

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 3 sites considered
- Current big-leaf parameterizations largely fail to capture the response mainly because of non-stomatal deposition

Abstract

Dry deposition is one of the driving factors behind ozone-meteorology relationships. 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 processes.

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 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 (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 can be an important factor driving the covariability of surface O_3 with meteorological conditions, especially during hot and dry episodes. For example, Kavassalis & Murphy (2017) argue that dry deposition would explain observed daily humidity- O_3 correlations, which common chemical transport models are not able to represent. Wang et al. (2017) likewise cite it as a factor in enhanced surface O_3 during seasonal drought that models are not able to fully reproduce. Dry deposition is also proposed as a driver of the summertime O_3 -temperature relationship (Kerr et al., 2019; Porter & Heald, 2019). Particularly hot and dry conditions in 2006

may have significantly reduced dry deposition, and therefore enhanced surface O₃ concentrations, over the United Kingdom that summer (Emberson et al., 2013).

This literature generally relies on the assumption that stomatal conductance, and therefore O₃ uptake, is suppressed by heat and dryness. Less attention has been given to how non-stomatal O₃ uptake may also change under such conditions. Low relative humidity may reduce cuticular O₃ uptake (Sun et al., 2016; Zhang et al., 2002), or high temperatures may promote cuticular O₃ 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 O₃ uptake, the inferred non-stomatal uptake could increase as a function of temperature (Kurpius & Goldstein, 2003; Wolfe et al., 2011). Dry soil may also promote O₃ 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 O₃ uptake to heat and dry anomalies is highly uncertain and biome-dependent (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 O₃ levels at the surface with a concomitant additional public health burden (Filleul et al., 2006), it is important to mechanistically understand O₃ dry deposition to correctly predict the changes in surface O₃ 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 (Lin et al., 2019).

We leverage multi-year O₃ flux measurements at several sites to explore the response of O₃ dry deposition under extreme dryness and heat. We select sites with co-located sensible heat, latent heat and CO₂ flux measurements, so that we can partition total O₃ 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 to investigate the following questions:

- 1) How does total, stomatal and non-stomatal O₃ 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 O₃ deposition during heat and dry episodes?

2 Datasets and method

We use long-term eddy covariance measurements of sensible heat (H), latent heat (LE), O₃, and CO₂ fluxes, and relevant auxiliary meteorological variables (e.g. air temperature, humidity, and radiation) from three sites: 1) Hyytiälä Forest (Hyy), Finland (Keronen et al., 2003; Mammarella et al., 2007); 2) Harvard Forest (Ha), Massachusetts, USA (Munger et al., 1996); and 3) 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.

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

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

where v_d is O₃ deposition velocity (inferred from the O₃ 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 & Hicks (1977)). We reject observations with negative or exceptionally high v_d ($> 3 \text{ cm s}^{-1}$) for quality control, and low turbulence (friction velocity $< 0.1 \text{ m s}^{-1}$) as v_d is mostly controlled by r_a rather than g_{c,O_3} under such condition.

We apply the Nelson et al. (2018) machine learning-based method to estimate ecosystem transpiration (Text S1). The resulting estimates of transpiration are then used to infer the stomatal conductance of water vapor ($g_{s,w}$) from the evaporative-resistive form of Penman-Monteith (PM) equation (Gerosa et al., 2007; Monteith, 1965), following Ducker et al. (2018). For comparison, we perform a second set of $g_{s,w}$ inferences with a simpler set of assumptions in evapotranspiration partitioning from Ducker et al. (2018). Stomatal conductance of O₃ (g_{s,O_3}) is then scaled from $g_{s,w}$ by the relative diffusivity between H₂O and O₃ molecules (Wesely, 1989):

$$g_{s,O_3} = \frac{g_{s,w}}{1.6} \quad (2)$$

The residual of v_d is then partitioned to estimate an apparent (or inferred) non-stomatal conductance (g_{ns,O_3}):

$$g_{ns,O_3} = g_{c,O_3} - g_{s,O_3} \quad (3)$$

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,O_3} , and g_{ns,O_3} 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. These approaches attempt to represent functional relations between O₃ deposition and environmental variables (Wong et al., 2019).

