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Key Points:
- Stomatal and cuticular deposition are inferred as drivers of day-to-day variability in deposition velocity
- Higher stomatal uptake increases deposition velocity on rainy days
- Observed interannual variability at Harvard Forest may reflect enhanced ozone deposition to dry soil

Supporting Information:
- Supporting Information S1

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Spatiotemporal Controls on Observed Daytime Ozone Deposition Velocity Over Northeastern U.S. Forests During Summer

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Abstract Spatiotemporal variability in ozone dry deposition is often overlooked despite its implications for interpreting and modeling tropospheric ozone concentrations accurately. Understanding the influences of stomatal versus nonstomatal deposition processes on ozone deposition velocity is important for attributing observed changes in the ozone depositional sink and associated damage to ecosystems. Here, we aim to identify the stomatal versus nonstomatal deposition processes driving observed variability in ozone deposition velocity over the northeastern United States during June–September. We use ozone eddy covariance measurements from Harvard Forest in Massachusetts, which span a decade, and from Kane Experimental Forest in Pennsylvania and Sand Flats State Forest in New York, which span one growing season each, along with observation-driven modeling. Using a cumulative precipitation indicator of soil wetness, we infer that high soil uptake during dry years and low soil uptake during wet years may contribute to the twofold interannual variability in ozone deposition velocity at Harvard Forest. We link stomatal deposition and humidity to variability in ozone deposition velocity on daily timescales. The humidity dependence may reflect higher uptake by leaf cuticles under humid conditions, noted in previous work. Previous work also suggests that uptake by leaf cuticles may be enhanced after rain, but we find that increases in ozone deposition velocity on rainy days are instead mostly associated with increases in stomatal conductance. Our analysis highlights a need for constraints on subseasonal variability in ozone dry deposition to soil and fast in-canopy chemistry during ecosystem stress.

1. Introduction

Tropospheric ozone is a potent greenhouse gas and an air pollutant harmful to humans and vegetation. It is also the primary source of the hydroxyl radical, which determines how long other air pollutants and reactive greenhouse gases stay in the atmosphere and regulates formation of some aerosols. Attributing variability and trends in tropospheric ozone concentrations requires quantifying both sources and sinks. The global models used to project atmospheric chemistry show that ozone dry deposition, which occurs when the gas is removed by the Earth's surface through surface-mediated reactions, is about 20% of global annual tropospheric ozone loss (Stevenson et al., 2006; Wild, 2007; Young et al., 2013). However, ozone dry deposition estimates vary by a factor of 2–3 across models (Hardacre et al., 2015; Wu et al., 2018), and a widely used ozone dry deposition parameterization does not simulate the strong observed variability in this sink (Clifton et al., 2017; Silva & Heald, 2018). Closer to the surface (i.e., the mixed layer), dry deposition is 30–95% of afternoon ozone loss over the United States (Fiore et al., 2002), implying that this sink may be an important control on ozone pollution. Earlier work has indeed shown a strong sensitivity of simulated ground-level ozone concentrations to ozone dry deposition over the northeastern United States (Val Martin et al., 2014; Walker, 2014), our region of study.

Ozone dry deposition to land occurs when the gas diffuses into pores on leaves (stomata) and reacts internally or when ozone is destroyed on other surfaces (*nonstomatal* pathways). Ozone uptake by stomata can be injurious to plants. On average, plant physiology observations show that chronic ozone exposure decreases stomatal conductance by 11% and photosynthesis by 21% (Lombardozzi et al., 2013). Ozone damage to plants impacts crop yields (Feng et al., 2008; Mauzerall & Wang, 2001; McGrath et al., 2015;

Morgan et al., 2003), local-to-global carbon and water cycling (Lombardozzi et al., 2015; Sun et al., 2012), and climate (Li et al., 2016; Sitch et al., 2007) and exacerbates ground-level ozone smog (Li et al., 2016; Sadiq et al., 2017).

Important nonstomatal deposition pathways over vegetation include surface-mediated chemical destruction on soil and leaf cuticles. Cuticular uptake occurs when ozone reacts with compounds on the leaf surface (Potier et al., 2017; Sun, Moravek, Trebs, et al., 2016). Water films from dew and rain may enhance cuticular uptake, but there is variability in the response to wetness observed in the field and laboratory (Altimir et al., 2006; Cape et al., 2009; Fuentes et al., 1992; Grantz et al., 1995, 1997; Lamaud et al., 2002; Massman, 2004; Pöschl & Shiraiwa, 2015; Potier et al., 2015; Turnipseed et al., 2009; Zhang et al., 2002). Previous work suggests that ozone dry deposition to rain-wet leaves may be low because rain cleanses the leaf surface of substances reactive with ozone (Finkelstein et al., 2000; Potier et al., 2017); this may explain some of the observed variability in the response to wetness. Microscopic water films that form when hygroscopic particles on leaf cuticles promote leaf-level increases in moisture may also enhance cuticular deposition (Burkhardt & Hunsche, 2013; Sun, Moravek, Trebs, et al., 2016). Most commonly, soil uptake of ozone is considered to occur through reaction with double carbon bonds in soil organic matter (Fowler et al., 2009; Wesely & Hicks, 2000), and there is strong evidence that ozone dry deposition to soil is inhibited by wetness (Bassin et al., 2004; Fares et al., 2014; Fumagalli et al., 2016; Massman, 2004; Sorimachi & Sakamoto, 2007; Stella et al., 2011), likely because moisture slows diffusion of ozone through soil pore spaces.

Laboratory and field measurements that isolate nonstomatal pathways advance fundamental process-level understanding (Cape et al., 2009; Fares et al., 2014; Fuentes & Gillespie, 1992; Fumagalli et al., 2016; Potier et al., 2017; von der Heyden, et al., 2016; Sun, Moravek, Trebs, et al., 2016) but are limited in constraining the relative importance of a specific deposition pathway at the ecosystem scale (i.e., what is measured through eddy covariance [EC] above the canopy). Interpreting ozone EC measurements relies on observation-driven modeling for resistances to turbulence, molecular diffusion, and individual deposition pathways (Altimir et al., 2006; Clifton et al., 2017; Lamaud et al., 2009; Launiainen et al., 2013; Rannik et al., 2012). Complicating matters, the observed ozone flux derived from EC measurements can include contributions from chemical destruction of ozone by nitrogen oxide (NO) and highly reactive biogenic volatile organic compounds (BVOCs) in the canopy air space (Dorsey et al., 2004; Goldstein et al., 2004). At vegetated observational sites worldwide, stomatal deposition is only 40–60% of the total deposition on average (Fowler et al., 2009), suggesting that in-canopy ambient chemistry (an *effective* deposition pathway) and/or nonstomatal deposition processes are important. Accurately partitioning ozone dry deposition by process is relevant not only for improving understanding of dry deposition and its impacts on vegetation but also for estimating secondary organic aerosol precursors that form when ozone reacts with BVOCs in the canopy air space (Holzinger et al., 2005; Kurpius & Goldstein, 2003; Wolfe et al., 2011).

Some recent studies suggest that stomatal deposition is an important control on day-to-day variability in surface ozone concentrations, including during extreme pollution episodes, as plants respond to moisture availability (Kavassalis & Murphy, 2017; Lin et al., 2017). However, unambiguous attribution of variations in observed ozone pollution is challenging due to individual depositional processes potentially having similar or offsetting relationships with meteorology and/or biophysics. For example, on hourly to seasonal timescales, effective nonstomatal deposition pathways may change with some of the same environmental conditions that influence stomatal conductance, such as air temperature or solar radiation (Coe et al., 1995; Coyle et al., 2009; Fowler et al., 2001; Fumagalli et al., 2016; Hogg et al., 2007; Rondón et al., 1993), soil moisture (Fumagalli et al., 2016; Massman, 2004), and humidity (Stella et al., 2011; Sun, Moravek, Trebs, et al., 2016; Zhang et al., 2002). Identifying the processes driving variability in the total observed ozone dry deposition through process modeling may bridge this gap and inform mechanistic modeling of surface ozone concentrations.

