emission was not suppressed (Fig. 3C).

BVOC may contribute to non-stomatal ozone uptake not only through reaction in the gas-phase chemistry in the canopy, but also inside the leaves. As previously noted (Velikova et al., 2005; Loreto and Fares, 2007), BVOCs may play an active role in removing ozone in the intercellular spaces. In this study, by using a formalism based on resistance analogies to calculate ozone fluxes we assume an intercellular ozone concentration equal to zero (Laisk et al., 1989), which thus takes into account the possible antioxidant action of BVOC or other antioxidants removing ozone from the intercellular spaces. A similar assumption is currently used in models for ozone risk assessment (Emberson et al., 2000).

4.2. Metrics for ozone risk assessment

Ozone metrics are often used to estimate the effective absorbed ozone dose for sensitive ecosystems, thus we use our observations here to assess the suitability of common metrics for ozone-risk assessment by comparing them to ozone fluxes. The correlations of a metric based on accumulated ozone concentrations (SUM0) with metrics based on accumulated total, stomatal and non-stomatal ozone fluxes were often low (Table 2), especially in summer which is a season of high photosynthetic activity and high ozone concentration (Fig. 3A). Low correlations between SUM0 and ozone fluxes were observed by Panek et al. (2002) in the same field site during the 1997 and 1998 growing seasons (R^2 = 0.36 and 0.38, respectively).

In summer, SUM0 correlated more strongly with the SUM-$FLUX_{nsto}$ than with SUMFLUX. This can be explained by the dependence of BVOC emissions and ozone formation on light and temperature which were highest during summer (Table 1). During this same period, the correlations of SUM0 with $SUMFLUX_{sto}$ were still poor because high temperatures and VPD moderately induced stomatal closure during this period of higher atmospheric ozone concentration. In spring, with fewer constraints to plant physiology and lower temperatures, SUM0 correlated better with SUM-$FLUX_{sto}$ than $SUMFLUX_{nsto}$. During fall, SUM0 correlated better with SUMFLUX and $SUMFLUX_{nsto}$, which suggests that ozone concentration and non-stomatal fluxes were influenced by similar

parameters even though daily temperature was decisively lower in fall than summer (13.6 °C vs 22.1 °C). Non-stomatal processes in the fall season (Table 1) still play a predominant role even if stomatal conductance is decreased due to lower physiological activity. This suggests that the parameters driving non-stomatal flux processes (e.g. deposition on surfaces, gas-phase chemistry reactions between ozone and BVOC) remained unchanged. The hypothesis that BVOC act as the main contributors to non-stomatal ozone fluxes during the fall season when temperatures are lower than summer, leads to the conclusion that temperature is not uniquely the driver of BVOC emission. The production of BVOC is known to continue even after a decrease of physiological activity (Lichtenthaler et al., 1997; Kesselmeier and Staudt, 1999), and partial stomatal closure, as found in laboratory experiment on drought stressed plants (Brilli et al., 2007). Future studies will need to clarify to what extent stomatal conductance controls BVOC emissions contributing to non-stomatal ozone uptake. Mechanical disturbance (Goldstein et al., 2004) and moisture (Schade et al., 1999) have also been shown to increase terpene emission at this site.

During winter, SUM0 poorly correlated with $SUMFLUX_{sto}$ and $SUMFLUX_{nsto}$. The low correlation with $SUMFLUX_{sto}$ could be due to stomatal closure even though there was considerable ozone concentration (between 20 and 55 ppb). The poor correlation of $SUMFLUX_{nsto}$ with SUM0 was mostly likely due to decreased BVOC emissions, which are constrained at low temperatures (the average daily temperature in winter was 5.9 °C). Of all the seasons, non-stomatal flux was the lowest in winter (14%, Table 1).

The second metrics of this study, AOT40, was calculated for the entire growing season. The best interannual correlation with the equivalent accumulated fluxes was with $SUMFLUX_{sto}$, but still was not statistically significant ($P = 0.49$). Similar results were observed using the same correlation exercise in spring and summer. The non-significance may be explained by the limited dataset (6 points, one per year) used to build the correlations and by the interannual variability.

