



## RESEARCH LETTER

10.1002/2016GL070923

## Key Points:

- Observed factor of 2 in interannual variability (IAV) of ozone dry deposition velocities, dominated by nonstomatal processes
- Stomatal conductance estimates from two observation-driven independent models show similar but weak IAV
- High-quality, long-term measurements needed to identify processes driving IAV in ozone dry deposition

## Supporting Information:

- Supporting Information S1

## Correspondence to:

O. E. Clifton,  
oclifton@ldeo.columbia.edu

## Citation:

Clifton, O. E., A. M. Fiore, J. W. Munger, S. Malyshev, L. W. Horowitz, E. Shevliakova, F. Paulot, L. T. Murray, and K. L. Griffin (2017), Interannual variability in ozone removal by a temperate deciduous forest, *Geophys. Res. Lett.*, *44*, 542–552, doi:10.1002/2016GL070923.

Received 19 AUG 2016

Accepted 23 NOV 2016

Accepted article online 5 DEC 2016

Published online 12 JAN 2017

Corrected 6 MAR 2017

This article was corrected on 6 MAR 2017. See the end of the full text for details.

## Interannual variability in ozone removal by a temperate deciduous forest

O. E. Clifton<sup>1,2</sup> , A. M. Fiore<sup>1,2</sup> , J. W. Munger<sup>3</sup> , S. Malyshev<sup>4,5</sup> , L. W. Horowitz<sup>5</sup> , E. Shevliakova<sup>5</sup> , F. Paulot<sup>5,6</sup> , L. T. Murray<sup>7</sup> , and K. L. Griffin<sup>1,2,8</sup> 

<sup>1</sup>Department of Earth and Environmental Sciences, Columbia University, New York, New York, USA, <sup>2</sup>Lamont-Doherty Earth Observatory of Columbia University, Palisades, New York, USA, <sup>3</sup>Division of Engineering and Applied Science and Department of Earth and Planetary Sciences, Harvard University, Cambridge, Massachusetts, USA, <sup>4</sup>Cooperative Institute for Climate Science, Princeton University, Princeton, New Jersey, USA, <sup>5</sup>National Oceanic and Atmospheric Administration Geophysical Fluid Dynamics Laboratory, Princeton, New Jersey, USA, <sup>6</sup>Program in Atmospheric and Oceanic Sciences, Princeton, New Jersey, USA, <sup>7</sup>Department of Earth and Environmental Sciences, University of Rochester, Rochester, New York, USA, <sup>8</sup>Department of Ecology, Evolution, and Environmental Biology, Columbia University, New York, New York, USA

**Abstract** The ozone (O<sub>3</sub>) dry depositional sink and its contribution to observed variability in tropospheric O<sub>3</sub> are both poorly understood. Distinguishing O<sub>3</sub> uptake through plant stomata versus other pathways is relevant for quantifying the O<sub>3</sub> influence on carbon and water cycles. We use a decade of O<sub>3</sub>, carbon, and energy eddy covariance (EC) fluxes at Harvard Forest to investigate interannual variability (IAV) in O<sub>3</sub> deposition velocities ( $v_{d,O_3}$ ). In each month, monthly mean  $v_{d,O_3}$  for the highest year is twice that for the lowest. Two independent stomatal conductance estimates, based on either water vapor EC or gross primary productivity, vary little from year to year relative to canopy conductance. We conclude that nonstomatal deposition controls the substantial observed IAV in summertime  $v_{d,O_3}$  during the 1990s over this deciduous forest. The absence of obvious relationships between meteorology and  $v_{d,O_3}$  implies a need for additional long-term, high-quality measurements and further investigation of nonstomatal mechanisms.

