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New Evidence for the Importance of Non-Stomatal Pathways in Ozone Deposition During Extreme Heat and Dry Anomalies

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Key Points:

- Responses of total ozone deposition to heat and dry anomalies vary considerably from site to site
- Non-stomatal deposition increases significantly during hot days in all three sites considered
- Current big-leaf parameterizations largely fail to capture the response mainly because of non-stomatal deposition

Supporting Information:

Supporting Information may be found in the online version of this article.

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Abstract Dry deposition could partially explain the observed response in ambient ozone to extreme hot and dry episodes. We examine the response of ozone deposition to heat and dry anomalies using three long-term co-located ecosystem-scale carbon dioxide, water vapor and ozone flux measurement records. We find that, as expected, canopy stomatal conductance generally decreases during days with dry air or soil. However, during hot days, concurrent increases in non-stomatal conductance are inferred at all three sites, which may be related to several temperature-sensitive processes not represented in the current generation of big-leaf models. This may offset the reduction in stomatal conductance, leading to smaller net reduction, or even net increase, in total deposition velocity. We find the response of deposition velocity to soil dryness may be related to its impact on photosynthetic activity, though considerable variability exists. Our findings emphasize the need for better understanding and representation of non-stomatal ozone deposition.

Plain Language Summary Ozone is an important air pollutant that can threaten both human and plant health. Removal of ozone from the atmosphere may be reduced during extremely hot or dry events due to how plants respond to such environmental conditions (governed by stomatal or non-stomatal processes separately). Using long-term observations at three different sites, we find that non-stomatal uptake generally increases on hot days, which can offset a reduction in stomatal uptake that is expected under the same conditions. The response to soil dryness is more complicated, but potentially related to responses in photosynthetic activity. Current models of on how ozone deposition affects surface ozone concentrations during hot and dry episodes are inaccurate because of their inability to represent non-stomatal responses.

1. Introduction

Surface ozone (O_3) is an important air pollutant with adverse effects on human health (Jerrett et al., 2009), and ecosystem productivity (Ainsworth et al., 2012; Tai et al., 2014; Wittig et al., 2009). One of its major atmospheric sinks is through dry deposition (Wild, 2007), referring to the removal of atmospheric trace chemicals by turbulent transport to the Earth surface (Wesely & Hicks, 2000). Terrestrial ecosystems are efficient sinks of surface O_3 because of both stomatal uptake and non-stomatal processes (e.g., uptake on cuticles and soil, or in-canopy gas-phase chemistry) (Fowler et al., 2009). Though process-level knowledge remains incomplete (Clifton et al., 2020), observational evidence indicates that O_3 dry deposition over terrestrial ecosystems exhibits strong variability from diurnal to interannual timescales (O. E. Clifton et al., 2017, 2019; Fares et al., 2010, 2012, 2014; Rannik et al., 2012; Ronan et al., 2020; Wong et al., 2019; Zona et al., 2014). Predictions of surface O_3 will benefit from a better understanding of the temporal dynamics of its dry deposition.

Dry deposition is expected to affect surface O_3 levels during hot and dry episodes. For example, the particularly hot and dry conditions in 2006 may have significantly reduced dry deposition, and therefore enhanced surface O_3 concentrations, over the United Kingdom that summer (Emberson et al., 2013). M. Lin et al. (2019) also argue that drought and heat-induced reduction in dry deposition contributes to the high surface O_3 over the central and eastern United States in summer 2012.

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This literature generally relies on the assumption that stomatal conductance, and therefore O_3 uptake, is suppressed by heat and dryness. Less attention has been given to how non-stomatal O_3 uptake may also change under such conditions. Low relative humidity may reduce cuticular O_3 uptake (Sun et al., 2016; Zhang et al., 2002), or high temperatures may promote cuticular O_3 uptake through faster surface reactions (Cape et al., 2009). In some forests where direct ozonolysis by biogenic volatile organic compounds (BVOC) plays an important role in O_3 uptake, the inferred non-stomatal uptake could increase as a function of temperature (Kurpius & Goldstein, 2003; Vermeuel et al., 2021; Wolfe et al., 2011). Dry soil may also promote O_3 uptake to soil (Mészáros et al., 2009; Stella et al., 2019; Stella, Loubet, et al., 2011). With these potentially competing pathways, the response of non-stomatal O_3 uptake to heat and dry anomalies is highly uncertain (e.g., Q. Li et al., 2019).

Extreme dryness and heat are expected to become more frequent and severe (Dai & Zhao, 2017; Meehl & Tebaldi, 2004; Perkins et al., 2012; Samaniego et al., 2018). Together with the empirical evidence that the above conditions could lead to increase in O_3 levels at the surface with a concomitant additional public health burden (Filleul et al., 2006), it is important to mechanistically understand O_3 dry deposition to correctly predict the changes in surface O_3 and related risks. Characterizing ecosystem responses to extreme events typically requires analysis of long-term monitoring data (Chu et al., 2017; Zscheischler et al., 2014) that enables comparisons across similar seasonal and phenological conditions.