Here, we examine ozone deposition velocity (v_d), obtained by dividing the ozone EC flux by the ozone concentration, at forests in the northeastern United States. We choose to examine v_d because (unlike the ozone flux) it is independent of variations in ozone concentrations and thus provides more insight into the underlying mechanisms controlling ozone dry deposition. We use ozone EC flux observations from 1990 to 2000 at Harvard Forest (central Massachusetts), the only eastern U.S. long-term monitoring site. We aim to identify which depositional processes control the observed variability in v_d, recognizing that the dominant process

may vary in space and time. In particular, we consider the roles that stomatal, cuticular, and soil deposition, as well as fast in-canopy chemistry, play on observed variability in v_d on daily and interannual timescales. We also use ozone EC flux observations from 1997 and 1998 at Kane Experimental Forest (northwestern Pennsylvania) and Sand Flats State Forest (upstate New York), respectively, in order to assess regional consistency in v_d variability and identify any limitations in our understanding of variation based solely on Harvard Forest data. Our focus is daytime (9 am to 4 pm) during summer (June–September) when both surface ozone concentrations and v_d are seasonally maximum over the northeastern United States.

2. Methods

2.1. Observations at Harvard Forest

Harvard Forest is a long-term ecological measurement site within a deciduous forest in central Massachusetts. Ozone EC fluxes are from the Environmental Measurements Site tower on the Prospect Hill Tract (42.53°N, 72.18°W; Munger et al., 1996). The dominant tree species around the tower are red oak (*Quercus rubra*), red maple (*Acer rubrum*), eastern hemlock (*Tsuga canadensis*), red pine (*Pinus resinosa*), and white pine (*Pinus strobus*). EC fluxes are measured at 29 m, and mean canopy height is 24 m. The full ozone EC data set spans 1990–2000, but complementary micrometeorological measurements are only available from 28 October 1991 onward (Munger & Wofsy, 1999b), so we mainly focus on 1992–2000. The fast ozone analyzer used for EC is ethylene chemiluminescence. For information on how v_d is calculated and filtered for outliers, see Text S1 in the supporting information. Daily total precipitation measurements are from the nearby Shaler Meteorological Station (Boose & Gould, 1999). For more details on leaf area index (LAI; Barford et al., 2001; Eisen & Plotkin, 2015; Munger & Wofsy, 1999a; Urbanski et al., 2007) and soil moisture measurements (Davidson et al., 1998; Davidson & Savage, 1999; Savage & Davidson, 2001), see Texts S2 and S3, respectively.

2.2. Observations at Kane Experimental Forest and Sand Flats State Forest

Kane Experimental Forest (41.595°N, 78.766°W) is a deciduous forest in northwestern Pennsylvania (Finkelstein et al., 2000). The dominant tree species around the flux tower are black cherry (*Prunus serotina*), red maple (*Acer rubrum*), sugar maple (*Acer saccharinum*), and hemlock (*Tsuga canadensis*). Ozone EC and other measurements are available from 29 April to 23 October 1997.

Sand Flats State Forest (43.565°N, 75.238°W) is a mixed forest in New York State (Finkelstein et al., 2000). The dominant tree species around the site are white pine (*Pinus strobus*), black cherry (*Prunus serotina*), sugar maple (*Acer saccharinum*), hemlock (*Tsuga canadensis*), and white spruce (*Picea glauca*). Ozone EC and complementary measurements are from 12 May to 20 October 1998.

The ozone EC measurement system used at Kane and Sand Flats is described in Meyers et al. (1998; see their appendices A1, A2, A5, and A6). For information on how v_d is calculated and filtered for outliers, see Text S1. The fast response ozone analyzer used measures the chemiluminescent reaction between ozone and eosin-y dye. Fluxes are from 36.4 (Kane) and 36.7 m (Sand Flats). Mean canopy heights are 22 (Kane) and 21.8 m (Sand Flats). Half-hourly precipitation measurements are available for Kane and Sand Flats. Other micrometeorological measurements are described in Meyers et al. (1998; see their Table 2) and Finkelstein et al. (2000). For more details on the LAI measurements at Kane and Sand Flats (Chason et al., 1991; Finkelstein, 2001; Meyers et al., 1998), see Text S2.

2.2.1. Leaf Wetness at Kane and Sand Flats

Leaf wetness measurements are available from Kane and Sand Flats but not for Harvard Forest. Leaf wetness was measured through electrical conductivity with a RM Young surface wetness sensor (Meyers et al., 1998) on a boom pointing away from the tower at 22 m at Kane and 21.8 m at Sand Flats (Finkelstein et al., 2000). Hourly leaf wetness values are between 0 and 1, averaged from measurements recorded every 10 s (raw measurements are 0 or 1). We assume that the leaf wetness measurements from the single instrument at each forest represent leaf wetness across the flux tower footprint. The measurements cannot detect moisture layers smaller than droplet size.

2.3. Stomatal Conductance Models

For Harvard Forest, we use three observation-driven estimates of stomatal conductance (g_s). The first two described below are modified slightly from Clifton et al. (2017) and are independent approaches. The first

g_s estimate employs water vapor EC fluxes; it is the Shuttleworth et al. (1984) inversion of the Penman-Monteith equation (hereafter P-M). Text S4 includes a full description of our methodology for P-M (Allen et al., 1998; Hogg et al., 2007; Lamaud et al., 2009; Launiainen et al., 2013; Moore et al., 1996; Novick et al., 2016; Wehr et al., 2017). The second g_s estimate is obtained from an optimal photosynthesis minimal transpiration model (Lin et al., 2015; Medlyn et al., 2011; hereafter *L15*). For this model, we employ gross primary productivity (GPP) inferred from observed carbon dioxide EC fluxes (Urbanski et al., 2007; Wofsy et al., 1993) as the best estimate of net photosynthesis at Harvard Forest. Note that we update the L15 g_1 parameter for red oak at Harvard Forest with the Franks et al. (2018) value. The third g_s estimate is the Wehr and Saleska (2015) empirical model (hereafter *W15*) for g_s at Harvard Forest and is based on leaf-to-air vapor pressure deficits, LAI, photosynthetically active radiation, and cloud coverage. This model is tuned to an inversion of P-M during dry periods (Wehr & Saleska, 2015) and so is not completely independent of our P-M g_s estimate. For all models, we calculate ozone g_s by multiplying g_s for water vapor or carbon dioxide by the ratio of ozone diffusivity to that of the respective gas (Massman, 1998). The three models are described in full in Text S4.

For the most part, we use the L15 and W15 g_s estimates to support our findings with P-M g_s. Clifton et al. (2017) find similar interannual variability in g_s estimates from L15 and P-M, so we are fairly confident that P-M represents g_s variations on this timescale. We are less confident in the ability of P-M g_s to represent subseasonal variability in g_s due to changes in evaporation with rain and aridity. When we investigate v_d and g_s on rainy versus dry days below, we only use L15 and W15 estimates because we expect P-M g_s to be influenced by enhanced evaporation after rainfall (e.g., Wehr et al., 2017). For Sand Flats and Kane, we only use P-M g_s because some of the parameters needed for L15 have not been inferred for these sites (doing so is beyond the scope of this manuscript) and W15 was designed specifically for Harvard Forest.