We focus on summer midday observations (9am – 3pm local time) when O₃ 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). Daily average observed and modeled v_d , 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)), and daily median observed and modelled g_{s,O_3} and g_{ns,O_3} , are computed for days with no more than two hours of missing midday v_d observations. Medians are used for g_{s,O_3} and g_{ns,O_3} as their distributions are less normal than the other variables (Ducker et al., 2018).

Finally, we define days with 10% highest midday average T , VPD , and 10% lowest midday 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 et al., 2012; Perkins & Alexander, 2013). Other days are labeled as “normal”.

All our statistical computing and v_d simulations are done with R version 3.6.0 (R Core Development Team, 2015).

3 Results

Table 1 compares the mean and standard deviation of midday average VPD , T , SWC , SW_{in} and GPP during “anomalous” days with rest of the sample population at each site. The mean midday T of 10% hottest days is 5.6 – 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 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 (+7% and -22% 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 , -58% in Blo and -26% in Ha).

Figure 1 summarizes the v_d , $g_{s,O3}$, and $g_{ns,O3}$ inferred from observations under normal and anomalous conditions, and compares them with predictions from the two big-leaf models. We calculate the significance of differences in response between the normal and anomalous days with a Wilcoxon Rank-Sum Test (Wilcoxon, 1945). Both the observed and modelled responses of v_d to anomalous conditions vary considerably across sites. Our results using either the Nelson et al. (2018) transpiration scheme or the simpler approach are qualitatively similar (Fig. S1), and we base our discussion in the main text on the former.

| | <i>T</i> (°C) | <i>VPD</i> (kPa) | <i>SWC</i> (%) | <i>SW_{in}</i> (W m ⁻²) | <i>GPP</i> (μmolC m ⁻² s ⁻¹) |
|---------------------|------------------|---------------------|-------------------|--|--|
| Hyttiälä | | | | | |
| <i>T</i> ≥ 90%ile | 24.9 ± 1.5* | 1.70 ± 0.41* | 25.6 ± 4.8* | 546 ± 91* | 8.43 ± 1.66 |
| <i>T</i> < 90%ile | 17.2 ± 2.9 | 0.81 ± 0.37 | 27.8 ± 6.9 | 399 ± 154 | 7.93 ± 1.99 |
| <i>VPD</i> ≥ 90%ile | 24.2 ± 2.1* | 1.83 ± 0.28* | 26.6 ± 5.2 | 591 ± 67* | 8.71 ± 1.57* |
| <i>VPD</i> < 90%ile | 17.3 ± 3.0 | 0.80 ± 0.35 | 27.6 ± 6.9 | 394 ± 150 | 7.89 ± 1.97 |
| <i>SWC</i> ≥ 10%ile | 18.7 ± 4.0 | 0.97 ± 0.53 | 18.0 ± 1.1* | 390 ± 145 | 7.02 ± 1.94* |
| <i>SWC</i> < 10%ile | 18.1 ± 3.7 | 0.92 ± 0.46 | 28.6 ± 6.3 | 422 ± 156 | 8.15 ± 1.80 |
| Blodgett | | | | | |
| <i>T</i> ≥ 90%ile | 28.9 ± 0.9* | 2.98 ± 0.27* | 16.6 ± 2.1 | 781 ± 108 | 11.2 ± 4.0 |
| <i>T</i> < 90%ile | 23.3 ± 3.3 | 2.04 ± 0.57 | 16.3 ± 3.0 | 776 ± 114 | 10.4 ± 4.3 |
| <i>VPD</i> ≥ 90%ile | 28.4 ± 1.2* | 3.09 ± 0.16* | 15.4 ± 1.7* | 770 ± 103 | 8.30 ± 4.31* |
| <i>VPD</i> < 90%ile | 23.4 ± 3.4 | 2.02 ± 0.55 | 16.4 ± 3.0 | 777 ± 115 | 10.7 ± 4.18 |
| <i>SWC</i> ≥ 10%ile | 23.3 ± 4.5 | 2.23 ± 0.75 | 13.7 ± 0.2* | 727 ± 130* | 4.47 ± 2.54* |
| <i>SWC</i> < 10%ile | 23.8 ± 3.3 | 2.11 ± 0.60 | 16.6 ± 2.9 | 808 ± 99 | 10.7 ± 4.04 |
| Harvard | | | | | |
| <i>T</i> ≥ 90%ile | 27.4 ± 1.3* | 2.34 ± 0.46* | 21.0 ± 8.4* | 672 ± 91* | 22.5 ± 4.5 |
| <i>T</i> < 90%ile | 20.6 ± 3.1 | 1.64 ± 0.44 | 27.4 ± 9.9 | 552 ± 206 | 20.5 ± 5.1 |
| <i>VPD</i> ≥ 90%ile | 25.9 ± 2.5* | 2.63 ± 0.22* | 25.7 ± 10.4 | 530 ± 158 | 22.9 ± 4.4 |
| <i>VPD</i> < 90%ile | 20.9 ± 3.3 | 1.61 ± 0.40 | 27.1 ± 9.8 | 570 ± 205 | 20.6 ± 5.1 |
| <i>SWC</i> ≥ 10%ile | 21.8 ± 4.0 | 1.61 ± 0.50 | 11.3 ± 1.8* | 595 ± 207 | 15.9 ± 4.3* |
| <i>SWC</i> < 10%ile | 21.4 ± 3.4 | 1.72 ± 0.46 | 28.5 ± 8.9 | 549 ± 192 | 21.6 ± 4.9 |