We leverage multi-year O_3 flux measurements at several sites to explore the response of O_3 dry deposition under extreme dryness and heat. We select sites with co-located sensible heat, latent heat and CO_2 flux measurements, so that we can partition total O_3 deposition into stomatal and non-stomatal pathways (Fares et al., 2012; Gerosa et al., 2005; Hogg et al., 2007; Stella, Personne, et al., 2011), and characterize associated ecosystem stress. This approach allows us the investigate the following questions:

1. How does total, stomatal and non-stomatal O_3 deposition change under heat and dry anomalies?
2. What are the plausible mechanisms and their potential ties to meteorology and ecosystem stress behind such changes?
3. Can big-leaf parameterizations used by regional and global models capture the variability in O_3 deposition during heat and dry episodes?

2. Datasets and Method

We use long-term eddy covariance (EC) measurements of sensible heat (*H*), latent heat (*LE*), O_3, and CO_2 fluxes, and relevant auxiliary meteorological variables (e.g., air temperature, humidity, and radiation) from three sites: (a) Hyytiälä Forest (*Hyy*), Finland (Keronen et al., 2003; Mammarella et al., 2007); (b) Harvard Forest (*Ha*), Massachusetts, USA (Munger et al., 1996); and (c) Blodgett Forest (*Blo*), California, USA (Fares et al., 2010). *Hyy* and *Blo* are characterized as needleleaf forests, while *Ha* is characterized as deciduous forest with scattered stands of needleleaf species. We include additional details of each site in Table S1 in Supporting Information S1.

Canopy conductance of O_3 ($g_{c,O3}$), representing the strength of the O_3 sink to the surface, is calculated by:

$$g_{c,O_3} = \left(v_{d,O_3}^{-1} - r_a - r_{b,O_3}\right)^{-1} \tag{1}$$

where v_d is O_3 deposition velocity (inferred from the O_3 flux and concentration measurements), r_a is the aerodynamic resistance (inferred based on widely accepted Monin-Obukhov similarity theory (Foken, 2006; Monin & Obukhov, 1954)), and r_b is the laminar boundary-layer resistance (calculated based on the formula proposed by Wesely and Hicks (1977)). We reject observations with low turbulence (friction velocity <0.1 m s^{-1}) as v_d is more likely to be controlled by r_a rather than $g_{c,O3}$, and often characterized by large random error (Rannik et al., 2012). This filter removes less than 1.2% of the daytime hourly observations (Table S1 in Supporting Information S1).

We apply three different strategies to infer canopy stomatal conductance of water vapor ($g_{s,w}$): (a) The evaporative-resistive form of Penman-Monteith (PM) equation (Gerosa et al., 2007; Monteith, 1965) with the Nelson et al. (2018) machine learning-based method to estimate ecosystem transpiration, (b) the PM equation with a simpler set of assumptions in evapotranspiration (*ET*) partitioning, and (c) a *GPP*-based estimate (Y. S. Lin et al., 2015; Medlyn et al., 2011). Detail descriptions of the methods, and the reasons supporting the use of

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method 1 are given in Text S1 in Supporting Information S1. Stomatal conductance of O_3 ($g_{s,O3}$) is then scaled from $g_{s,w}$ by the relative diffusivity between H_2O and O_3 molecules (Wesely, 1989):

$$g_{s,O_3} = \frac{g_{s,w}}{1.6} \tag{2}$$

The residual of v_d is then partitioned to estimate an apparent (or inferred) non-stomatal conductance ($g_{ns,O3}$):

$$g_{ns,O_3} = g_{c,O_3} - g_{s,O_3} \tag{3}$$

Regional and global models tend to use big-leaf parameterizations of v_d (Hardacre et al., 2015; Pleim & Ran, 2011; Simpson et al., 2012). To investigate their performance, we model v_d, $g_{s,O3}$, and $g_{ns,O3}$ with two widely-used big-leaf parameterizations: the Wesely scheme (Wesely, 1989), and the Zhang scheme (Zhang et al., 2003). Details of each are given in Table S2 in Supporting Information S1.

We focus on summer daytime observations (9a.m.–3p.m. local time) when O_3 deposition is highest and boundary-layer turbulence is most developed (Freire et al., 2017). The definition of summertime for each site is taken from previous studies (Clifton et al., 2017; Fares et al., 2010; Rannik et al., 2012) (see Table S1 in Supporting Information S1). Daily average observed and modeled v_d, $g_{s,O3}$, $g_{ns,O3}$, air temperature (*T*), vapor pressure deficit (*VPD*), incoming solar radiation (SW_{in}), soil water content (*SWC*) and gross primary productivity (*GPP*, "GPP_NT_VUT_REF" from FLUXNET 2015 (Pastorello et al., 2020)) are computed for days with no more than 2 hours of missing daytime v_d observations.

Finally, we define days with 10% highest daytime average *T*, *VPD*, and 10% lowest daytime average *SWC* as "anomalously" hot (high *T*), dry air (high *VPD*), and dry soil (low *SWC*) days respectively. The choice of 90th percentile provides reasonable sample size and corresponds to accepted definitions of anomalous events (Perkins & Alexander, 2013; Perkins et al., 2012). Other days are labeled as "normal".

