Annual ozone deposition to a Sierra Nevada ponderosa pine plantation

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Abstract

Ozone concentration and ecosystem scale fluxes were measured continuously from June 1999 to June 2000 above a ponderosa pine plantation at Blodgett Forest, an Ameriflux site located ~ 75 km northeast of Sacramento, CA (1300 m). The ponderosa pine trees were most active during the summer but maintained a low level of activity during the fall, winter, and spring. Cumulative ozone flux for the year was 127 mmol m^{-2} with the contribution for each season being 37% for summer, 18% for fall, 15% for winter, and 30% for spring. The high levels of cumulative ozone deposition over non-summer seasons indicate that significant ozone damage may occur during times when ozone concentrations are not at their maximum. Ozone flux is dependent upon both ozone deposition velocity (O$_3$ V_d, how effective the ecosystem is at taking up ozone) and ambient ozone concentration but was found to be more closely related to O$_3$ V_d than to ozone concentration. The relationships between O$_3$ V_d (and therefore ozone flux) and the controlling climatic variables were dynamic over the year, changing mainly with water status and phenology. Understanding how the relationship between ozone deposition and its driving variables interact and change over the year is therefore critical to understanding potential ozone damage to vegetated ecosystems. Additionally, we found that commonly used ozone exposure metrics such as SUM0 (sum of all ozone exposure during the day) were poor predictors of ozone uptake (flux) unless periods of ecosystem stress, such as drought, were excluded.
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1. Introduction

Tropospheric ozone along with its photochemical precursors are transported downwind from Sacramento and the surrounding areas into the northern Sierra Nevada Mountains (Cahill et al., 1996). Ozone levels out of compliance with both federal and California ozone standards are routinely observed in this region (Bauer et al., 2000; Duckworth and Crowe, 1979). These high levels are of concern for ecosystem health. Ozone enters the plant through the stoma and causes the breakdown of chlorophyll and inhibits productivity through reduction in photosynthesis and stomatal conductance, premature leaf abscission, and decreases in leaf size (Arbaugh et al., 1998; Bytnerowicz, 1996; Sasek and Richardson, 1989; Taylor et al., 1982; Temple et al., 1993; Unsworth and Ormrod, 1982). Ponderosa pine (*Pinus ponderosa*) is one of the plants most susceptible to ozone damage in the Sierra Nevada Mountains (Miller and McBride, 1988).

High levels of ozone do not automatically result in plant damage: to impact plant processes ozone must first diffuse into the leaf through the stoma. Currently, evaluation of the impacts of ozone on tree health are

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based on ozone exposure (i.e., concentration) rather than actual dose (i.e., flux). The National Ambient Air Quality Standards characterizes ozone levels harmful to humans and vegetation in terms of ambient concentration. In addition, a suite of ozone metrics based on concentration have been developed to relate ozone concentration to effects of ozone on forest health in polluted areas. The most common metrics being employed are the daytime cumulative concentration indices with various threshold levels such as SUM0, SUM06, SUM08, W126, and AOT40 (for descriptions of these indices refer to Blankenship and Stefanski, 2001; Lee et al., 1988; Lefohn and Benedict, 1982; Legge et al., 1995; Musselman and Massman, 1999; Panek et al., 2002). Recent reviews of ozone metrics as applied to natural ecosystems indicate that these metrics often do not adequately characterize pollutant loading to vegetation (Emberson et al., 2000; Fuhrer, 2000; Legge et al., 1995; Massman et al., 2000; Musselman and Massman, 1999).

The poor performance of the ozone metrics in representing ozone uptake in some natural ecosystems stems from the fact that ozone uptake depends on both ozone concentration and stomatal conductance. Any factor that influences stomatal conductance but not ambient concentration (or vice versa) will cause the relationship between ozone concentration and flux to become decoupled (Larson and Vong, 1990; Taylor et al., 1988). The current metrics disregard physiological and environmental factors that control stomatal conductance such as phenology, soil moisture, vapor pressure deficit, air temperature, and sunlight. In cases where periods of high photosynthesis coincide with elevated ozone levels, such as crops and eastern US forests, the ozone metrics based on concentration may be an appropriate and convenient tool to monitor and assess impacts of ozone on plant health. However, in cases where stomatal conductance increases/decreases without concurrent changes in ozone concentration the ozone metrics based solely on concentration are likely to be inadequate. For example, Bauer et al. (2000) and Panek and Goldstein (2001) found that late-summer drought which causes lowered stomatal conductance in ponderosa pine trees in the northern Sierra Nevada Mountains can cause reduced ozone uptake regardless of high ozone concentration while Arbaugh et al. (1998) reported a similar finding for ponderosa pine trees in the southern Sierra Nevada Mountains. Panek et al. (2002) compared direct measurements of summertime ozone flux into a ponderosa pine plantation in the northern Sierra Nevada Mountains with the most common ozone metrics and found that SUM0 (defined as the sum of 14-h daytime ozone concentration) best corresponded to ozone uptake; however, only at times when the stomata were not limited by soil moisture.