### 1. Introduction

Tropospheric ozone (O<sub>3</sub>) is a potent greenhouse gas, deleterious to human health and vegetation, and central to the atmospheric chemistry controlling the removal of air pollutants and reactive greenhouse gases. Attributing observed variability and long-term trends in tropospheric O<sub>3</sub> to specific processes requires a clear understanding of major O<sub>3</sub> sinks [e.g., Wild, 2007]. Global atmospheric chemistry models suggest that O<sub>3</sub> dry deposition, the process by which O<sub>3</sub> is taken up by Earth's surface, is 20% of the annual global tropospheric O<sub>3</sub> loss [Lelieveld and Dentener, 2000; Stevenson et al., 2006; Wild, 2007; Young et al., 2013]. However, O<sub>3</sub> deposition is highly parameterized and varies widely across these models [Hardacre et al., 2015]. Poor mechanistic understanding of the processes leading to O<sub>3</sub> deposition [Zhang et al., 2003; Pleim and Ran, 2011; Wolfe et al., 2011] precludes our ability to characterize variability in this sink accurately. Here we examine interannual variability (IAV) in O<sub>3</sub> deposition velocities ( $v_{d,O_3}$ ) at Harvard Forest, a broadleaf deciduous forest in Massachusetts (MA), USA, using 11 years of O<sub>3</sub> eddy covariance (EC) measurements.

Turbulence above a forest facilitates contact between vegetation and ambient O<sub>3</sub>, but the dominant control on daytime  $v_{d,O_3}$  is usually the canopy resistance [Fuentes et al., 1992; Gao and Wesely, 1995; Mikkelsen et al., 2004], which has stomatal and nonstomatal components [e.g., Fowler et al., 2009]. Stomatal uptake of O<sub>3</sub> is around 40–60% of the total [Fowler et al., 2009] and can be injurious to vegetation [e.g., Wittig et al., 2009; Ainsworth et al., 2012], thereby changing the ability of vegetation to act as an O<sub>3</sub> and carbon sink and transpire water vapor [Sitch et al., 2007; Sun et al., 2012; Lombardozzi et al., 2013]. Variability in nonstomatal deposition is poorly characterized [Fowler et al., 2009; Rannik et al., 2012; Neiryck et al., 2012]. Recent field-based evidence suggests that nonstomatal processes include thermal decomposition and light-mediated and aqueous chemical reactions on vegetation and soil [Fowler et al., 2009; Ganzeveld et al., 2015; Fumagalli et al., 2016]. If deposition is considered to include all of the processes leading to O<sub>3</sub> loss below the top of the canopy, then chemical reactions with biogenic volatile organic compounds (BVOCs) or nitrogen oxide (NO) in canopy air are nonstomatal pathways. However, distinguishing between nonstomatal deposition to surfaces and in-canopy O<sub>3</sub> chemical destruction is relevant for estimating the production of secondary organic aerosol precursors [e.g., O'Dowd et al., 2002; Hallquist et al., 2009].

Several long-term studies show that nonstomatal  $O_3$  deposition dominates the total on a multiyear average basis (e.g., pine plantation [Fares *et al.*, 2010], moorland [Fowler *et al.*, 2001], spruce forest [Mikkelsen *et al.*, 2004], and mixed temperate forest [Neiryck *et al.*, 2012]). However, stomatal  $O_3$  deposition dominates the multiyear mean total at a subalpine site [Turnipseed *et al.*, 2009] and a boreal forest [Rannik *et al.*, 2012]. Although several observational studies demonstrate IAV in flux and some include analysis on IAV in canopy, stomatal, and/or nonstomatal components [Munger *et al.*, 1996; Fowler *et al.*, 2001; Mikkelsen *et al.*, 2004; Gerosa *et al.*, 2009; Fares *et al.*, 2010; Rannik *et al.*, 2012], we lack a complete evaluation of IAV in stomatal versus nonstomatal deposition and the relative contributions to IAV in total deposition.

The present understanding of the controls on variability in  $v_{d,O_3}$  over temperate deciduous forests is informed mainly by short-term observational studies [e.g., Fuentes *et al.*, 1992; Finkelstein *et al.*, 2000]. The decade-long  $O_3$  EC data set from Harvard Forest is unique for temperate deciduous forests. Here we explicitly quantify IAV over 11 years, focusing on  $v_{d,O_3}$  in order to probe variability in the strength of this  $O_3$  sink irrespective of near-surface  $O_3$  concentrations. We extend our summertime analysis to stomatal and nonstomatal  $O_3$  deposition and attempt to identify environmental drivers of the  $v_{d,O_3}$  IAV. Knowledge of IAV in the depositional sink is necessary to interpret observed long-term trends and IAV in surface  $O_3$ .