3. Results and Discussions

Table 1 compares the mean and standard deviation of daytime average *VPD*, *T*, *SWC*, SW_{in}, and *GPP* during "anomalous" days with rest of the sample population at each site. The mean daytime *T* of 10% hottest days is 5.7°C–7.7°C higher than the average of other summer days. As *VPD* is partly dependent on temperature through the strong relationship between saturated vapor pressure and air temperature (Alduchov & Eskridge, 1996), high *T* naturally increases *VPD*. At *Hyy* and *Blo*, many high *T* days (~30) overlap with high *VPD* days. At *Ha*, this co-occurrence is less common (14 days). Still, we find enough distinction between the populations and ecological impacts of high *T* and high *VPD* days that they can be studied separately. *GPP* shows slight increases or no changes during both hot and high *VPD* days at *Hyy* and *Ha*, while at *Blo* hot days and high *VPD* days have opposing responses on *GPP* (+4% and −20%, respectively). At all three sites, dry soil days have little overlap with either high *T* or high *VPD* (2–9 days), providing a mostly distinct condition to study. Dry soil conditions are associated with suppressed *GPP*, though to varying degrees across all sites (−14% in *Hyy*, −59% in *Blo* and −24% in *Ha*).

Figure 1 summarizes the v_d, $g_{s,O3}$, and $g_{ns,O3}$ inferred from observations under normal and anomalous conditions obtained from the Nelson et al. (2018) transpiration scheme, and compares them with predictions from the two big-leaf models. We calculate the significance of differences in response (medians) between the normal and anomalous days with a Wilcoxon Rank-Sum Test (Wilcoxon, 1945). Both the observed and modeled responses of v_d to anomalous conditions vary considerably across sites.

3.1. Heat and High *VPD* Anomalies

During the 10% hottest days, observed v_d is −0.08 cm s^{-1} (14%) lower at *Hyy*, but +0.10 cm s^{-1} (16%) higher over *Blo*. At *Ha* v_d is slightly reduced but the difference is not statistically significant. We find that the inferred $g_{s,O3}$ shows strong declines at *Hyy* (−0.15 cm s^{-1}, 37%), but does not decline significantly at *Blo* and *Ha*. At all three sites, the inferred $g_{ns,O3}$ is significantly higher during hot days (+0.10 to +0.18 cm s^{-1}). The overall v_d response to extreme heat is therefore determined by whether the reduction in $g_{s,O3}$ can compensate for the increase in $g_{ns,O3}$.

Table 1
Average Daytime (9a.m.–3p.m.) Mean VPD, T, SWC, SW_{in} and GPP From Days With and Without Anomalous Conditions for All Three Sites

	T (°C)	VPD (kPa)	SWC (%)	SW_{in} (W m^{-2})	GPP (μmolC m^{-2} s^{-1})
Hyytiälä					
T ≥ 90%ile	24.9 ± 1.5*	1.60 ± 0.42*	25.6 ± 4.8*	546 ± 92*	8.43 ± 1.66
T < 90%ile	17.2 ± 2.9	0.76 ± 0.39	27.6 ± 6.9	392 ± 157	7.84 ± 2.03
VPD ≥ 90%ile	23.6 ± 2.6*	1.75 ± 0.28*	26.6 ± 5.5	598 ± 57*	8.58 ± 1.64*
VPD < 90%ile	17.4 ± 3.2	0.75 ± 0.37	27.5 ± 6.8	387 ± 152	7.81 ± 2.02
SWC < 10%ile	18.5 ± 4.0	0.85 ± 0.58	17.9 ± 1.2*	415 ± 158	6.91 ± 1.93*
SWC ≥ 10%ile	18.1 ± 3.7	0.86 ± 0.47	28.4 ± 6.2	377 ± 153	8.05 ± 1.97
Blodgett					
T ≥ 90%ile	28.9 ± 1.0*	3.00 ± 0.29*	16.6 ± 2.0	780 ± 114	10.7 ± 5.2
T < 90%ile	23.2 ± 3.5	2.02 ± 0.58	16.2 ± 3.0	778 ± 106	10.3 ± 4.3
VPD ≥ 90%ile	28.5 ± 1.3*	3.10 ± 0.18*	15.6 ± 1.7*	768 ± 102	8.45 ± 4.30*
VPD < 90%ile	23.2 ± 3.6	2.00 ± 0.57	16.4 ± 3.0	779 ± 114	10.6 ± 5.16
SWC < 10%ile	22.9 ± 5.6	2.19 ± 0.82	13.7 ± 0.2*	725 ± 127*	4.32 ± 2.56*
SWC ≥ 10%ile	24.0 ± 3.3	2.11 ± 0.61	16.6 ± 2.9	809 ± 98	10.6 ± 4.29
Harvard					
T ≥ 90%ile	27.3 ± 1.3*	1.31 ± 0.40*	20.9 ± 8.3*	669 ± 92*	22.5 ± 4.5
T < 90%ile	20.6 ± 3.1	0.82 ± 0.46	27.6 ± 9.9	547 ± 209	20.4 ± 5.2
VPD ≥ 90%ile	24.9 ± 2.1*	1.66 ± 0.17*	21.6 ± 8.7*	727* ± 84	20.6 ± 5.2
VPD < 90%ile	20.9 ± 3.5	0.78 ± 0.41	27.7 ± 9.9	540 ± 204	20.6 ± 4.6
SWC < 10%ile	21.8 ± 3.9	1.08 ± 0.53	11.4 ± 1.9*	589 ± 207	16.2 ± 4.6*
SWC ≥ 10%ile	21.3 ± 3.5	0.86 ± 0.48	28.7 ± 8.9	543 ± 196	21.4 ± 5.0