Most previous studies on ozone deposition to vegetated ecosystems have focused on the summer months (e.g., Affre et al., 2000; Cieslik and Labatut, 1997; Hicks et al., 1989; Massman, 1993; Padro et al., 1991; Pederson et al., 1995) because that is when the highest ozone concentrations occur and this coincides with the growing season for most plants. Some work on winter ozone deposition (Padro et al., 1992; Pilegaard et al., 1995) and year-round ozone deposition (Mikkelsen et al., 2000; Munger et al., 1996; Pio and Feliciano, 1996; Wieser et al., 2000) has been done, but trends in annual ozone deposition to natural ecosystems remain largely unexplored. CO_2 flux measurements by Law et al. (2000) showed that ponderosa pine in eastern Oregon have the potential for active gas exchange between senescence and bud break: they reported that 50–70% (depending on year) of the annual carbon uptake occurred outside the growing season. The seasonality of pine physiological activity can be quite variable in regions with strong seasonality in weather. The manner in which ozone exposure coincides with plant activity level is therefore likely to be critical in determining total dose of ozone over the course of the year. Additionally, it has been recognized that plants can protect themselves from ozone damage primarily by preventing ozone uptake through stomatal closure or by detoxification of the ozone-generated free radicals by antioxidants in the apoplast. Phenology and environmental conditions have been found to affect both stomatal conductance (e.g., Baldocchi et al., 1987; Jarvis, 1976; Zeiger et al., 1987) and antioxidant levels in conifers (e.g., Anderson et al., 1992; Doulis et al., 1993; Esterbauer and Grill, 1978; Hauslauden et al., 1990; Madamanchi et al., 1991). Given that ozone uptake and defense systems are dynamic on a seasonal timescale, understanding year-round patterns in ozone uptake is critical in assessing impacts of ozone on forest health.

The goals of this paper are to: (1) investigate seasonal and diurnal patterns of ozone concentration, and ozone deposition velocity (O_3 V_d); (2) examine how ozone concentration and O_3 V_d combine to create the observed seasonality in ozone flux; and (3) evaluate the efficacy of the ozone metric SUM0 by examining its correlation with ozone flux year-round.

2. Methods and materials

Measurements were made from a 12 m tower located in a ponderosa pine plantation owned by Sierra Pacific Industries (located adjacent to Blodgett Forest Research Station) near Georgetown, California ($38°53'42.9''$N, $120°37'57.9''$W) at 1300 m elevation (Fig. 1). The forest upwind of the tower, comprising the sampled footprint, is a homogeneous canopy of trees dominated by ponderosa pine (*Pinus ponderosa*) with a leaf area index
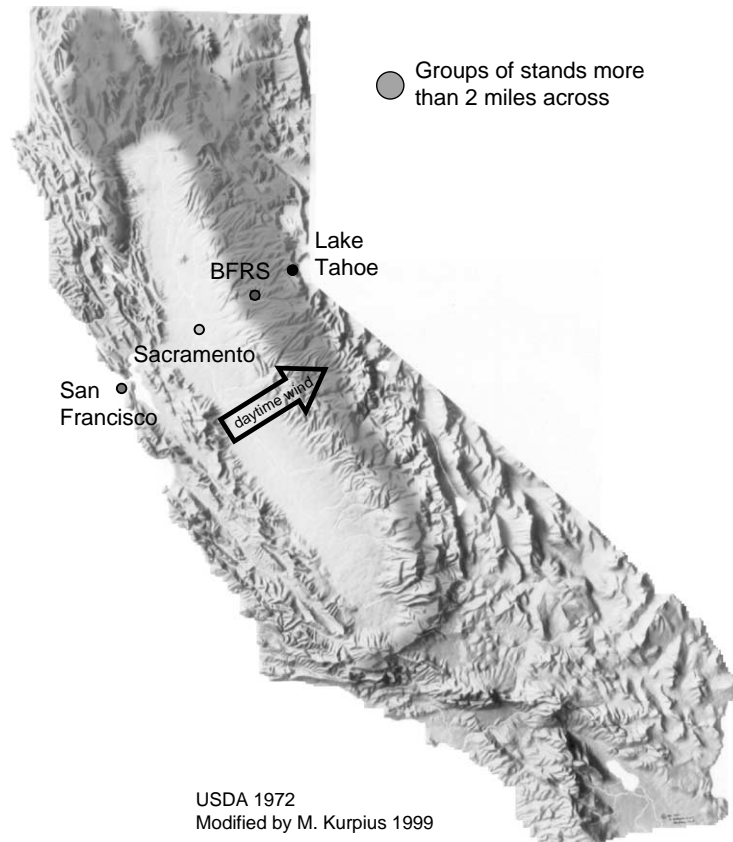
Fig. 1. Map of California showing Blodgett Forest Research Station (BFRS), daytime air mass trajectory around Sacramento, and distribution of ponderosa pine trees.

of 3.6. During the measurement period the trees were 7–8 yr old and ~ 5 m high. Following common management practices, shrubs were removed in June 1999. The region is characterized by a Mediterranean climate. Mean yearly precipitation for this area is 163 cm (75% as rain, 25% as snow) with the majority of precipitation falling between September and May and little or no rain in the summer.

Ozone concentration and ecosystem scale ozone flux, along with relevant environmental variables were measured continuously from June 1999 to June 2000. Ozone concentration was measured using a UV photometric ozone analyzer (Dasibi 1008-RS, Glendale CA). Ozone flux was determined as the half-hour average of the covariance between the instantaneous deviation from the mean vertical wind and instantaneous deviation from the mean ozone at 12 m above the ground. High frequency (10 Hz) wind data were obtained using a three-axis sonic anemometer (ATI Electronics Inc., Boulder, CO). High frequency (10 Hz) ozone data were obtained using a fast response chemiluminescent ozone analyzer built by Jim Womack (National Oceanic and Atmospheric Administration—Atmospheric Turbulence and Diffusion Division) based on a design by Hans Gusten (Gusten and Heinrich, 1996). The fast response ozone data was calibrated to the UV photometric ozone analyzer, which provided a stable reference. By convention, negative flux represents flux into the ecosystem. The environmental measured variables included photosynthetically active radiation (PAR) (Li-Cor Inc., Lincoln, NE), air temperature (Vaisala Inc., Woburn, MA), and soil moisture (Campbell Scientific Inc., Logan, UT). Vapor pressure deficit (VPD) was determined as the difference between saturated and measured vapor pressure at ambient air temperature above the plantation. Ozone deposition velocity (O_3 V_d), the rate at which ozone is deposited to the ecosystem, was calculated as ozone flux normalized for concentration. In an actively transpiring ecosystem, stomatal conductance is the most dynamic and influential component of O_3 V_d. For a complete list of measurements and additional descriptions of the field site and instrumentation see Bauer et al. (2000), Goldstein et al. (2000) and Schade and Goldstein (2001).