In general, SUM0 better correlated with non-stomatal fluxes during the warm seasons because non-stomatal ozone fluxes driven by BVOC emissions were not as constrained by summer drought stress and because both ozone concentration and BVOC emissions increase with temperature. Our results which show that AOT40 and SUM0 do not correlate well with $SUMFLUX_{sto}$ during all times of physiological activity support the general consensus that exposure-based metrics are not the most suitable index for ozone-risk assessment (Matyssek et al., 2007). Although we did not have evidence of plant damage to be correlated with accumulated stomatal fluxes, we provide a quantification of interannual and seasonal ozone dose absorbed through stomata which may serve for future ozone-risk assessment purposes. Future studies should address identification of threshold levels for accumulated stomatal ozone fluxes for *P. ponderosa*, similarly to the research carried out on other tree species like Beech and Birch (Karlsson et al., 2004; UNECE, 2004).

A modelling approach (e.g. Emberson et al., 2000; Tuovinen et al., 2007; Tuovinen, 2009; Simpson et al., 2007) was not evaluated in this study, but represents a valid alternative to estimate stomatal ozone fluxes especially when a direct measure of water and ozone fluxes is not available at a specific location. The core of most of these models is a multiplicative algorithm to calculate stomatal conductance to ozone that takes into account several parameters such as the maximum stomatal conductance, light conditions, temperature, and vapour pressure deficit. This common approach investigates stomatal flux into leaves at the top of the canopy ("Big leaf concept"), and is less sensitive to non-stomatal processes removing ozone within the canopy such as the BVOC–ozone reactions described in this paper. The data collected during our 6 years of measurements could be useful for model parameterization, considering that a source of uncertainty for those models is often the estimation of the maximal stomatal conductance (Tuovinen et al., 2007), and could serve to calibrate canopy models introducing a resistance term representing BVOC reactions with ozone in canopy.

5. Conclusions

Six years of continuous measurements produced a robust dataset which allowed us to investigate the controls on ozone fluxes in a *P. ponderosa* ecosystem. We measured total ozone flux and separated it into stomatal and non-stomatal fluxes to assess the actual ozone flux into plants and to test exposure and flux-based metrics.

In agreement with previous research carried out on this conifer ecosystem at an earlier stage of development, we found that stomatal ozone uptake contributed less than non-stomatal uptake (which we attribute mainly to gas-phase reactions between ozone and BVOCs) to the total ozone flux during the growing seasons, indicating that less than half the deposited ozone enters through stomata and contributes to ozone damage. This is particularly interesting considering that ozone taken up through stomata is thought to be responsible for detrimental effects on vegetation. For the first time, we used PTR-MS to measure fluxes of BVOC oxidation products, and showed a diurnal cycle which matches a combination of terpene fluxes and non-stomatal ozone fluxes. In conclusion, the main finding of this study is that non-stomatal mechanisms are the dominant processes contributing to ozone removal, and this is likely happening in ecosystems which produce BVOC such as mono-terpenes and sesquiterpenes, two classes of terpenoids which rapidly react with ozone in the gas phase.

The predominance of non-stomatal sinks for ozone may be increased in the future if increases in temperatures occur. Higher temperatures will result in an increase of BVOC emission, thus increasing the magnitude of non-stomatal ozone sinks in BVOC-emitting ecosystems. Higher ozone concentrations in the future could also cause a depression in stomatal conductance which presumably leads to a decrease in ozone stomatal fluxes. We showed that non-stomatal ozone fluxes are the dominant process in the warm seasons, with plant physiology controlling BVOC emission in a lower extent than temperatures. In the future, we predict this seasonal difference could be even larger.

Another aim of our research was to test how well common metrics of accumulated ozone exposure (SUM0 and AOT40) correlate with total ozone flux, stomatal ozone flux ($SUMFLUX_{sto}$) and non-stomatal ozone flux ($SUMFLUX_{nsto}$). Measuring ozone concentration and calculating the metrics of accumulated ozone exposure is easier than measuring ozone fluxes, for which more sophisticated monitoring devices are required, and allows for a simpler standardization of sampling procedures and inter-comparison between different monitored sites. However, the poor correlation of SUM0 and AOT40 with $SUMFLUX_{sto}$ for this ponderosa pine ecosystem, in which summer drought is not usually a severe constraint for plant physiology, leads to the conclusion that metrics based on accumulated concentrations are poor predictor of ozone fluxes. In parallel, the correlation between SUM0 and total ozone flux or $SUMFLUX_{nsto}$ was higher, indicating that total and non-stomatal ozone fluxes are more tightly coupled to ozone exposure than is stomatal ozone uptake. This higher correlation between non-stomatal ozone fluxes and ozone concentration especially during summer was driven by the temperature-dependence of both BVOC emission which largely contribute to $SUMFLUX_{nsto}$ and ozone concentration.

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