Note. Asterisks indicate statistically significant ($p < 0.01$) difference between extreme and non-extreme days.

We find that neither the Wesely nor Zhang parameterization captures the increases in inferred $g_{ns,O3}$, and therefore do not correctly capture the observed responses of v_d to extreme heat. At *Hyy*, competing errors in the Zhang parameterization (overpredicting the reduction in $g_{s,O3}$ and underpredicting the reduction in $g_{ns,O3}$) result in an overall reduction in v_d that is comparable to that inferred by observations. Still, the Zhang parameterization tends to capture the reduction in $g_{s,O3}$ better than the Wesely parameterization. This is not surprising, since the former includes land cover-specific stomatal response to *T* and *VPD*, while $g_{s,O3}$ in the Wesely parameterization lacks any *VPD* dependence (and has fixed optimal temperature for stomatal opening irrespective of plant type and climate).

We find that high *VPD* generally leads to stronger reductions in inferred $g_{s,O3}$ at all sites, with either weaker (*Ha*) or no increases (*Hyy* and *Blo*) in $g_{ns,O3}$. At *Hyy*, the v_d change with high *VPD* (−0.09 cm s^{-1}, −15%) is comparable to that during heat anomalies. In contrast, high *VPD* at *Blo* reduces v_d by −0.06 cm s^{-1} (−10%, not significant at 95% level), attributable to the stronger reduction in $g_{s,O3}$ (−0.11 cm s^{-1}) and the lack of response in the inferred $g_{ns,O3}$. At *Ha*, the reduction in inferred $g_{s,O3}$ (−0.11 cm s^{-1}) and increase in inferred $g_{ns,O3}$ (+0.11 cm s^{-1}) largely offset each other, leading to an insignificant response in v_d.

The Zhang parameterization, which includes stomatal response to VPD, captures the reductions in observed v_d and inferred $g_{s,O3}$ at *Hyy* and *Blo* under high *VPD* conditions. Yet in addition it also predicts significant reduction in $g_{ns,O3}$ at *Ha* due to low relative humidity, resulting in a large reduction in v_d not supported by the observations. The Wesely parameterization does capture the inferred responses of v_d and individual components at *Blo* within statistical uncertainty. At *Ha*, it predicts no changes in either $g_{s,O3}$ or $g_{ns,O3}$, contradicting with our inference, but yields similar overall changes in v_d. In *Hyy* the responses are similar to those during extreme heat. We conclude that successfully predicting the reduction in $g_{s,O3}$ does not necessarily guarantee accurate modeling of v_d during high *VPD* days, due to the difficulty of reproducing the response of apparent $g_{ns,O3}$.