3. Results and Discussion

In the following sections, we present our results according to a series of hypotheses describing the patterns we observe in the v_d data sets; the titles of the sections reflect the hypotheses most supported by our findings. Our earlier work concludes that the strong interannual variability in observed v_d at Harvard Forest is not caused by uptake through stomata (Clifton et al., 2017). Here, we expand upon our prior analysis to examine several possible drivers of observed variations in v_d on daily and interannual timescales at Harvard Forest and compare the measurements at Harvard with those at two other northeastern U.S. forests with growing-season measurements for a single year. We investigate the roles of each effective deposition pathway: stomata, leaf cuticles, soil, and ambient in-canopy chemistry. For cuticular deposition, we probe the roles of rain-wet versus dew-wet leaves separately and a third case: when leaves appear dry but may be covered by microscopic water films caused by leaf-level increases in humidity. In terms of ambient in-canopy chemistry, NO concentrations are typically not high enough at Harvard Forest to impact ozone fluxes (Munger et al., 1996). The highly reactive BVOCs that impact observed ozone fluxes are generally not expected at Harvard Forest (McKinney et al., 2011) because the forest is mostly dominated by red oak, red maple, and eastern hemlock. However, red and white pines are ~20% of the trees in the flux tower footprint when wind comes from the northwest (NW), a dominant wind sector (Moody et al., 1998; Munger et al., 1996). Measurements from the laboratory and field at sites other than Harvard Forest suggest that red and white pines emit small amounts of β-caryophyllene (a sesquiterpene), α-humulene (a sesquiterpene), and α-terpinene (a monoterpene; Bouvier-Brown et al., 2009; Calogirou et al., 1999; Duhl et al., 2008; Geron et al., 2000; Goldstein et al., 2004; Helmig et al., 1999, 2007), which are BVOCs reactive enough to influence the ozone EC flux (Richters et al., 2015; Shu & Atkinson, 1994). Emission of BVOCs can increase during periods of ecosystem stress (Duhl et al., 2008; Hansen & Seufert, 1999; Niinemets, 2010; Ormeño et al., 2007) and from the mechanical disturbance of rain (Haase et al., 2011; Helmig et al., 1998; Holzinger et al., 2006).

To examine day-to-day variability in v_d, we calculate daytime (9 am to 4 pm) medians. Two hours of missing data are allowed per daytime value. For interannual variability, we examine summertime (June–September) averages for each year, which we calculate with a bootstrapping technique (Text S5). For interforest differences in v_d, we use a weekly value calculated with an 11-day moving average centered on the current daily median. Three days of missing values are allowed in the moving average.

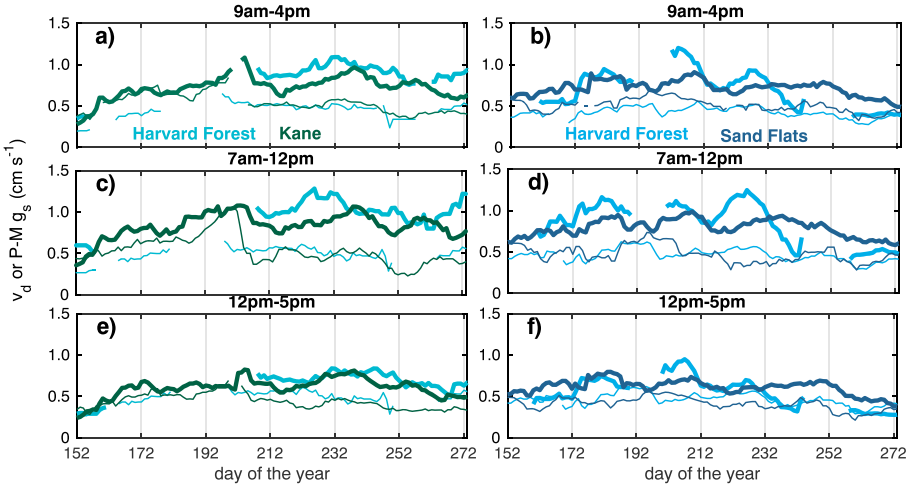

Figure 1. The progression of daytime (9 am to 4 pm; top panel), morning (7 am to 12 pm; middle panel) and afternoon (12–5 pm; bottom panel) weekly mean observed ozone deposition velocity (v_d; thick lines) and P-M stomatal conductance (g_s; thin lines) over June to September 1997 at Harvard Forest and Kane (first column) and 1998 at Harvard Forest and Sand Flats (second column). Note that the v_d filtering method used for Harvard Forest in this figure is different from that used in other figures for consistency with the filtering method for Kane and Sand Flats (Text S1). For g_s, we do not remove values with low VPD here.

3.1. Uptake by Dew-Wet Leaves Contributes to Interforest Differences in v_d

Figure 1 shows weekly mean v_d and PM g_s during 1997 at Harvard Forest and Kane and 1998 at Harvard and Sand Flats for the daytime (9 am to 4pm), morning (7 am to 12 pm), and afternoon (12 pm to 5 pm). Daytime v_d is higher at Harvard versus Kane when observations are available at Harvard (Figure 1a) and is similar between Harvard and Sand Flats at the beginning of the summer but higher at Harvard in the middle and lower at Harvard at the end (Figure 1b). When daytime v_d is higher at Harvard Forest versus the short-term sites, morning v_d is usually higher (Figures 1c and 1d), but afternoon is not (Figures 1e and 1f), suggesting that higher daytime v_d at Harvard is largely driven by higher morning v_d there.

The lack of consistent interforest differences in PM g_s between Harvard and Kane implies that g_s does not explain the consistent interforest differences in v_d. For the most part, interforest differences in v_d between Harvard and Sand Flats are also not explained by differences in P-M g_s. In particular, with respect to higher morning v_d at Harvard versus Sand Flats, higher g_s may contribute to higher v_d during days 212–232 but not otherwise. From the P-M estimate, we infer that a process other than stomatal deposition and restricted to, or at least with a dominant influence during, the morning likely contributes substantially to the interforest differences in v_d.

We suggest that the higher observed morning v_d at Harvard Forest during 1997 and 1998, relative to Kane and Sand Flats, respectively, may be due to higher ozone dry deposition to dew-wet leaves at Harvard. This may result from higher LAI at Harvard (by 1–2 m^2/m^2) or more rain at Kane and Sand Flats (June to September rainfall is 253 mm [Harvard] versus 405.9 mm at [Kane] for 1997 and 322 mm [Harvard] versus 377.8 mm at [Sand Flats] for 1998) that leads to fewer compounds that are reactive with ozone on leaf cuticles. Note that differences in aerodynamic resistance as estimated with Monin-Obuhkov Similarity Theory due to higher measurement height at Sand Flats and Kane do not contribute substantially to interforest differences in v_d (not shown).

3.2. Stomatal and Dry-Cuticular Deposition Contribute to Day-to-Day Variability in v_d

In order to separate the drivers of day-to-day variability in v_d from the drivers of seasonality and interannual variability, we calculate daily anomalies in daytime median v_d and related variables by subtracting the 30-day backward running mean daytime median. We require at least 7 days to have data for the 30 days. We find that anomalies in g_s correlate with anomalies in observed v_d at Harvard (Figure 2), at least for P-M and W15 estimates. The lower correlation between v_d and L15 g_s anomalies relative to P-M and W15 may