3. Results

3.1. Seasonal patterns in climate and ozone

Conditions for summer 1999 (days 153–243) were typical with very little rain (1.73 cm), low soil moisture, and high PAR, air temperature, and vapor pressure deficit (VPD) (Fig. 2). Ozone concentration was high for the duration of the summer (daytime mean concentrations of ~ 60–80 ppb) (Fig. 3). Ozone flux and ozone deposition velocity (O_3 V_d) were high for most of the summer with daytime mean values of -40 to $-65 \, \mu mol \, m^{-2} \, h^{-1}$ and 0.5–$0.8 \, cm \, s^{-1}$ for ozone flux and O_3 V_d, respectively. O_3 V_d decreased during shrub removal ($\sim$ days 165–185) causing a decrease in ozone flux but both returned to pre-shrub removal levels after.

The hot, dry conditions of the summer continued into fall 1999 (days 244–334): air temperature and VPD were high while soil moisture continued to decrease until day 300 (Fig. 2). There was no additional rain during this early period of the fall. Ozone concentration in the fall remained at high summer levels until day 290. In contrast, O_3 V_d began to drop at the beginning of the fall (day 243) causing ozone flux to drop. Ozone flux and O_3 V_d, dropped to $10 \, \mu mol \, m^{-2} \, h^{-1}$ and $0.2 \, cm \, s^{-1}$, respectively, by day 300 (Fig. 3). The rainy season began around day 300 resulting in a marked increase in soil moisture and a decrease in air temperature and VPD. Shortly after the onset of the rainy season, ozone concentration dropped by one-half while O_3 V_d and ozone flux increased more than two-fold. The ponderosa pine plantation received 21.4 cm rain between days 300 and 334.

Winter 2000 (days 335-60) was cold and wet with 79.3 cm of precipitation and low PAR (Fig. 2). While the daytime air temperature occasionally approached $0°C$, daytime freezing temperatures were rare. Daytime air temperatures were most often 5–$10°C$. During this period, ozone concentration became low and fairly constant (daytime mean of 20–40 ppb). Ozone flux was also low (daytime mean values of -10 to $-20 \, \mu mol \, m^{-2} \, h^{-1}$) while O_3 V_d was moderate and variable (daytime mean O_3 V_d of 0.2–$0.6 \, cm \, s^{-1}$) (Fig. 3).

Spring 2000 (days 61–151) had periodic rain that maintained moderately high soil moisture. The rainy periods were punctuated by sunny warm periods (Fig. 2) that had high PAR and moderate air temperatures. Ozone concentration increased slightly at the beginning of spring but remained moderate (40–60 ppb) all spring. O_3 V_d substantially increased from $\sim 0.3 \, cm \, s^{-1}$ at day 60 to $\sim 0.7 \, cm \, s^{-1}$ by day 140 (Fig. 3). Consequently, ozone flux increased from ~ -20 to $-40 \, \mu mol \, m^{-2} \, h^{-1}$ over this period.

Over the year, daytime mean ozone concentration was found to vary by a factor of two–three with the extremes occurring in mid summer and winter. O_3 V_d varied by a factor of three–four with the high periods occurring in late spring and late summer, when PAR was high but VPD low. The minimum O_3 V_d occurred in mid fall just before the onset of the rainy season. Ozone flux exhibited a roughly eight-fold change with the maximum occurring in mid summer and the minimum occurring in mid fall. Ozone flux was found to be more closely related to O_3 V_d ($r^2 = 0.64$) than to ozone concentration ($r^2 = 0.45$) for daytime mean values.

3.2. Seasonal patterns in O_3 V_d and VPD

Previous work at this site (Bauer et al., 2000) showed that VPD was the most important climatic driver of O_3 V_d on a day to day timescale during the summer but that the relationship between O_3 V_d and VPD was also dependent on other climatic variables and phenology. To examine how the relationship between O_3 V_d and VPD varied with changing weather conditions over the course of a year we calculated slope, intercept, and Pearson correlation coefficients for the relationship between daytime mean O_3 V_d and VPD for selected periods of the year (Table 1).

The first time period was in mid to late summer (days 196–236). This period was after the shrub removal but before fall shutdown and severe water stress. We found a strong ($r^2 = 0.79$) negative relationship between O_3 V_d and VPD. The second period (days 240–280) was in early to mid fall and represents the period of fall shutdown and very low soil moisture. During this period the relationship between O_3 V_d and VPD diminished, as indicated by an r^2 of 0.08. Following a period of cool days and the first rain, there was an increase in O_3 V_d. The days in late fall after this partial recovery (days 280–320) show that the correlation between O_3 V_d and VPD re-emerged but was not as strong as in mid summer ($r^2 = 0.68$). Days 20–60 were in the heart of the rainy and cold period that existed in mid to late winter and extended into early spring. O_3 V_d and VPD were positively related during this period but the strength of the relationship was very weak ($r^2 = 0.11$). Days 95–115 represent one of the intermittent dry periods of the spring. Based on CO_2 flux data, we determined that the trees were photosynthesizing at this time. During this time period, the relationship between O_3 V_d and VPD again became negative; however, the relationship was only moderately strong ($r^2 = 0.50$). The final time period was in late spring (days 125–155) when O_3 V_d showed a marked increase. The trees were approaching bud break during this period and did not show a relationship with O_3 V_d ($r^2 = 0.09$).