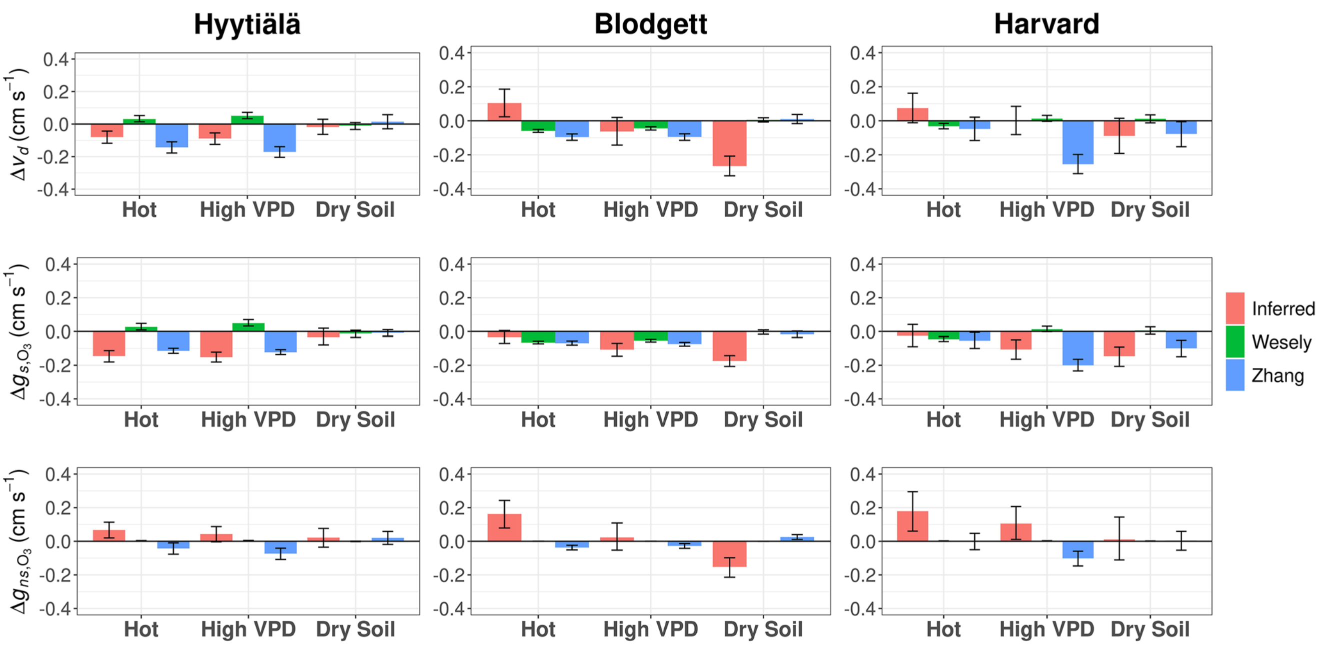

Figure 1. Differences in medians summer daytime (9a.m.–3p.m.) v_d, $g_{s,O3}$, and $g_{ns,O3}$ between anomalous and normal days derived from the evapotranspiration partitioning method proposed by Nelson et al. (2018). Error bars indicate 95% confidence interval (constructed following Bauer, 1972) for the differences in medians.

It has generally been proposed that heat and dryness leads to reduction in g_s, causing reduction in v_d and worse O_3 air quality (Emberson et al., 2013; Huang et al., 2016; M. Lin et al., 2019). Less attention is given to the potential importance of responses in $g_{ns,O3}$ under similar conditions. While we generally see the expected reduction in g_s under hot or high *VPD* conditions, there is a variable response in the apparent $g_{ns,O3}$. Consequently, the impact on overall v_d can vary. The increases in $g_{ns,O3}$ inferred during hot conditions may partially enhance or offset the reduction in $g_{s,O3}$ at *Hyy* (Figures 1 vs. S2 in Supporting Information S1), while dominating the overall response of v_d to anomalous conditions at *Blo* and *Ha*. Common big-leaf deposition models are unable to predict these responses in $g_{ns,O3}$, highlighting a need for better understanding the relationship between non-stomatal O_3 uptake and anomalous conditions.

We examine the possible factors (Clifton et al., 2020) and their potential contributions to the inferred increase in $g_{ns,O3}$ during hot days:

1. During hot days, latent heat may mostly come from the cooler shaded leaves instead of the hotter sunlit leaves (e.g., He et al., 2018). The inferred $g_{s,w}$ may be low-biased comparing to normal days (Text S2 in Supporting Information S1). This implies that both the decrease in g_s and increase $g_{ns,O3}$ may be exaggerated during hot days. Yet if we accept the general ecophysiological theory that g_s decreases with heat anomalies, the increases in inferred $g_{ns,O3}$ at *Blo* and *Ha* are qualitatively robust. On the other hand, this adds to the doubt of robustness of the inferred changes of $g_{ns,O3}$ in *Hyy*, where the signal is small, and the carbon-based partitioning (Figure S2 in Supporting Information S1) suggests reductions instead of increases in $g_{ns,O3}$.
2. Using an experimentally-determined activation energy (30 kJ mol^{-1}) (Cape et al., 2009) and assuming an O_3 cuticular conductance of 0.1 cm s^{-1} during normal days representative of model estimates over dense forests (Clifton et al., 2019; Simpson et al., 2012), we estimate that the increase in cuticular uptake during hot days would contribute approximately 0.042, 0.025 and 0.030 cm s^{-1} to total increases in $g_{ns,O3}$ at *Hyy*, *Blo* and *Ha*, respectively. This is not enough to explain the inferred magnitude of increase in $g_{ns,O3}$ over *Blo* and *Ha*.
3. Using a base emission of at most 3.5 ng N m^{-2} s^{-1} for ordinary days (Munger et al., 1996; Pilegaard et al., 2006; Wolfe et al., 2011), a standard temperature-dependence function for soil NO emission (Steinkamp & Lawrence, 2011), and the assumption that at most 0.8 mol of O_3 is removed by each mole of soil NO emitted (Kurpius & Goldstein, 2003), we calculate that during the increase in soil NO during hot days translates to no more than 0.002 cm s^{-1} increase in v_d over the three sites, which is negligible.