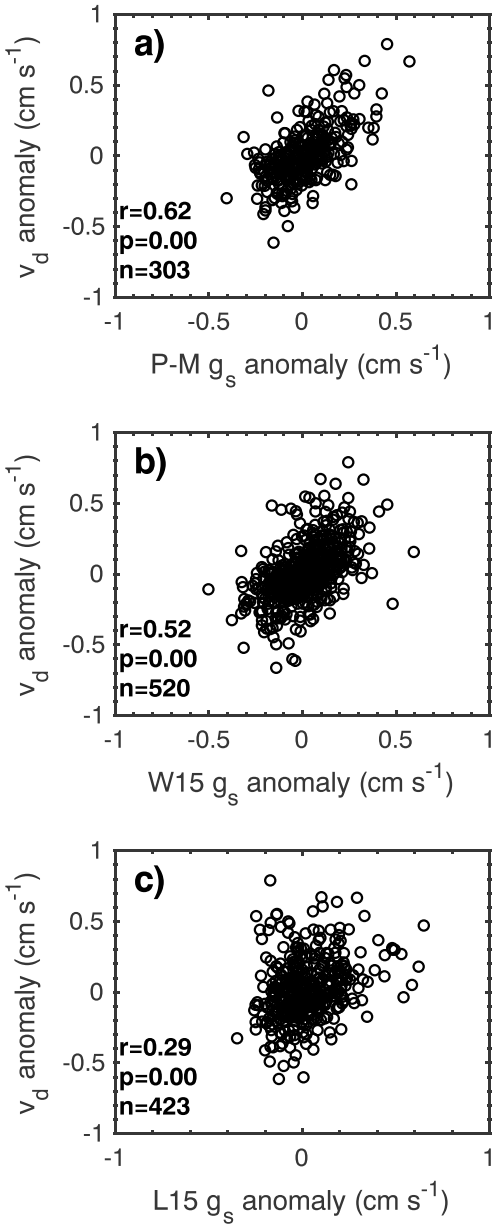

Figure 2. June–September daily ozone deposition velocity (v_d) and stomatal conductance (g_s) anomalies at Harvard Forest for 1992–2000. The anomalies represent the deviation from monthly scale values for each year. The text in the lower-hand corner shows the Pearson correlation coefficient (r), the p value for the null hypothesis (p), and the number of observations (n). For r and p, values are rounded to the hundredth decimal place.

stem from a failure of the estimated GPP used for net photosynthesis in L15 to capture wind sector differences in GPP inferred from isotopic measurements (Wehr et al., 2016). Indeed, if we exclude hours when wind comes from the NW, the relationship between v_d and L15 g_s anomalies improves ($r = 0.51$, $n = 215$, $p = 0.00$).

We apply multiple linear regression to build our understanding of the controls on day-to-day variability in v_d. Relative humidity anomalies, in addition to P-M g_s anomalies, are an important predictor of day-to-day variability in v_d anomalies at Harvard Forest (adjusted $R^2 = 0.43$) and Kane (adjusted $R^2 = 0.48$). Only relative humidity is a significant predictor of day-to-day variability in v_d at Sand Flats, but it does not explain much of the variation in v_d there. Table 1 includes coefficients for each predictor and the y intercept, the number of observations, the root mean square error, and the adjusted R^2 for each model, and Text S6 includes more details on the multiple linear regression. Because both field and laboratory evidence suggest a strong (exponential) dependence of this pathway on humidity (Altimir et al., 2006; Lamaud et al., 2009; Sun, Moravek, Trebs, et al., 2016; Zhang et al., 2002), we hypothesize that the humidity predictor represents dry-cuticular uptake.

3.3. Observed Interannual Variability in v_d

3.3.1. Ozone Uptake by Soil Drives the Interannual Variability in v_d

There is a negative correlation between summertime cumulative precipitation and v_d (Figure 3a; $r = -0.55$, $p = 0.08$), suggesting that the process or processes that controls the interannual variation in observed v_d increases with decreases in water availability (e.g., soil water content and aridity). Because ozone dry deposition to soil decreases with soil moisture (Fares et al., 2014; Fumagalli et al., 2016; Massman, 2004; Stella et al., 2011), we first use v_d modeling to explore whether this negative correlation stems from ozone dry deposition to soil. More specifically, we apply the Massman (2004) nonstomatal deposition model (see Text S7 for details), which distinguishes deposition to wet versus dry soil. We use the P-M estimate for g_s in the estimate of v_d with the Massman (2004) nonstomatal deposition model. Text S7 includes descriptions of the resistance framework used and the resistances to turbulence and molecular diffusion (Businger et al., 1971; Foken, 2006, 2008; Högström, 1988; Meyers et al., 1998; Paulson, 1970; Wesely & Hicks, 1977; Wu et al., 2015).

Because some years lack soil moisture measurements at Harvard Forest, we use a simple precipitation-based indicator of wet soil to determine whether the soil is wet or dry. If cumulative precipitation since 1 June for any given day in the summer is higher than the linear increase from 0 on 1 June to 450 mm on 30 September (black lines in Figure 4), then we consider the soil to be wet otherwise, the soil is dry. While we acknowledge that this is a fairly crude indicator of soil moisture, the mean correlation coefficient between the indicator and observed soil moisture is 0.77 for 5 out of 6 years when there are soil moisture measurements at Harvard Forest (Figure 5). The indicator does not agree with observed soil moisture in 1995 (Figure 5a), but precipitation measurements are missing from the first half of that summer. In the calculation of summertime cumulative precipitation, we assume that days with missing data (shown by the red triangles in Figure 4) have 1990–2000 monthly mean precipitation. The comparison of 1995 soil moisture measurements to the indicator (Figure 5a) suggests that this is not the best assumption; we thus have less confidence interpreting estimated v_d from 1994 and 1995, years with long periods of missing precipitation data (Figures 4c and 4d).

Table 1
Coefficients (Estimates ± Standard Errors) for the Multiple Linear Regression on Daily v_d Anomalies at Each Forest

	y intercept	P-M g_s anomaly	RH anomaly	n	Adjusted R^2	RMSE
Harvard Forest	0.014 ± 0.010	*0.929 ± 0.064*	*0.005 ± 0.001*	291	0.43	0.138
Kane	*0.077 ± 0.020*	*0.720 ± 0.159*	*0.010 ± 0.002*	58	0.48	0.14
Sand Flats	−0.006 ± 0.018	N/A	*0.003 ± 0.001*	94	0.04	0.179

Note. RH is relative humidity, n is the number of observations used in the model, RMSE is the root mean square error. Italics denote $p < 0.05$ for predictors. N/A means that we do not regress v_d on that variable because the variable is not a significant predictor. All models are statistically significant ($p < 0.05$).

Figure 3b shows v_d estimated with the Massman (2004) nonstomatal deposition model, which underestimates the range of the observed interannual variability. We tune the Massman (2004) model by adjusting its resistances for ozone dry deposition to wet and dry soil from 500 and 100 s/m (Massman, 2004), respectively, to 10,000 and 200 s/m. The original values are based on a synthesis of resistances inferred from observations across several land use types and represent the approximate average of the observational synthesis, but values span ~10 to 1,100 s/m. The use of the *tuned* resistances lowers v_d during all years, by 0.1 cm/s in low v_d years (1992 and 1996), effectively reducing estimated ozone dry deposition to soil to 0% during these years (Figure 6), and by 0.06 to 0.1 cm/s in other years. There is an improved and now statistically significant correlation between estimated and observed v_d on interannual timescales for the Massman (2004) tuned estimate (i.e., $r = 0.71$, $p = 0.03$ for the tuned Massman, 2004, estimate versus $r = 0.57$, $p = 0.11$ for the original Massman, 2004, estimate). However, even with the tuned estimate, the magnitudes of the lowest and highest summertime mean observed v_d are not captured (Figures 3b and 6). For example, v_d is underestimated during 1997, 1998, and 1999 (Figures 3b and 6). In general, biases in our estimate of soil resistance may stem from neglecting changes in vertical variation and spatial heterogeneity in soil moisture and organic content. Future chamber measurements of soil ozone fluxes (e.g., Fumagalli et al., 2016) at Harvard Forest would be useful for isolating seasonal variation in ozone dry deposition to soil and pinpointing drivers. We now explore the evidence, or lack thereof, for dominant contributions from other effective nonstomatal deposition processes to the observed interannual variation in v_d.