3.3. Diurnal patterns

The diurnal patterns of ozone concentration showed a morning dip in concentration before sunrise followed by
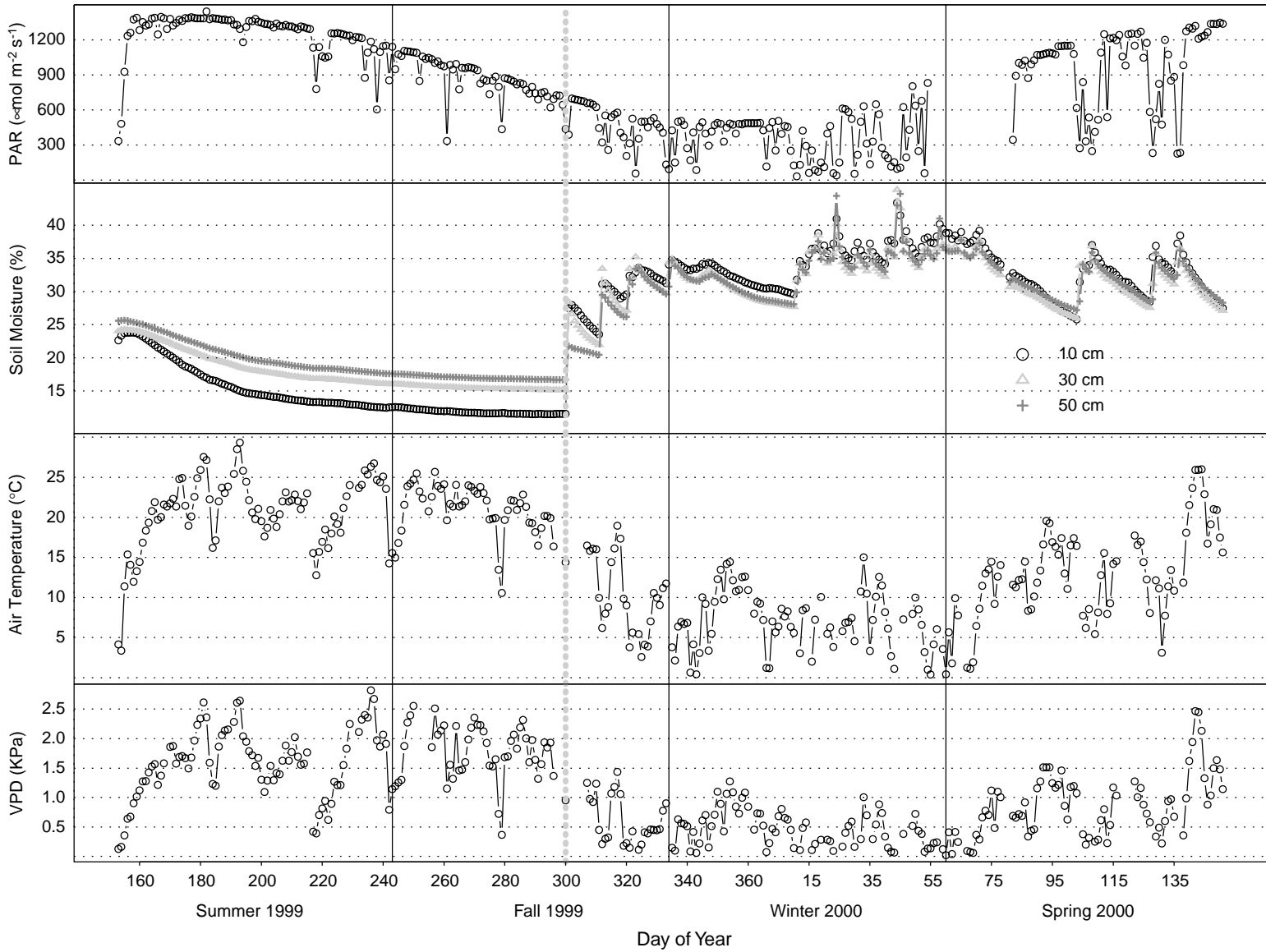
Fig. 2. Daytime (hours 800–1800) mean climatic variables. Dotted vertical line represents the onset of the rainy season.
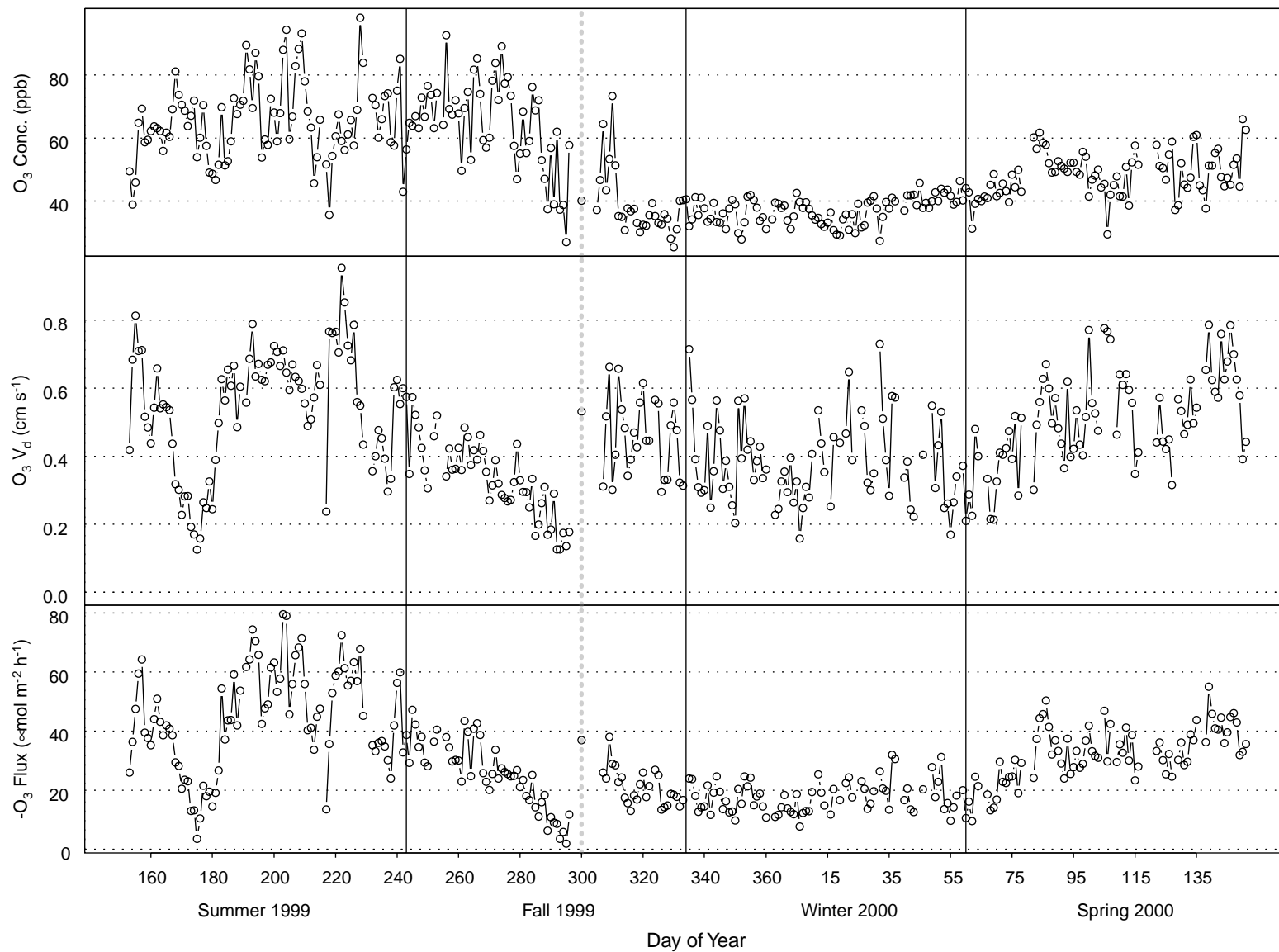
Fig. 3. Daytime (800–1800) mean ozone concentration, flux, and deposition velocity. Dotted vertical line represents the onset of the rainy season. Note that negative flux represents flux into the ecosystem.