Table 1. Average midday mean VPD , T , SWC , SW_{in} and GPP from days with and without anomalous conditions for all three sites. Asterisks indicate statistically significant ($p < 0.01$) difference between extreme and non-extreme days.

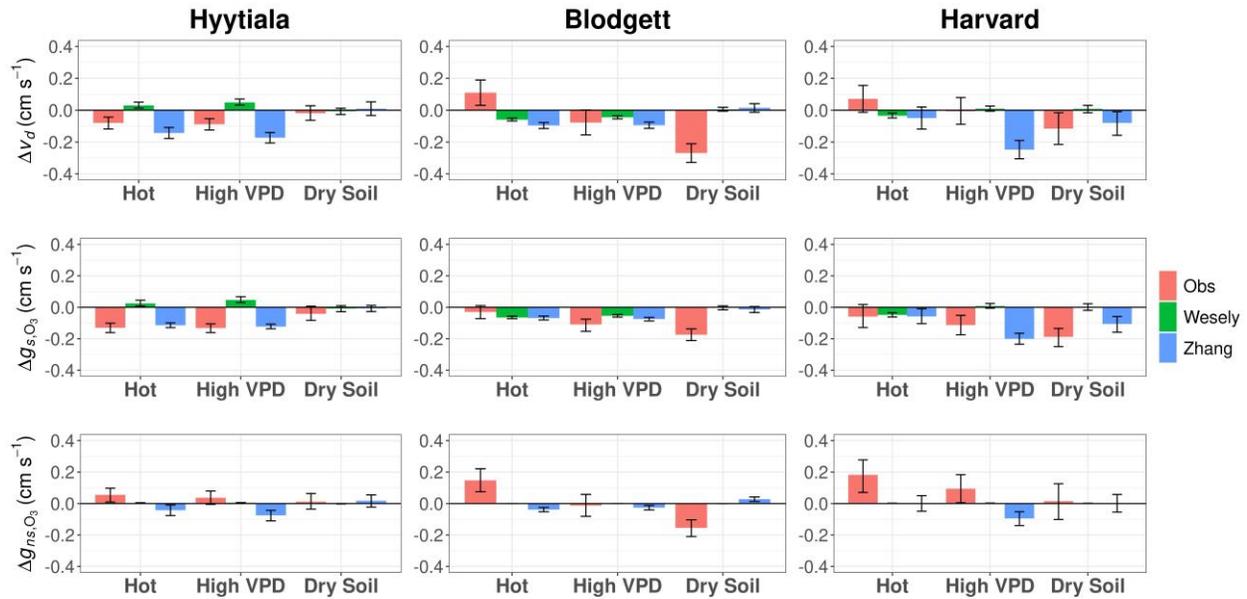


Figure 1. Differences in summer midday (9am – 3pm) v_d , $g_{s,O3}$ and $g_{ns,O3}$ between anomalous and normal days derived from the evapotranspiration partitioning method proposed by Nelson et al. (2018). Error bars indicate 95% confidence interval (constructed following Bauer, 1972) for the differences.