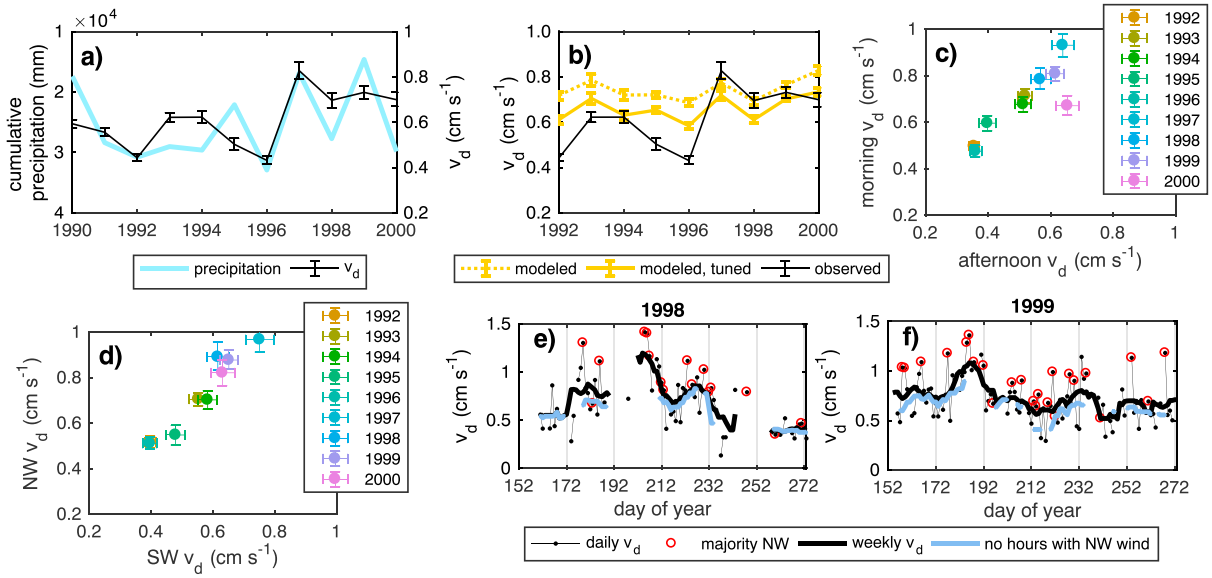

Figure 3. (a) June–September observed daytime mean v_d and cumulative precipitation at Harvard Forest. Note that left y axis for precipitation is reversed. (b) June–September observed and estimated daytime mean v_d at Harvard Forest (see Text S7 and section 3.3.1 for a description of the models). (c) June–September observed v_d for morning (7 am to 12 pm) versus afternoon (12 pm to 5 pm) at Harvard Forest. (d) June–September observed daytime v_d at Harvard Forest, composited by the dominant wind directions. SW is between 180° and 270°, and NW is wind direction greater than 270°. For (a) through (d), averages and 95% confidence intervals are calculated using a bootstrapping technique (see Text S5). (e and f) Daily and weekly daytime observed v_d during June–September 1998 and 1999 at Harvard Forest. Red open circles indicate days when the wind is mostly coming from the NW (this is defined as when more than five (out of eight) daytime hours have wind coming from the NW). Light blue indicates weekly v_d excluding hours with NW wind from the weekly average.

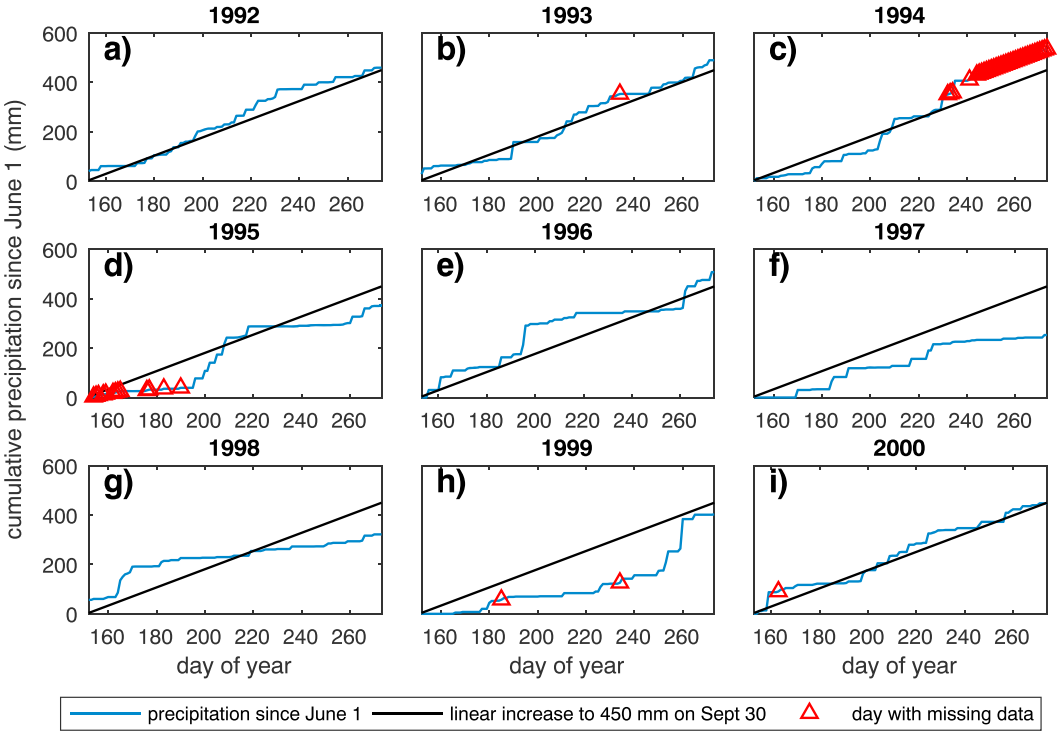

Figure 4. Cumulative precipitation from 1 June to 30 September (blue) and linear increase in precipitation from 0 at June 1 to 450 mm at 30 September (black) at Harvard Forest. We replace any days with missing data (red triangles) with 1990–2000 monthly averages. We use whether cumulative precipitation is above or below the linear increase as an indicator of soil wetness.

3.3.2. Deposition to Dry Cuticles Likely Does Not Contribute to the Interannual Variation in v_d

Based on the strong expected dependence of dry-cuticular deposition on relative humidity, one line of evidence that dry-cuticular deposition does not drive interannual variability in observed v_d is that the ranking of years in terms of relative humidity does not agree with that for observed v_d at Harvard Forest ($r = -0.29$, $p = 0.44$). A laboratory study finds that dry-cuticular uptake by *outdoor* leaves is higher on average by a factor of 1.8 than clean leaves for relative humidity above 45% (Sun, Moravek, Trebs, et al., 2016). If rain cleans

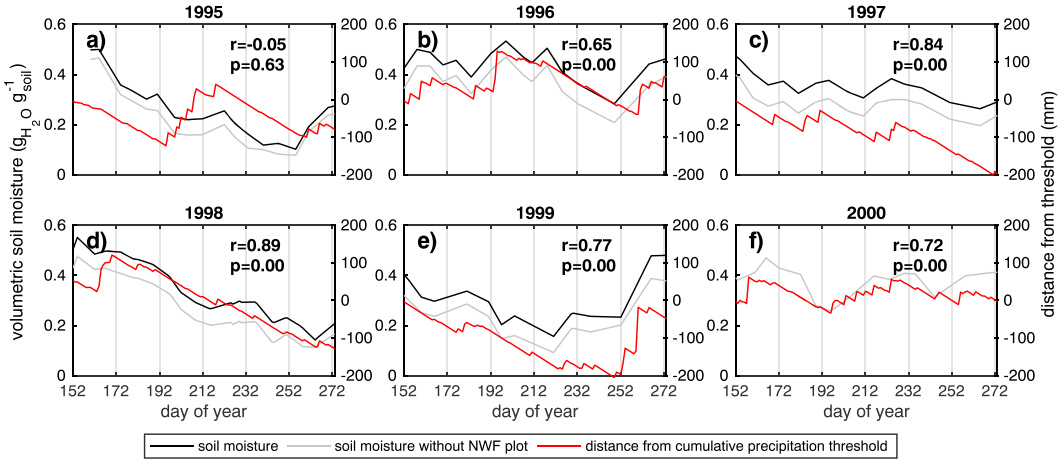

Figure 5. Observed versus estimated soil moisture at Harvard Forest for years with soil moisture measurements. We estimate whether soil is wet or dry with whether cumulative precipitation is above or below a threshold (see Figure 4). The distance from that threshold is shown in red here. For observed soil moisture, there are six plots used to obtain the site-level average shown in black here; one, called "NWF," is missing data from 2000, so we show the average of all plots except NWF in gray for all years. For more details on the soil moisture observations, see Text S3. The text in the upper right corner shows the Pearson correlation coefficient (r) between red and gray lines and p value for the null hypothesis (p). For r and p, values are rounded to the hundredth decimal place.