Table 1
Slope, intercept, and squared Pearson coefficient (r^2) for the relationship between O_3 V_d and VPD at selected times of the study period

Time period	Slope	Intercept	r^2
Mid–late summer (days 196–236)	−0.22	0.97	0.79
Early–mid fall (days 240–280)	−0.05	0.50	0.08
Late fall (days 280–320)	−0.21	0.62	0.68
Winter and early spring: cold, rain periods (days 20–60)	0.20	0.26	0.11
Mid spring: dry period (days 95–115)	−0.22	0.74	0.50
Late spring: near bud break (days 125–155)	0.06	0.50	0.10

Fig. 4. Seasonal patterns of diurnal ozone concentration deposition velocity (O_3 V_d) and flux.

an increase to an afternoon high (Fig. 4). This pattern was pronounced in summer, fall, and spring while the winter ozone concentration showed little change over the course of the day. The overall magnitude of ozone concentration was highest in the summer followed by fall, then spring, and then winter. The diurnal patterns in ozone concentration were strongly correlated with the diurnal patterns of air temperature ($r^2 = 0.82$). The diurnal pattern of O_3 V_d had a morning spike that was apparent in all seasons, with spring having the most pronounced spike. In summer, fall, and spring O_3 V_d decreased after noon. In winter O_3 V_d remained steady and even increased slightly in the afternoon before decreasing with PAR to low nighttime values. O_3 V_d was slightly higher in summer than spring and both seasons were substantially higher than in fall and winter. The seasonal diurnal patterns were most closely related to PAR ($r^2 = 0.86$). Ozone flux increased rapidly in the morning, remained relatively constant through the midday, and then decreased in late afternoon. Ozone flux was highest in summer followed by spring, then fall, then winter. The seasonal diurnal patterns of ozone flux were more closely related to O_3 V_d ($r^2 = 0.94$) than to ozone concentration ($r^2 = 0.15$).

3.4. SUM0 and ozone flux

SUM0 was calculated as the sum of the 14-h daytime (0600–2000 PST) ozone concentration. Ozone flux ($\mu mol\,m^{-2}$) was summed for the same hours as SUM0