4. Temperature generally promotes emissions of BVOC (Guenther et al., 1995). As certain monoterpenes or sesquiterpenes can rapidly scavenge O_3 (Atkinson & Arey, 2003; Yee et al., 2018), higher temperatures may promote the inferred non-stomatal O_3 deposition through reactions with these BVOC. Though not directly verified by observations, this hypothesis is supported by our finding of larger increases in $g_{ns,O3}$ at *Blo* and *Ha*, where previous work has argued for the influence of BVOC on O_3 uptake (Clifton et al., 2019; Fares et al., 2010; Goldstein et al., 2004; Kurpius & Goldstein, 2003), and the contrast at *Hyy* where BVOC are not considered important sinks of O_3 in general (Rannik et al., 2012; Zhou et al., 2017).

3.2. Soil Dryness Anomalies

We find less consistency in the response of v_d, $g_{s,O3}$ and $g_{ns,O3}$ to dry soil days. Rather than being roughly equally distributed across different years (as is the case with high *T* and high *VPD* days), the driest soil days tend to be concentrated over prolonged episodes within particular years. Therefore, we analyze these dry soil episodes individually and use *GPP* observations to gauge the level of ecosystem stress. This helps elucidate how different levels of drought stress may affect O_3 deposition.

At *Hyy* the criteria of tenth percentile leads to identification of short and long dry soil episodes (<10 days in 2003, 2005, 2013; 16 days in 2009 and 11 days in 2010). In all cases, the impacts of soil dryness on *GPP* are relatively modest (−20% to −5%), and the range of mean daytime v_d across individual episodes is large (0.41–0.65 cm s^{-1}). We find no consistent relationship between *SWC*, *GPP*, other meteorological variables and v_d over the five episodes (Table S3 in Supporting Information S1). This implies that the dry soil anomalies at *Hyy* may not all be significant enough to trigger consistent responses in O_3 dry deposition. With temperature and *VPD* conditions similar to other days (Table 1), the models likewise predict little change in v_d, $g_{s,O3}$ and $g_{ns,O3}$ to dry soil anomalies here.

At *Ha*, the dry soil days mainly occur in late August of 1995 and early August of 1999, and stronger down-regulation of *GPP* is also observed (−25% in 1995 and −21% in 1999). The 2 years have very distinct mean daytime v_d during dry soil days (0.43 cm s^{-1} in 1995 vs. 0.77 cm s^{-1} in 1999), and this difference is explained by differences in the apparent $g_{ns,O3}$ (−0.07 cm s^{-1} in 1995 vs. + 0.32 cm s^{-1} in 1999 relative to average) rather than $g_{s,O3}$ (−0.19 cm s^{-1} in 1995 vs. −0.20 cm s^{-1} in 1999 relative to average). The 1999 episode has slightly higher temperature, *VPD* and lower *SWC* (Table S3 in Supporting Information S1). Given the uncertainty in EC-based *GPP* estimates in *Ha* (Wehr, Munger, et al., 2016), it is difficult to judge how different the ecosystem stress during these two episodes is. It might require highly specific ecosystem processes or events (e.g., Clifton et al., 2019; Urbanski et al., 2007), rather than simply relying on meteorological and *GPP* observations, to explain the huge difference in $g_{ns,O3}$ between the two episodes. The Zhang parameterization partially responds to soil dryness by reducing $g_{s,O3}$. The model predicts a reduction in average v_d comparable to observation when all dry days are considered, but it is not able to simulate the difference between the 1995 and 1999 episodes specifically. The Wesely parameterization, meanwhile, produces no significant response to soil dryness.

At *Blo*, all but one 39 dry soil days originate from the one single episode in August and September 2004. Strong concurrent reductions in mean daytime v_d (−0.27 cm s^{-1}, −42%) are observed, and reductions in both $g_{s,O3}$ (−0.17 cm s^{-1}, −58%) and $g_{ns,O3}$ (−0.15 cm s^{-1}, −40%) are inferred. That summer was characterized by average *T* but extremely low spring rainfall, and the coincident decline in *GPP* (−65%), suggests that the ecosystem may have been under prolonged and severe drought stress. Neither the Wesely and Zhang parameterizations are able to capture the reduction in g_s, due to the lack of explicit dependence on *SWC*. However, we note that other v_d parameterizations with explicit g_s dependence on *SWC* (Centoni, 2017; Emberson et al., 2000; Meyers et al., 1998; Simpson et al., 2012; Valmartin et al., 2014) may likewise not produce the reduction in v_d due to simplistic representations of $g_{ns,O3}$. While monoterpene emissions in pine forests are generally a function of temperature and less related to ecosystem productivity due to storage (Bouvier-Brown et al., 2009), the strong reduction in photosynthetic capacity here may still have hampered the de novo emissions of monoterpene (Schurgers et al., 2009), reducing the inferred $g_{ns,O3}$.

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4. Conclusions

We use three long-term O_3 EC datasets to quantify the response of O_3 dry deposition, and inferred stomatal and non-stomatal deposition, to heat and dry anomalies. Despite distinct environmental and ecological conditions, we generally find:

1. Inferred stomatal conductance is consistently reduced when the air or soil become extremely dry (high *VPD* or low *SWC*).
2. During hot days, especially when heat is not strong enough to suppress photosynthetic activity, inferred non-stomatal conductance tends to increase.
3. The magnitudes of changes in inferred stomatal and non-stomatal conductance during heat and dry anomalies are generally comparable.
4. Current big-leaf parameterizations tend to perform poorly compared to the observations partly because of their inability to reproduce the changes in apparent non-stomatal deposition.