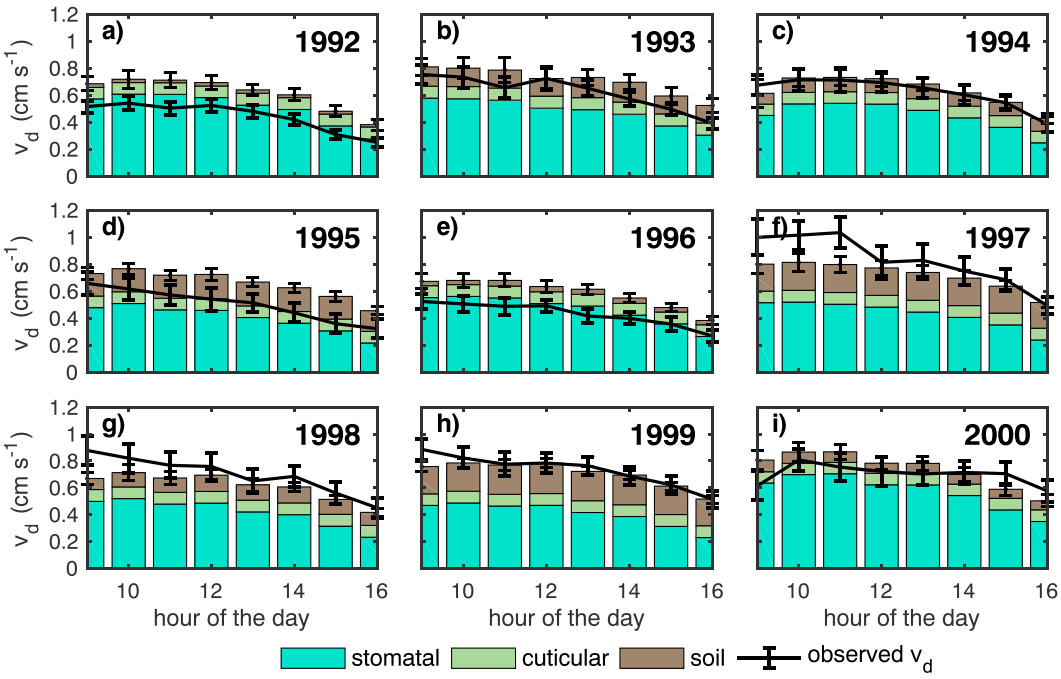

Figure 6. June–September hourly mean ozone deposition velocity (v_d) for 9 am to 4 pm at Harvard Forest as observed (black lines) and estimated (bars) with the tuned Massman (2004) model (see Text S7 and section 3.3.1). Colors indicate contributions from stomata, dry leaf cuticles, and soil to estimated v_d. Error bars indicate two standard errors across all values for a given hour.

cuticles of compounds that react with ozone, then summertime rainfall may be important to account for in deposition models. Indeed, as previously discussed, the highest v_d years, 1997, 1998, and 1999, are low-rainfall years (defined by summertime total precipitation), and lowest v_d years are high-rainfall years, 1992 and 1996 (Figure 3a). Typical deposition models suggest that multiyear daytime mean dry-cuticular conductance ($g_{cut,dry}$) at Harvard Forest is 0.10–0.11 cm/s (Massman, 2004; Zhang et al., 2002). If we assume a $g_{cut,dry}$ average of 0.105 cm/s and a factor of 1.8 difference in $g_{cut,dry}$ between high and low rainfall years based on the findings of Sun, Moravek, Trebs, et al. (2016), then $g_{cut,dry}$ would range from 0.075 to 0.14 cm/s. This is not sufficient to explain the observed interannual variation in v_d, and incorporating this variation into v_d estimated with the tuned Massman (2004) model shown in Figure 6 would not change estimated v_d substantially.

3.3.3. High Deposition to Dew-Wet Cuticles May Contribute to High v_d During 1997

We assume that the presence of dew on leaves is restricted to the morning and examine how interannual variability in morning v_d compares with afternoon. Because the observed interannual ranking of years in summertime mean v_d is largely consistent for the morning and afternoon (Figure 3c), we do not expect that enhanced ozone dry deposition to dew-covered leaves drives the ranking. However, for 1997, morning v_d is particularly enhanced relative to afternoon (Figures 3c and 6f), suggesting that a process isolated to the morning contributes to the high observed v_d this year. We hypothesize that enhanced dew-wet cuticular uptake of ozone contributes to high v_d during 1997. Summer 1997 has low rainfall (Figure 4) but is the second coolest summer on record from 1992 to 2014 at Harvard Forest with a June–September daily average of 16.9 °C. Cool and dry summers like 1997 may facilitate high uptake of ozone by dew-wet cuticles because dew may not evaporate from the leaves as quickly as other summers and rain may not wash away compounds with which ozone reacts.

3.3.4. Deposition to Rain-Wet Cuticles Does Not Likely Contribute to the Interannual Variation in v_d

For investigating the influence of rain-wet cuticles on interannual variability in v_d, we are limited to daily total precipitation measurements at Harvard Forest (rather than high-frequency precipitation and leaf wetness measurements like at Kane and Sand Flats). Nonetheless, our findings from Kane and Sand Flats suggest that the v_d response to rain is consistent throughout the day (Figure 7a), suggesting that we can use a v_d

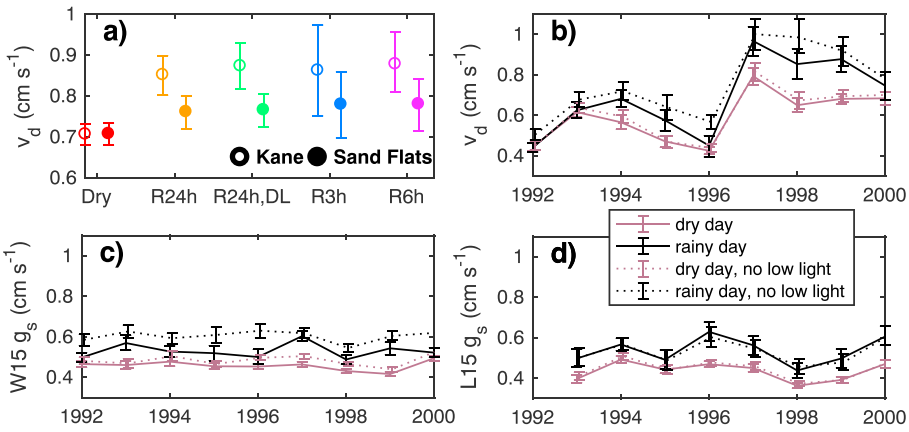

Figure 7. (a) June–September daytime mean ozone deposition velocity (v_d) at Kane (open circles) and Sand Flats (closed circles) composited by precipitation and leaf wetness. *Dry* excludes data with rain in the last 24 hr, R24h only includes data with rain in the last 24 hr, *R24h, DL* only includes data with rain in the last 24 hr and hourly leaf wetness less than 0.1 (i.e., dry leaves), and *R3h* (R6h) only includes data with rain in the last 3 (6) hr. For all composites in (a), we exclude hourly data when rain occurs during that hour of measurement. June–September daytime mean (b) v_d, (c) W15 stomatal conductance (g_s), and (d) L15 g_s at Harvard Forest on rainy versus dry days. Dotted lines represent when hourly low light conditions (i.e., defined as photosynthetically active radiation at 28 m less than 500 μmol/m^2/s) are excluded. For all plots, averages and 95% confidence intervals are calculated using a bootstrapping technique (see Text S5).

rainy day composite to investigate the processes driving higher v_d on rainy days. Year-to-year variations in v_d on rainy versus dry days at Harvard are not consistent with a role for rain-wet cuticles in driving the observed interannual variability in v_d because the interannual variability in v_d on rainy versus dry days is similar (Figure 7b). If rain-wet cuticles were a major contributor to the interannual variability, then we would instead expect to find that rainy days drive the interannual variability in v_d.