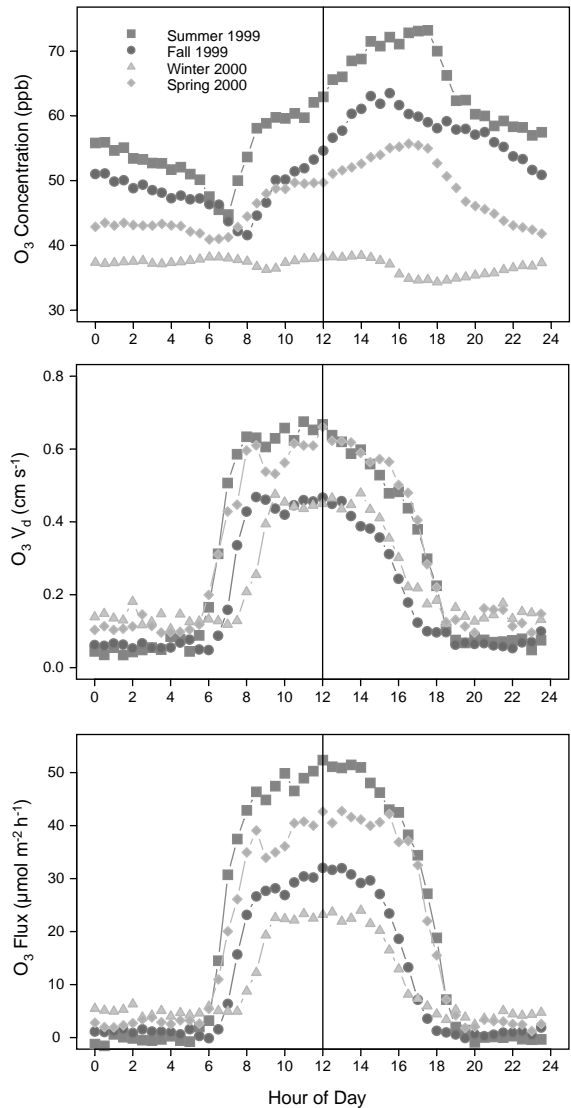and regressed against SUM0 (ppb h) (Fig. 5). The daily summed data for the year show that there was a relationship between ozone flux and SUM0; however, the relationship was not strong ($r^2 = 0.36$) when all the data except the period of shrub removal were included. The strength of the relationship between SUM0 and ozone flux for the year substantially improved when data from the late summer/early fall period—the period when stomatal aperture was limited by drought stress—were also removed ($r^2 = 0.67$). This relationship was much weaker for each individual season: $r^2 = 0.22$ for summer 1999, $r^2 = 0.31$ for fall 1999, $r^2 = 0.001$ for winter 2000, and $r^2 = 0.49$ for spring 2000.
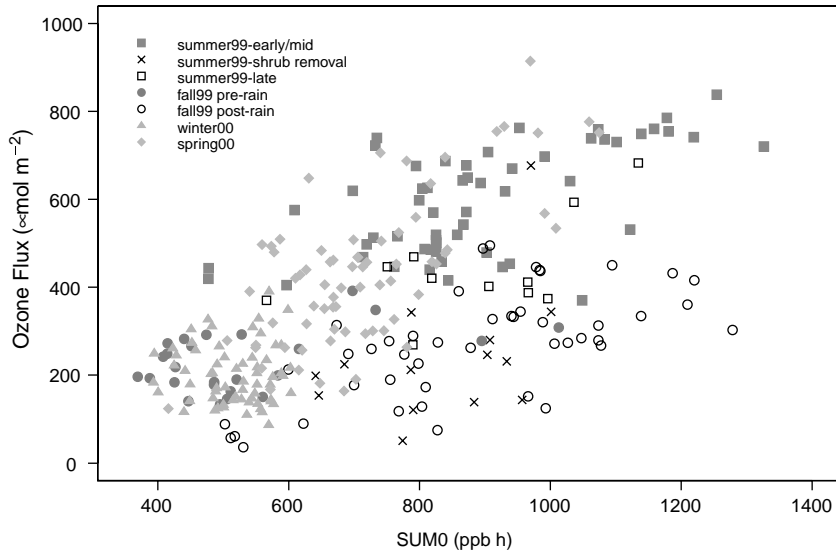
Fig. 5. Daily (14 h) summed ozone flux versus daily summed ozone concentration (SUM0).

3.5. Total ozone flux

The highest ozone deposition per season occurred during the summer, comprising 37% of the yearly daytime ozone flux (Table 2). While summer had the highest deposition for any single season, the majority of ozone deposition (63%) occurred outside the summer months during fall, winter, and spring.

4. Discussion

Ozone flux to an ecosystem depends on both ozone concentration and capacity for uptake by the ecosystem (i.e., O_3 V_d). Here, we examined the relative importance of ozone concentration and O_3 V_d, along with their driving variables, in determining ozone flux at both the seasonal and diurnal timescale. In light of the dual dependence of ozone uptake on concentration and deposition velocity we also discuss the appropriateness of using concentration based metrics to protect tree health.

4.1. Seasonal patterns

Ozone concentration and O_3 V_d had distinct seasonal patterns as dictated by their driving variables. Ozone concentration was lowest in the winter and highest in the summer, due to the dependence of ozone production on chemical precursors, sunlight (Haagen-Smit, 1952) and air temperature (Sillman and Samson, 1995). The two periods of highest O_3 V_d occurred in late spring and late summer when conditions of high PAR coincided with low VPD. The lowest O_3 V_d occurred when drought

Table 2
Cumulative ozone flux to ponderosa pine plantation

Time period	Flux (mmol m^{-2})	Percent (%)
Summer 1999 (days 153–243)	47.3	37
Fall 1999 (days 244–334)	22.3	18
Winter 2000 (days 335–60)	19.0	15
Spring 2000 (days 61–151)	38.1	30
Total	126.8	—

stress caused stomatal closure in late summer and early fall. Ozone flux is directly related to both ozone concentration and O_3 V_d so that increases in ozone concentration or O_3 V_d generally result in higher ozone flux. However, due to the dual dependence of ozone flux on ozone concentration and O_3 V_d, the highest ozone fluxes did not occur during the periods of highest ozone concentration or O_3 V_d but rather when ozone concentration and O_3 V_d were both moderate. This happened because the highest levels of ozone concentration occurred when the air temperature was very high. High air temperatures are accompanied by high VPD which caused stomatal closure and hence low O_3 V_d. Conversely, high O_3 V_d occurred when VPD was low and so air temperature and ozone concentration were also low.

Understanding how the meteorology and phenology combine to affect year-round ozone flux is critical to

assessing the potential effects of ozone on vegetation. However, it is implausible to directly measure ozone flux at numerous locations throughout the world. We propose instead to couple the extensive ozone concentration monitoring network with model estimates of stomatal conductance to determine ozone flux at broader spatial scales. Year-round direct measurements at selected locations would have to be integral to this scheme in order to test models, especially in sensitive ecosystems.