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 $+0.11 \text{ cm s}^{-1}$ (17%) 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* (-0.13 cm s^{-1} , 35%), 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 $+0.18 \text{ cm s}^{-1}$). 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 $g_{ns,O3}$.

We find that neither the Wesely nor Zhang parameterization captures the increases in $g_{ns,O3}$ inferred by observations, 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 -0.08 cm s^{-1} (-12%), attributable to the stronger reduction in g_{s,O_3} (-0.11 cm s^{-1}) and the lack of response in the inferred g_{ns,O_3} . At *Ha*, the reduction in inferred g_{s,O_3} (-0.11 cm s^{-1}) and increase in inferred g_{ns,O_3} ($+0.09 \text{ cm s}^{-1}$) largely offset each other, leading to an insignificant response in v_d .

As the response of v_d to high *VPD* is generally dominated by g_{s,O_3} , the Zhang parameterization (which includes stomatal response to *VPD*) performs more satisfactorily in its response to these conditions. The Zhang parameterization also predicts significant reduction in g_{ns,O_3} at *Ha* due to low relative humidity, resulting in a large reduction in v_d not inferred by the observations. The Wesely parameterization does capture the responses of v_d and individual components at *Blo* within statistical uncertainty. At *Ha*, it predicts no changes in either g_{s,O_3} or g_{ns,O_3} , contradicting the observations, 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,O_3} does not necessarily guarantee accurate modelling of v_d during high *VPD* days, due to the difficulty of reproducing the response of apparent g_{ns,O_3} .

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,O_3} 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,O_3} . Consequently, the impact on overall v_d can vary. The increases in g_{ns,O_3} inferred during hot conditions may partially offset the reduction in g_{s,O_3} at *Hyy*, 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,O_3} , highlighting a need for better understanding the relationship between non-stomatal O_3 uptake and anomalous conditions.

Several mechanisms may explain the increase in apparent g_{ns,O_3} with high temperatures:

1) During hot days, latent heat may mostly come from the cooler shaded leaves instead of the hotter sunlit leaves. Canopy temperature may be overestimated, and the inferred $g_{s,w}$ may underestimate the true $g_{s,w}$. This implies that both the decrease in g_s and increase g_{ns,O_3} 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,O_3} at *Blo* and *Ha* are qualitatively robust.

2) Dry cuticular O_3 uptake may increase with temperature. 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,O_3} at *Hyy*, *Blo* and *Ha*, respectively. This is not enough to explain the observed magnitude of increase in g_{ns,O_3} over *Blo* and *Ha*.

3) 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,O_3} 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 H_{yy} 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,O_3} and g_{ns,O_3} 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 H_{yy} the criteria of 10th 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 midday v_d across individual episodes is large (0.43 to 0.68 $cm\ s^{-1}$). This implies that the dry soil anomalies at H_{yy} 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,O_3} and g_{ns,O_3} 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 (-28% in 1995 and -20% in 1999). The two years have very distinct mean midday v_d during dry soil days (0.44 $cm\ s^{-1}$ in 1995 vs 0.79 $cm\ s^{-1}$ in 1999), and this difference is explained by differences in the apparent g_{ns,O_3} (-0.06 $cm\ s^{-1}$ in 1995 vs +0.32 $cm\ s^{-1}$ in 1999 relative to average) rather than g_{s,O_3} (-0.20 $cm\ s^{-1}$ in 1995 vs -0.18 $cm\ s^{-1}$ in 1999 relative to average). Clifton et al. (2019) suggest that the high v_d during 1999 may be attributable to elevated BVOC emissions due to drought stress. As both GPP and SWC are lower during the 1995 dry soil episode than the 1999 one, we postulate that the drought stress during 1995 may have been strong enough to suppress BVOC emissions, resulting in lower g_{ns,O_3} and explaining the discrepancy in g_{ns,O_3} between the two episodes (Niinemets, 2010). The Zhang parameterization partially responds to soil dryness by reducing g_{s,O_3} . 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 38 dry soil days originate from the one single episode in August and September 2004. Strong concurrent reductions in mean midday v_d (-0.27 $cm\ s^{-1}$, -42%) are inferred, due to reductions in both g_{s,O_3} (-0.17 $cm\ s^{-1}$, -57%) and g_{ns,O_3} (-0.15 $cm\ s^{-1}$, -54%) are observed. That summer was characterized by average T but extremely low spring rainfall, and the coincident decline in GPP (-58%), 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,O_3} . 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,O_3} .