3.3.5. In-Canopy Ambient Chemistry May Contribute to Periods of High v_d During 1998 and 1999

The red and white pines in the instrument footprint at the Harvard Forest flux tower are only in the NW wind sector. The similar ranking of years in summertime mean v_d when wind comes from the NW versus southwest (SW; the other dominant wind direction) in Figure 3d suggests that the process, or processes, driving the strong interannual variability in v_d is forest wide. If in-canopy chemistry related to highly reactive BVOC emissions from red and white pines were a main driver of the observed interannual variation, then we would expect to find sector-dependent variations. For 1998 and 1999, however, NW v_d is 1.45 and 1.35 times higher than SW v_d, respectively, relative to 1.15 to 1.31 for other years, suggesting that a process isolated to the NW may contribute to the high summertime mean v_d during 1998 and 1999. We hypothesize that highly reactive BVOC emissions are high enough under ecosystem stress during 1998 and 1999 to influence ozone fluxes at some points during these summers. Evidence for this includes the following: The highest peaks in weekly v_d during late July 1998 and late June to early July 1999 are for the most part driven by high v_d when wind comes from the NW (Figures 3e and 3f), and 1998 and 1999 are known to be years with ecosystem stress. For 1998, ecosystem stress, perhaps associated with stunted canopy growth, likely from springtime weather events (e.g., severe thunderstorms in May and a frost event in early June), may be the cause of low photosynthetic capacity for the following couple of years (Urbanski et al., 2007). June–September 1999, which is the second hottest summer on record at Harvard Forest from 1992 to 2014, had a daily mean air temperature of 19.3 °C, and there was yearlong severe drought ending in late September 1999 (Savage & Davidson, 2001). That the high v_d episode occurs earlier rather than later during summer 1999 (Figure 3f) agrees with observational evidence from other ecosystems that sesquiterpene emissions can be elevated under drought stress but decrease when drought is severe (Duhl et al., 2008; Hansen & Seufert, 1999; Niinemets, 2010; Ormeño et al., 2007).

Previous work has used an exponential air temperature dependence of observed ozone fluxes as an indicator of the influence of highly reactive BVOCs on ozone fluxes (Goldstein et al., 2004; Kurpius & Goldstein, 2003) because BVOC emission from trees tends to increase exponentially with temperature. As in this earlier work, we find an exponential dependence of hourly 9 am to 4 pm observed ozone fluxes on air temperature during summers 1998 and 1999 when wind comes from the NW (Figures 8a, 8d, and 8g). However, we do not find a similar relationship for v_d (Figures 8b, 8e, and 8h), suggesting that accounting for variations in ozone

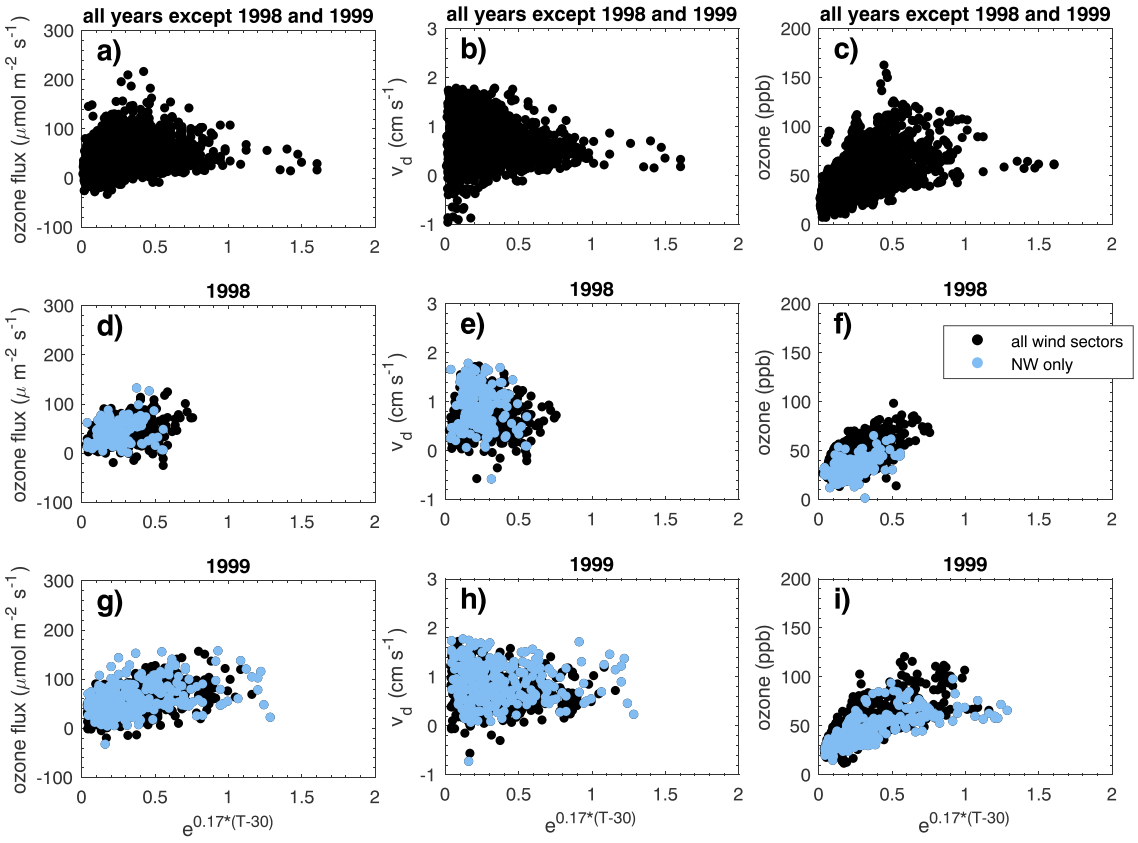

Figure 8. Hourly observed ozone fluxes (shown as positive here; μmol $O_3/m^2/s$), deposition velocities (v_d; cm/s), and concentrations (ppb) versus an exponential temperature (T) dependence for 9 am to 4 pm during June–September 1998 and 1999 (years where we hypothesize highly reactive biogenic volatile organic compounds play a role) versus other years at Harvard Forest. Blue indicates hours when wind comes from the NW because trees that emit highly reactive biogenic volatile organic compounds are only in the NW wind sector.

concentrations may be necessary to deduce the role of chemistry on observed ozone dry deposition and/or dependencies of individual depositional pathways on temperature or other environmental conditions may mask a v_d dependence on temperature (e.g., Wolfe et al., 2011). There is also an exponential dependence of the ozone fluxes on temperature for other years, but the relationship is stronger for 1998 and 1999 (Figures 8a, 8d, and 8g). For example, the regression coefficients describing an exponential fit for June–September 1998 and 1999 when wind comes from the NW are 66.1 and 62.5 (unitless) compared to 32.7 for other years, and the adjusted R^2 is 0.08 and 0.16 compared to 0.05; see also Text S8 and Table S2. The R^2 may not be much higher for 1998 than other years because ecosystem stress reduced photosynthetic capacity (Urbanski et al., 2007) and may have decreased synthesis and thus emission of highly reactive compounds (Niinemets, 2010), rather than only changing temperature-dependent emission. Nonetheless, we find it challenging to attribute the temperature dependence of the ozone fluxes to BVOC emission, or any single process, because of the strong temperature dependence of ozone concentrations (Figures 8c, 8f, and 8i). Ozone concentrations are well known to be correlated with air temperatures in this region during the summer, largely reflecting synoptic-scale meteorology (e.g., Camalier et al., 2007).