4.2. Controls on O_3 V_d

Day to day and seasonal changes in ozone flux were more closely related to O_3 V_d than to ozone concentration. Similar finding have been reported at the ecosystem scale by Wieser et al. (2000) and Mikkelsen et al. (2000) on Norway spruce and cembran pine. Therefore, the factors that control O_3 V_d (PAR, VPD, air temperature, soil moisture, and phenology) should have a greater effect on ozone flux than the factors that control ozone concentration (hydroxyl radical, hydrocarbons, oxides of nitrogen, light, and air temperature). We found that the relationships between O_3 V_d (and therefore ozone flux) and the climatic variables were dynamic over the year, changing mainly with water status and phenology. The ecosystem was most effective at taking up ozone (i.e., had the highest O_3 V_d), under conditions of moderate to high PAR, soil moisture greater than 12–13%, low VPD, and during periods of high physiological activity. Air temperature was also an important climatic variable in defining the period of peak O_3 V_d because it influences budbreak and therefore photosynthetic rates for the trees in late spring. The highest O_3 V_d was observed in late spring through mid summer as a result of the combination of these factors.

The largest decrease observed in O_3 V_d during this measurement period occurred in the beginning of fall when low soil moisture, low PAR, and senescence all occur. The low O_3 V_d during that period was mostly the result of soil moisture levels getting below a critical threshold ($\sim$12–13% in the top 10–20 cm) when the trees shut their stomata to conserve water (see Bauer et al., 2000 for additional comment on this threshold). O_3 V_d increased after the rain at day 300 but did not return to late spring and summer values indicating that phenology (fall senescence) and/or decreasing PAR also caused decreasing O_3 V_d.

While PAR, soil moisture and air temperature were critical climatic variables in defining the peak period of O_3 V_d, it was VPD that was most important in determining the day to day variability in O_3 V_d. This has previously been observed at this site during summer (Bauer et al., 2000); however, the variability of this relationship throughout the year has not previously been reported. O_3 V_d was closely correlated to VPD on a daily timescale during dry periods of active photosynthesizing; however, drought, cold and rainy weather, and phenology (senescence and budbreak) caused O_3 V_d to be relatively unresponsive to changes in VPD. Although the relationship between O_3 V_d and VPD was most often negative, we observed a positive correlation in winter to early spring, and late spring. With near-freezing temperatures in winter and early spring, it is plausible that increases in air temperature would result in both increases in VPD and in tree physiological activity, so that the weak positive correlation we observed during the winter and early spring was really a response to increasing temperature rather than increasing VPD. This agrees with results of Wieser et al. (2000) who found a significant relationship between maximum stomatal conductance and the previous nights minimum temperature.

Stomatal deposition is generally believed to be the most dynamic ozone sink and the one that controls the diurnal and seasonal patterns (c.f., Wieser et al., 2000); however, deposition to surfaces and chemical reactions, mainly NO and hydrocarbons, probably play some role in total ozone deposition at this site. For example, there is often a pulse in NO emission from soil (see Pilegaard et al., 1995) and a pulse in hydrocarbon emissions (Schade and Goldstein, 2001; Schade et al., 1999) after rain events following a drought. Reaction with NO and hydrocarbons could account for some of the increase in ozone flux after the rain event around day 300. In addition to this pulsing, the biogenic emission of NO and hydrocarbons is exponential with temperature and therefore, could also contribute to the relationship between ozone flux and temperature. Ozone deposition to surfaces is generally small (-2–$-10\,\mu mol\,m^{-2}\,h^{-1}$) and constant (see review by Massman, 1996) and so does not likely contribute to the observed ozone patterns.

4.3. Diurnal patterns

The diurnal patterns in ozone concentration were strongly correlated with the diurnal patterns of air temperature. Ozone production rates are positively correlated with air temperature (e.g., Sillman and Samson, 1995) primarily due to the effect of temperature on emissions of chemical precursors to ozone and their reaction rates in the atmosphere. The diurnal pattern of ozone concentration deviated from that of air temperature in the morning and in the afternoon. The morning decrease in ozone concentration was due to trees becoming active after sunrise and taking up ozone when the air was stably stratified with little vertical or horizontal mixing. The late afternoon rise in ozone concentration coincides with the transport time of ozone and its chemical precursors from the valley below to the mountains (Dillon et al., 2002).

The diurnal pattern of O_3 V_d was markedly different from concentration. A morning spike in O_3 V_d was apparent in all seasons, with spring having the most pronounced spike. The morning peak in O_3 V_d was also seen in canopy conductance data and is likely due to a rapid opening of stomata to their maximum aperture for the day when light levels are high enough to cause the stomata to open and when the water status is at its most favorable. In summer, fall, and spring O_3 V_d decreased after noon. In winter O_3 V_d remained steady and even increased slightly in the afternoon before decreasing with PAR to low nighttime values. O_3 V_d was slightly higher in summer than spring and was substantially lower in fall and winter. CO_2 flux data at this site show that the trees were most active during the spring and summer, but that photosynthesis occurred year-round indicating that the trees were active year-round. The seasonal diurnal patterns were most closely related to PAR with effects of VPD superimposed (e.g., morning spike and afternoon decrease).

Ozone flux had diurnal patterns with features from both ozone concentration and O_3 V_d. The diurnal pattern of ozone flux showed a rapid morning increase driven by O_3 V_d. However, rather than decreasing after noon as O_3 V_d did, ozone flux remained relatively constant through the midday in all seasons due to afternoon increases in ozone concentration. Ozone flux decreased with O_3 V_d in late afternoon. Similarly, Mikkelsen et al. (2000) reported that high O_3 V_d in the morning and high ozone concentration in the afternoon resulted in an equal ozone flux over the day for an evergreen forest in Denmark. The diurnal patterns of ozone flux were more closely tied to O_3 V_d than to ozone concentration, resulting in a decoupling of ozone concentration and ozone flux in early morning and afternoon (see also Bauer et al., 2000). Due to high O_3 V_d in the morning, ozone flux was highest in the morning when ozone concentration was low to moderate. Late afternoon decoupling of ozone concentration and flux occurred only in summer. During this summer afternoon decoupling, ozone flux was decreasing when ozone concentration was reaching its highest level. For fall, winter and spring the maximum ozone concentrations occurred while ozone flux was still high.