Current global models typically utilize  $O_3$  dry deposition routines based on the Wesely [1989] parameterization (“the Wesely scheme”) [e.g., Hardacre *et al.*, 2015]. This scheme is designed to represent the diel cycle of deposition on time scales of at least a few weeks and coarse spatial resolution [Wesely, 1989]. The Wesely scheme is a resistance-in-series parameterization that includes resistances posed by turbulence, molecular diffusion, and the canopy, which incorporates stomatal and nonstomatal resistances. The rates of nonstomatal deposition in the Wesely scheme do not vary with meteorology aside from solar radiation and canopy wetness.

We show substantial IAV in  $v_{d,O_3}$  from  $O_3$  EC measurements at Harvard Forest. This IAV is not simulated by a widely used chemistry-transport model with a modified Wesely scheme. We use the wealth of meteorological and biophysical observations at Harvard Forest to investigate  $O_3$  dry deposition in a traditional resistance-in-series framework, acknowledging limitations with this approach [Baldochi *et al.*, 1987; Erismann *et al.*, 1994; Wesely and Hicks, 2000]. By using independent methods to determine stomatal conductance and estimating nonstomatal conductance as the residual from the total canopy conductance, we probe the changing roles of stomatal versus nonstomatal  $O_3$  deposition from year to year.

## 2. Methodology

### 2.1. Observations at Harvard Forest

Observations are from the red oak-dominated Environmental Measurement Site at Harvard Forest (42°538′N, 72°171′W) in MA, USA [Munger and Wofsy, 1999b]. We calculate 11 years (1990–2000) of hourly  $O_3$  deposition velocities ( $v_{d,O_3}$ ) from  $O_3$  eddy covariance (EC) fluxes and concentrations from 5 m above mean canopy height (24 m) [Munger *et al.*, 1996] (Text S1 in the supporting information). Other Harvard Forest micrometeorological and biophysical observations are described in section 2.2, Table S1 in the supporting information, and Texts S2 and S3.

### 2.2. Resistance-in-Series Framework

$O_3$  dry deposition is typically described in a resistance-in-series framework analogous to the treatment of resistances in Ohm’s law for electrical circuits:

$$v_{d,O_3} = (R_a + R_b + R_c)^{-1} \quad (1)$$

Using the  $v_{d,O_3}$  from  $O_3$  EC and other observations at Harvard Forest under this framework, we separate the total resistance ( $v_{d,O_3}^{-1}$ ) into aerodynamic ( $R_a$ ), quasi-laminar ( $R_b$ ), and canopy ( $R_c$ ) resistances. We focus on stomatal and nonstomatal contributions to canopy conductance ( $R_c^{-1}$ ), examining 1 June to 15 September (JJAS15) averages for all quantities as this framework breaks down when the canopy is not fully developed. Averaging across summer also serves to minimize the uncertainty on all components calculated with hourly observations.

The aerodynamic resistance ( $R_a$ ) is the resistance posed by turbulence and derived from Fick's law. See Text S2 for details on the parameterization used [Paulson, 1970; Businger *et al.*, 1971; Högström, 1988; Foken, 2006, 2008; Meyers *et al.*, 1998; Wu *et al.*, 2015]. The quasi-laminar resistance ( $R_b$ ) is the resistance posed by molecular diffusion in the boundary layer that forms around individual canopy elements. We adopt the Wesely and Hicks [1977] formulation commonly used in the current generation of global models [e.g., Ganzeveld and Lelieveld, 1995; Wang *et al.*, 1998; Emmons *et al.*, 2010] as described in Text S2. Using formulations of  $R_b$  that address limitations to the K-theory approach [Massman, 1999] or the lack of information about leaf length scales [Jensen and Hummelshøj, 1995, 1997] in the formulation used has little influence on our results. We calculate hourly canopy resistance ( $R_c$ ) using equation (1) and invert to get hourly canopy conductance ( $g_c$ ). Uncertainties in our  $g_c$  estimate result from uncertainties in turbulent flux observations [Goulden *et al.*, 1996; Richardson *et al.*, 2006] and in the parameterizations of  $R_a$  and  $R_b$  (Text S2). We remove outliers by requiring hourly  $g_c$  to fall within the mean  $\pm 3$  standard deviations of the hourly time series during JJAS15 1992–2000 (i.e., we retain 99.7% of the data;  $\mu = 0.51 \text{ cm s}^{-1}$  and  $\sigma = 0.96 \text{ cm s}^{-1}$ ). We assume that  $g_c$  is the sum of parallel uptake pathways: stomatal conductance ( $g_s$ ) and nonstomatal conductance ( $g_{ns}$ ) [e.g., Massman *et al.*, 1994].