4 Discussion

We use three long-term O_3 eddy covariance 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,O_3} 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, Paulot, et al., 2020; Zhang et al., 2003), tend to instead predict reductions in g_{ns,O_3} 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,O_3} 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,O_3} and g_{ns,O_3} 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,O_3} 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,O_3} 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; 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.

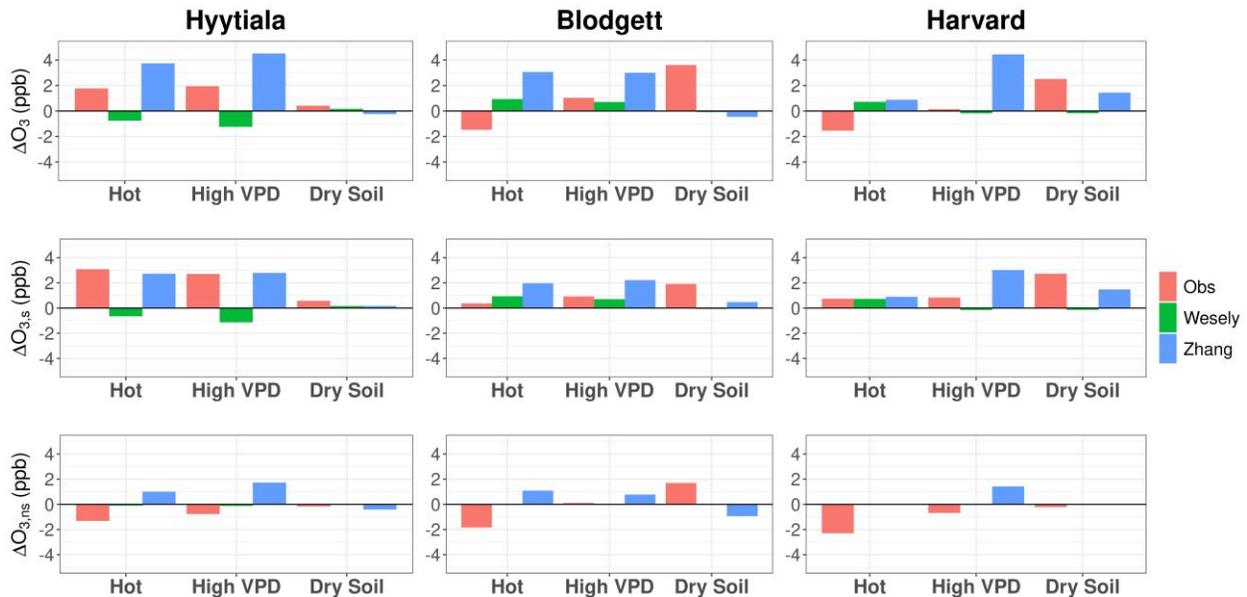


Figure 2. Estimated effect of observed (“Obs”) and modelled (“Wesely” and “Zhang”) v_d difference in anomalous days on surface ozone (ΔO_3) and its component attributable to stomatal ($\Delta O_{3,s}$) and non-stomatal pathways ($\Delta O_{3,ns}$).

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 in Figure 2, following the approach of Wong et al. (2019) (see Supplemental Text), 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 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, Fiore, 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).

Given the functional diversity of plants, the scarcity of observation (Clifton et al., 2020), and the importance of the spatiotemporal dynamics of dry deposition on understanding and prediction of surface O₃ (Baublitz et al., 2020; Clifton et al., 2020; M. Lin et al., 2017, 2019; Wong et al., 2019), and vegetation impacts (Mills et al., 2011; Ronan et al., 2020), direct O₃ flux observations must be expanded in both space and time to deepen our understanding of surface O₃ 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 O₃ deposition (Silva et al., 2019).

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