3.4. Stomatal Deposition Leads to Higher v_d on Rainy Days

On average across 1992–2000, g_s is 0.07 and 0.11 cm/s higher on rainy days versus dry days at Harvard Forest, for W15 and L15 estimates, respectively. This pattern holds across most individual years (Figures 7c and 7d). Higher g_s on rainy days is consistent with previous work showing enhanced photosynthesis rates at Harvard Forest on rainy days, which the authors attribute to cooler leaves and higher canopy humidity (Medvigy et al., 2010). Here, we only use W15 and L15 estimates due to the direct influence of rain on evaporation, which introduces errors into our P-M estimate. While g_s is higher on rainy days, v_d is not always

enhanced (see 1992, 1993, and 1996 in Figure 7b). If, however, we remove hours with low light (i.e., defined as photosynthetically active radiation at 28 m less than 500 μmol/m^2/s) from the v_d composite, then v_d does increase on rainy days in all years (compare differences between dashed lines versus solid lines in Figure 7b). From this analysis, we infer that g_s controls much of the v_d response to rainy days, although g_s does not explain the full v_d response during 1997, 1998, and 1999, suggesting that another process, or processes, contributes to the high v_d on rainy days during these years.

We use high-frequency leaf wetness and precipitation measurements at Kane and Sand Flats (not available at Harvard Forest) to investigate whether deposition to rain-wet cuticles drives the increase in v_d on rainy days. v_d is similar on rainy days when leaves are dry at the time of measurement (Figure 7a), which suggests that ozone uptake by rain-wet cuticles does not lead to the increase in v_d on rainy days.

If highly reactive BVOCs are emitted at Harvard during years with ecosystem stress and increase under the mechanical disturbance of rain, then this could explain why v_d on rainy days in 1998 and 1999 is relatively higher than during other years. For 1997 we do not know of any ecosystems stressors that would enhance in-canopy chemistry contributions to the high v_d on rainy days.

An underlying assumption of our hypothesis that decreases in ozone dry deposition to soil with rain drive the observed interannual ranking of years in v_d is that ozone dry deposition to soil is suppressed after rain (assuming that soil moisture is substantially enhanced then). The fact that the interannual ranking of observed v_d is largely consistent on rainy and dry days is therefore inconsistent with that hypothesis. That chemistry contributes to the high v_d on rainy days in 1998 and 1999 in part reconciles this discrepancy.

4. Conclusions

Here, we probe the roles of ozone dry deposition to plant stomata, leaf cuticles, and soil, as well as fast ambient chemistry on observed variations in summertime ozone deposition velocity at Harvard Forest in the northeastern United States using a decade's worth of ozone EC flux observations and observation-driven modeling. We compare our findings from Harvard to data sets available from Sand Flats State Forest and Kane Experimental Forest, two nearby short-term monitoring sites with observations during years when there were also observations at Harvard. We examine changes in ozone deposition velocity on rainy days and interforest differences, as well as daily and interannual variations in ozone deposition velocity. We conclude that the following hypotheses are most consistent with the data:

1. Stomatal deposition enhances v_d on rainy days
2. Uptake by dew-wet leaves leads to interforest v_d differences
3. Stomatal and dry-cuticular deposition contribute to day-to-day variability in v_d
4. Suppression of soil uptake when soil is wet drives interannual variability in v_d
5. Uptake by dew-wet leaves leads to high v_d at Harvard during 1997
6. In-canopy chemistry associated with stress contributes to high v_d during 1998 and 1999

We summarize the findings and implications related to these hypotheses below.

With high-frequency measurements of precipitation and leaf wetness at the two short-term observational sites, we show that ozone dry deposition to rain-wet cuticles does not drive the mean increase in ozone deposition velocity on rainy days there. At Harvard Forest, we use two stomatal conductance models that do not directly depend on observed water vapor fluxes (and thus are less sensitive to assumptions about evaporative fluxes) to show that increases in stomatal deposition mostly drive increases in ozone deposition velocity on rainy days. We explore variability in the response to rain at Harvard Forest and hypothesize that when especially high deposition velocities occur on rainy days in years with ecosystem stress, they may indicate enhanced loss from reaction with highly reactive BVOCs. Targeted short-term measurements after rain events of in-canopy processes related to ozone dry deposition are needed to confirm this hypothesis. Our findings suggest that parameterizations that do not account for the influence of changes in the canopy microclimate after rain on stomatal conductance (e.g., Wesely, 1989) or increase cuticular deposition with leaf wetness (e.g., Zhang et al., 2002) are unlikely to capture the higher ozone deposition observed on rainy days accurately.

Our analysis shows substantial same-year differences in morning ozone deposition velocity between nearby forests. Morning interforest differences are not explained by our best estimate of stomatal conductance. We infer that higher morning deposition velocity at Harvard stems from higher cuticular deposition to dew-wet leaves. This hypothesis is supported by similar stomatal conductance, higher LAI, and lower rainfall at Harvard Forest versus the short-term observational sites. In a summer with low rainfall, there may be more compounds adhered to cuticles (i.e., not washed away) that are available to react with ozone when the leaves are wet with dew.

Our analysis also shows that stomatal deposition drives some day-to-day variability in ozone deposition velocity. In addition to stomatal conductance, we find that relative humidity is a significant predictor of daily variability in ozone deposition velocity. We hypothesize that increases in deposition velocity with humidity represent cuticular deposition to dry leaves on the basis of previous field and laboratory studies identifying a strong humidity dependence of this depositional pathway.

On interannual timescales, there is a negative correlation between summertime ozone deposition velocity and cumulative rain over summer at Harvard Forest. Stomatal conductance does not contribute to the interannual ranking of years in ozone deposition velocity (Clifton et al., 2017). Therefore, the effective nonstomatal deposition process, or processes, driving the interannual variation in ozone deposition velocity is high during dry summers, moderate during average-rainfall summers, and low during wet summers. We suggest that the process driving this observed interannual variability is ozone dry deposition to soil because there is substantial field evidence supporting reductions in uptake by soil with increases in soil moisture. As a heuristic, we use a simple model to describe ozone deposition velocity and changes in soil uptake with soil moisture to show that the rankings of years for estimated and observed ozone deposition velocity are similar. Our findings suggest that distinguishing ozone dry deposition to wet versus dry soil should be included in models such as Wesely (1989) and Zhang et al. (2002). We also hypothesize that high dew-wet cuticular deposition during 1997 and in-canopy chemistry during 1998 and 1999 contribute to the high ozone deposition velocities observed during these summers. We emphasize that measurements of highly reactive BVOC emissions during periods of ecosystem stress, subseasonal changes in ozone deposition to soil with soil moisture and organic content, and changes in cuticular uptake to dew-covered leaves (e.g., before and after rainfall) at Harvard Forest are needed to pinpoint the exact contributions of each process and more broadly to confirm or falsify our hypotheses. Our work suggests that on interannual timescales effective nonstomatal deposition generally decreases with rainfall, a response that opposes the response of plant stomatal activity to water availability. Understanding which response drives observed variability in ozone deposition velocity on various timescales at other monitoring sites worldwide will strengthen our ability to project changes in ozone dry deposition with a changing climate.

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