$$g_c = g_s + g_{ns} \quad (2)$$

We calculate hourly  $g_s$  using two independent process-level models driven by observations from Harvard Forest. One model incorporates carbon dioxide ( $\text{CO}_2$ ) EC flux, and the other uses water vapor ( $\text{H}_2\text{O}$ ) EC flux.

### 2.3. Stomatal Conductance ( $g_s$ ) Models

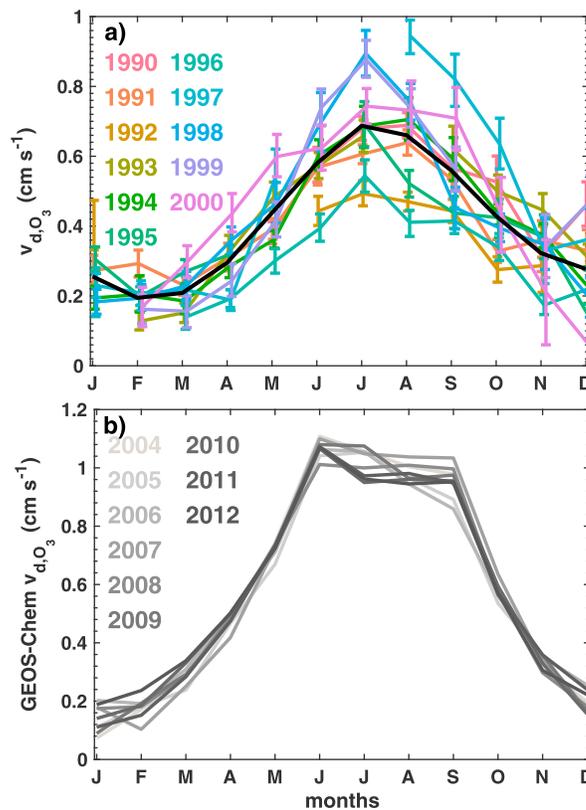
For an estimate of  $g_s$  based on  $\text{H}_2\text{O}$  EC, we use the Shuttleworth *et al.* [1984] inversion of the Penman-Monteith equation (hereafter, P-M). We account for the roughly 10% of the observed  $\text{H}_2\text{O}$  flux that comes from below the canopy [Moore *et al.*, 1996] by subtracting 10% of hourly  $\text{H}_2\text{O}$  flux before use in P-M, noting that this may be an oversimplification that fails to capture short-term variability. The second  $g_s$  estimate, based on  $\text{CO}_2$  EC, uses the Lin *et al.* [2015]  $g_s$  model (hereafter, L15) based on optimization of photosynthesis and minimization of transpiration [Cowan and Farquhar, 1977; Medlyn *et al.*, 2011]. We employ gross primary productivity (GPP) at Harvard Forest [Urbanski *et al.*, 2007] as the best estimate of net photosynthesis for L15 (GPP may be an upper limit as leaf respiration is not accounted for). We scale both  $g_s$  estimates for  $\text{H}_2\text{O}$  by the ratio of  $\text{O}_3$  diffusivity to  $\text{H}_2\text{O}$  diffusivity (0.61). See Text S3 for details.

We also use the single-point version of the Geophysical Fluid Dynamics Laboratory (GFDL) land model version 3 (LM3) [Shevliakova *et al.*, 2009; Milly *et al.*, 2014] configured for Harvard Forest and driven by Sheffield *et al.* [2006] meteorology (combination of reanalysis products and recent observation-based data sets) to examine  $g_s$ . LM3 simulates  $g_s$  according to Leuning [1995] with modification for water stress [Milly *et al.*, 2014]. When the simulated leaf area index goes to zero in LM3 due to drought [Milly *et al.*, 2014] during August 1991 and 1997 and September 1999, we consider  $g_s$  as missing data.