The consistent reduction in inferred g_s during high *VPD* and low *SWC* days is expected from plant ecophysiological theory (Granier et al., 2007; Jarvis, 1976; Y. S. Lin et al., 2015; Medlyn et al., 2011). This response is sometimes reproduced by specific big-leaf dry deposition models if the influence of *VPD* is directly accounted for. In contrast, while previous literature has discussed the positive relationship between T and non-stomatal O_3 deposition (Fares et al., 2010; Kurpius & Goldstein, 2003), and the possibility of positive relationship between v_d and T when ozonolysis from BVOC is a major in-canopy O_3 sink (Wolfe et al., 2011), we explicitly show that $g_{ns,O3}$ significantly increases during hot days. This behavior is not captured in the common big-leaf dry deposition models. Even more "advanced" big-leaf deposition models that consider how leaf wetness and relative humidity increases cuticular deposition (Clifton et al., 2020; Zhang et al., 2003), tend to instead predict reductions in $g_{ns,O3}$ during hot days.

We propose faster thermal decomposition on dry cuticles and increased emissions of highly reactive BVOC as plausible mechanisms behind the high inferred $g_{ns,O3}$ during hot days at the sites we considered. The uncertainty in leaf temperature, and the potential bias in inferring $g_{s,w}$ due to the impossibility to distinguish between sunlit and shaded canopy under our framework, should also be considered when interpreting the changes in inferred stomatal and non-stomatal uptake.

On the other hand, we find less consistency in the responses of v_d, $g_{s,O3}$ and $g_{ns,O3}$ to dry soil, which is a more direct indicator of water availability to plants. Taking *GPP* as a proxy of ecosystem stress status, we hypothesize that the varying intensity of soil dryness may have distinct impacts on O_3 deposition because of impacts on plant ecophysiology (Medrano et al., 2002), BVOC emissions (Niinemets, 2010), or both. Previous work has suggested that drier soils can generally increase soil O_3 deposition (Fares et al., 2014; Massad et al., 2019; Mészáros et al., 2009; Stella, Loubet, et al., 2011), but since we do not infer a consistent increase in $g_{ns,O3}$ during dry soil days, such an effect may not be universally important in these particular ecosystems. Our definition of dry soil days allows us to examine the effects across a range of soil dryness, but selection based on closeness to soil wilting point in the future may yield more consistent insight across sites due to the direct ecophysiological relevance.

While we use the commonly observed responses of BVOC emissions to heat and drought stress to argue for potential role of BVOC ozonolysis in the response of $g_{ns,O3}$ to heat and dry anomalies, it must be noted that stresses are also able to alter the composition of emitted BVOC, and, therefore potentially the total O_3 reactivity (Bonn et al., 2019; S. Li et al., 2017; Niinemets, 2010; Peñuelas & Staudt, 2010). This may play a role in the response of O_3 dry deposition during hot and dry anomalies, but the precise mechanisms remain largely unknown.

This work highlights the importance of changes in both stomatal and non-stomatal pathways in the response of O_3 deposition during hot and dry anomalies, and the general inability of big-leaf parameterizations to reproduce the inferred responses in total v_d. This may lead to considerable error in predicting and attributing surface O_3 changes during hot and dry episodes. We estimate the direct impacts on O_3 to a first order using sensitivity simulations from GEOS-Chem (Figure 2) following the approach of Wong et al. (2019) (see Text S3 in Supporting Information S1), and find differences in O_3 during heat and dry anomalies of up to 3–5 ppb that would not be correctly reproduced by the big leaf models. Modeling stomatal O_3 uptake can be readily improved by applying more updated ecophysiological theories (Centoni, 2017; Lei et al., 2020; Valmartin et al., 2014), but our findings imply important limitations in our understanding of the environmental controls on non-stomatal O_3 deposition. These