4.4. Implications for forest health

Ozone exposure, most often represented as daytime (14 h) summed concentration, is the metric most commonly used to assess potential harm to vegetation, even though uptake (i.e., flux) is the more biologically relevant measure. Therefore, it is important to know how representative ozone exposure indices such as SUM0 are of ozone flux. We found that SUM0 was a poor predictor of ozone flux when all the data were used: SUM0 explained 36% of the variability in ozone

deposition. When the data from the late summer/early fall drought period were removed, SUM0 explained 67% of the variability in ozone flux. Our findings suggest that ozone exposure could be used with moderate success to assess potential harm to trees if the phenological and climatic conditions that cause decoupling between ozone concentration and flux are accounted for. However, this means that an understanding of changes in stomatal conductance (or O_3 V_d) must accompany use of the ozone metrics. Moreover, the relationships between SUM0 and ozone flux for each individual season were poor, thus it is important to have year-round data to relate ozone exposure to ozone flux.

The SUM0 metric is based on the premise that total ozone dose during the day is more important to tree health than short-term, high doses of ozone. If it is the acute high doses that determine damage (Musselman et al., 1983) then it is critical to understand the hourly coupling of ozone concentration and ozone flux. For example, in our case it would be necessary to consider late afternoon coupling between ozone concentration and flux to determine if high levels of late afternoon ozone would be potentially harmful. Further, use of the SUM06 or SUM08 metrics (defined as the sum of the 14-h daytime ozone concentration exceeding 60 and 80 ppb, respectively) would be inappropriate if the periods of high ozone concentrations did not coincide with high ozone fluxes. The afternoon decoupling between ozone concentration and ozone flux may explain the poor performance of the SUM06 and SUM08 metrics in relating to ozone uptake at this site reported by Panek et al. (2002). For an extensive review of how the wider suite of ozone metrics performed at our site refer to Panek et al. (2002).

Most studies on ozone deposition focus on the summer months because that is when ozone concentration and plant photosynthesis are typically the highest. This work shows that ozone deposition during summer months made up only 37% of annual ozone deposition while deposition during fall, winter, and spring accounted for 63% of annual ozone deposition. In areas with higher summer drought stress and/or warmer winters, such as that in Southern California, we would expect a smaller proportion of seasonal ozone uptake to occur during summer. Given the higher levels of ozone in the southern Sierra Nevada, the timing of peak physiological activity and peak ozone concentrations is critical.

Given the expected seasonality of ozone uptake, it is interesting to note that damage to needles in the Sierra Nevada Mountains is generally observed in late summer, when drought stress should be limiting ozone uptake. There are a number of possible reasons for the decoupling between the timing of maximum ozone uptake and observed damage. One possibility is that drought stress exacerbates ozone stress. Another

possibility is that high levels of ozone prior to the onset of drought could cause damage to guard cells and the loss of stomatal control. This would result in high uptake of ozone even when the trees are drought stressed. It is also possible that drought and reduced carbon uptake due to stomatal closure could impair the defense systems. Musselman and Massman (1999) propose that plants may be more susceptible to ozone damage during periods of low metabolic activity due to lowered defense systems. Antioxidants are one of the most important defense mechanisms for a plant and have pronounced seasonal changes in conifer needles (Anderson et al., 1992; Doulis et al., 1993; Esterbauer and Grill, 1978; Hauslauden et al., 1990; Madamanchi et al., 1991). If the trees cannot keep up with the antioxidative demand, as may occur during drought-stressed periods, damage will occur.

Even though damage is not visible during winter, this period represents a potentially vulnerable time. Antioxidant levels have been found to significantly increase at the dormancy induction period, but it is unclear whether the antioxidant pools can be maintained through the winter due to lowered metabolism of dormant trees. For example, Oquist et al. (1978) reported that the antioxidant reserves for the winter were not sufficient to provide protection from photo-oxidation injury in the late winter and early spring in Scots pine growing in northern Sweden. Unless the reserves are high enough to deal with all potential oxidation damage over the dormant period, or the trees can replenish pools during the winter, we suggest that moderate levels of ozone could be more harmful in the non-summer months than higher levels in the summer.

5. Conclusion

Nearly two-thirds of the total annual ozone deposition occurred during non-summer months indicating that significant ozone damage may be occurring when ozone damage is not at its maximum. Both ozone concentration and O_3 V_d were important in driving the seasonal patterns in ozone flux but ozone flux was more closely related to O_3 V_d. Further, the relationships between O_3 V_d (and therefore ozone flux) and the climatic variables driving plant physiology were not static over the year, changing mainly with water status and phenology. Understanding how climate and phenology interact to change the efficiency of ozone uptake by an ecosystem is therefore a key step in improving models of ozone deposition. The transitions between the rainy and dry seasons were not only important in driving patterns in O_3 V_d through climate and phenology, but also greatly affected ozone concentration. Climate change could have a large impact on the timing of these transitions, thus altering ambient ozone concentration

and deposition patterns. Finally, we found the ozone index, SUM0, to be a poor predictor of ozone uptake because major changes in the ecosystems ability to take up ozone, such as drought or budbreak, are not accounted for. Modeling O_3 V_d and combining this information with ozone exposure provides a promising way to improve the ozone exposure indices for natural ecosystems.

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