## 3. Interannual Variability (IAV) in Monthly Mean $\text{O}_3$ Deposition Velocity ( $v_{d,\text{O}_3}$ )

We examine here seasonal cycles of monthly daytime mean  $v_{d,\text{O}_3}$ . We define daytime as 09:00 A.M. to 03:00 P.M. because there is daylight during this time period for all months of the year. During summer, some years have consistently high (1998 and 1999) or low (1992 and 1996) monthly daytime mean  $v_{d,\text{O}_3}$  (Figure 1a). In each month, monthly daytime mean  $v_{d,\text{O}_3}$  during the lowest versus highest year differs by about a factor of 2. Using a bootstrapping technique (Text S4), we find that for each month, the highest and lowest monthly daytime mean  $v_{d,\text{O}_3}$  are significantly different from each other at a 95% confidence level (Figure 1a). The shapes of the  $v_{d,\text{O}_3}$  seasonal cycles also differ by year, with the caveat that missing data prevent an illustration of the complete seasonal cycle during several years. Monthly daytime mean  $\text{O}_3$  fluxes differ by about a factor of 2 in each month (Figure S1 in the supporting information), but the ranking by year and seasonality of  $v_{d,\text{O}_3}$  does not simply follow that of the fluxes.

The substantial IAV in  $v_{d,\text{O}_3}$  from Harvard Forest  $\text{O}_3$  eddy covariance (EC) observations is not apparent in 9 years (2004–2012) of daytime mean  $v_{d,\text{O}_3}$  at Harvard Forest in the Goddard Earth Observing System–Chemistry model (GEOS-Chem) (Figure 1b), a widely used chemistry-transport model with a modified Wesely scheme [Wang *et al.*, 1998; Bey *et al.*, 2001; van Donkelaar *et al.*, 2008] and driven by observed meteorology [Rienecker *et al.*, 2011]. While we only have hourly  $v_{d,\text{O}_3}$  for the years 2004–2012 available from this



**Figure 1.** Monthly daytime (09:00 A.M. to 03:00 P.M.) mean  $v_{d,O_3}$  at Harvard Forest (a) calculated using a bootstrapping technique (Text S4) on  $v_{d,O_3}$  from  $O_3$  eddy covariance observations and (b) from GEOS-Chem (v9-02; <http://geos-chem.org>; 42°N, 73°W; deciduous land cover type). Black indicates the multiyear mean, and the colors denote the individual years in Figure 1a; the shades of grey denote the individual years in Figure 1b. The error bars in Figure 1a indicate the 95% confidence intervals. If the percentage of days with missing data for any hour between 09:00 A.M. and 03:00 P.M. for a particular month and year is greater than 75%, then the monthly mean is not included.

responsible for the observed IAV in  $v_{d,O_3}$  is crucial to ensure that key processes are incorporated into  $O_3$  deposition parameterizations in the models used to interpret observations and to project changes under emissions and climate scenarios.

The tendency for monthly daytime mean  $v_{d,O_3}$  to remain consistent in magnitude during a given summer implies a role for environmental controls that persist over seasonal time scales. We seek to identify climate drivers of this IAV but find no obvious relationship between 1 June and 15 September (JJAS15) mean  $v_{d,O_3}$  and net radiation, photosynthetically active radiation, temperature, atmospheric vapor pressure deficit, relative humidity, precipitation [Boose and Gould, 1999], wind speed, wind direction, friction velocity,  $O_3$  concentration or bud break [Jeong et al., 2012] at Harvard Forest, or statewide Palmer Drought Severity Index (Table S1). Soil NO emissions are unlikely to contribute substantially to  $v_{d,O_3}$  at Harvard Forest [Munger et al., 1996; Horii et al., 2004].