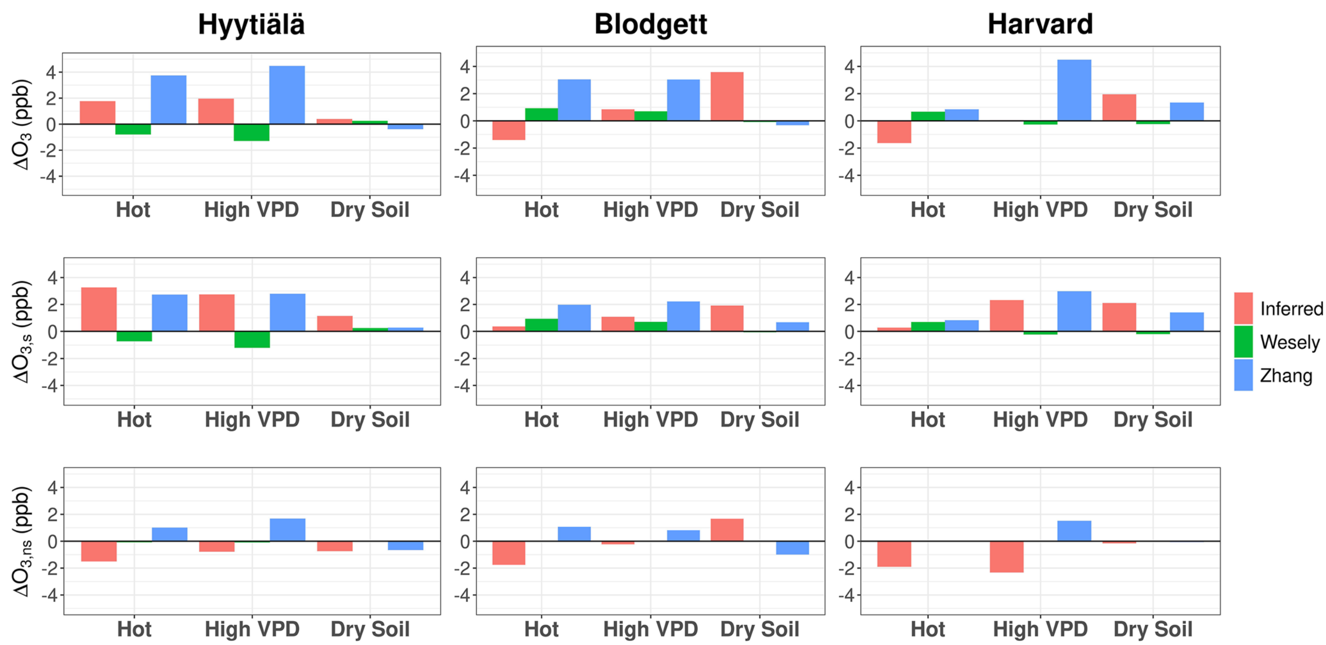

Figure 2. Estimated effect of observationally-inferred ("Inferred") and modeled ("Wesely" and "Zhang") v_d difference in anomalous days on surface ozone (ΔO_3) and its component attributable to stomatal ($\Delta O_{3,s}$) and non-stomatal pathways ($\Delta O_{3,ns}$). The sensitivity of surface O_3 to v_d (β) is derived from the simulations of Wong et al. (2019).

are best addressed with a combination of direct O_3 flux and other concurrent measurements (e.g., soil moisture, BVOC speciation, canopy wetness) measurements (Clifton et al., 2020). Simultaneous monitoring of O_3 and BVOC oxidation products fluxes may provide a novel and effective tool to study non-stomatal ozone deposition from in-canopy BVOC ozonolysis (Holzinger et al., 2005; Vermeuel et al., 2021).

Our work is an example that demonstrates the potential of applying data-driven techniques to help partition *ET* and infer g_s, which is crucial to partition the changes in v_d into stomatal and non-stomatal components. Data-driven techniques require only basic meteorological measurements in addition to EC fluxes, making them highly applicable to cross-site and long-term studies, providing a promising way to improve water vapor-based inference of g_s. Yet the discrepancies in estimated *ET* partitioning between different data-driven methods can be substantial (Nelson et al., 2020). Machine learning models might also be prone to overfitting, which we test in Table S4 in Supporting Information S1. The potential effects of overfitting on *ET* partitioning remains warrants future study, but we also find that our conclusions from this approach are consistent with other accepted portioning techniques (Text S1 in Supporting Information S1). Thus, the machine-learning technique could help alleviate, but does not fully eliminate, the limitations of water vapor-based inference of g_s. Further evidence from independent inferences of g_s by other means (e.g., sap flux, CO_2 flux, OCS flux (e.g., Wehr, Commane, et al., 2017)) will be particularly valuable.

Given the functional diversity of plants, the scarcity of observation (O. E. Clifton et al., 2020), and the importance of the spatiotemporal dynamics of dry deposition on understanding and prediction of surface O_3 (Baublitz et al., 2020; Clifton et al., 2020; M. Lin et al., 2019, 2017; Wong et al., 2019), and vegetation impacts (Mills et al., 2011; Ronan et al., 2020), direct O_3 flux observations must be expanded in both space and time to deepen our understanding of surface O_3 concentrations with global change. Longer observational datasets with greater spatial density have the added benefit of potentially allowing big-data type approaches to model the complex phenomenon of O_3 deposition (Silva et al., 2019).

Data Availability Statement

Ozone flux measurements from Harvard Forest is available through J. W. Munger et al. (1996), and retrieved from Harvard Forest Data Archive. Ozone flux measurements from Hyytiälä Forest is available through Keronen et al. (2003), and retrieved from SmartSMEAR. Ozone flux measurements from Blodgett Forest is available from Fares et al. (2010). Additional site characteristics is obtained from biomass inventory data (HF069) of Harvard Forest Archive for Harvard (W. Munger and Wofsy, 2021) and Launiainen et al. (2016) for Hyytiälä. The processed data directly used in this analysisd; is freely available in the Boston University Institutional Repository, open BU (https://open.bu.edu/handle/2144/43002).

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