Recent field-based work [Mikkelsen et al., 2000; Kurpius and Goldstein, 2003; Goldstein et al., 2004; Hogg et al., 2007; Fares et al., 2010, 2012, 2014; Rannik et al., 2012; Neiryneck et al., 2012; Launiainen et al., 2013] conflicts as to whether in-canopy  $O_3$  destruction by BVOCs such as terpenoids is a key nonstomatal pathway determining variability in observed  $O_3$  deposition. Using June–August mean monoterpene emissions simulated by GEOS-Chem (Table S1), we find that a high  $v_{d,O_3}$  year, 1999, matches a high year for monoterpene emission, while 1992 and 1996 are low years for both monoterpene emission and  $v_{d,O_3}$ . This finding implies that in-canopy

$2^\circ \times 2.5^\circ$  v9-02 simulation, examination of 1990–2000 daily mean  $v_{d,O_3}$  from a  $4^\circ \times 5^\circ$  v9-01-03 simulation shows a similar lack of IAV. The factors controlling IAV in monthly mean  $v_{d,O_3}$  are therefore not represented adequately in GEOS-Chem. As Walker [2014] demonstrates a strong sensitivity of surface  $O_3$  over the eastern U.S. to  $v_{d,O_3}$  in GEOS-Chem, the poor representation of IAV may lead to model overemphasis of the role of emissions on observed  $O_3$  IAV.

Our understanding of  $v_{d,O_3}$  over temperate deciduous forests has been largely based on  $O_3$  EC data sets that span a few years or less: at Kane Experimental Forest from 1997 [Finkelstein et al., 2000; Finkelstein, 2001; Zhang et al., 2001, 2002, 2006], Harvard Forest from 1990 to 1994 [Munger et al., 1996] and from 2000 [Wu et al., 2011], and Camp Borden from 1988 [Fuentes et al., 1992; Padro, 1996]. The IAV in 11 years of  $v_{d,O_3}$  suggests that model development with short-term (weeks to a few years) observations over temperate deciduous forests may restrict model representation to capturing the dynamics of solely high or low  $v_{d,O_3}$  years. The lack of IAV in models may contribute to intermodel and model-observation differences that span a factor of 2 in  $v_{d,O_3}$  [Schwede et al., 2011; Park et al., 2014; Val Martin et al., 2014; Hardacre et al., 2015]. Understanding the mechanisms

reactions between terpenoids and  $O_3$  may contribute to IAV in  $v_{d,O_3}$ , although the yearly ranking of monoterpene emission magnitude does not simply explain the observed  $v_{d,O_3}$  ranking (Table S1).

Figure 1a shows the steep declines in  $v_{d,O_3}$  after July during 1995, 1996, 1998, and 1999, all years with late-summertime soil moisture deficits [Savage and Davidson, 2001]. For other years, the decline is weaker or shifts to after August–September. The occurrence of drought at Harvard Forest thus may be an important control on the timing of the  $v_{d,O_3}$  downturn at the end of summer, with the caveat that soil moisture was not measured during several years.

Half of the full range of JJAS15 daytime mean  $v_{d,O_3}$  ( $0.43 \text{ cm s}^{-1}$ ) is spanned by years with severe drought (1995 and 1999 [Savage and Davidson, 2001]; Table S1). One of these years, 1999, is a high summertime  $v_{d,O_3}$  year, whereas daytime mean  $v_{d,O_3}$  during the other year, 1995, is  $0.01\text{--}0.14 \text{ cm s}^{-1}$  less than the multiyear mean (Figure 1a). During August–October 1997, a year without a late-summertime drought [Savage and Davidson, 2001], the magnitude of  $v_{d,O_3}$  is at least  $0.11\text{--}0.19 \text{ cm s}^{-1}$  higher than other years (Figure 1a). Concurrent, longer-term observations of soil moisture and  $O_3$  deposition are needed to pinpoint the role of drought on the ranking of  $v_{d,O_3}$  across years at temperate deciduous forests.

Leaf area index (LAI) is a primary driver of seasonality in observed  $v_{d,O_3}$  [Gao and Wesely, 1995; Finkelstein et al., 2000] and long-term trends in simulated  $v_{d,O_3}$  [Ganzeveld et al., 2010; Wu et al., 2012; Fu and Tai, 2015], but its role in IAV of  $v_{d,O_3}$  is unknown. LAI observations at Harvard Forest from 1998 to 1999 and 2005 to 2014 [Munger and Wofsy, 1999a] (Text S2) indicate that LAI during June 1998 is  $0.54$  and  $0.57 \text{ m}^2 \text{ m}^{-2}$  lower than 1999 and the multiyear mean, respectively, due to stunted canopy growth [Urbanski et al., 2007]. June daytime mean  $v_{d,O_3}$  during 1998, however, is about the same magnitude as 1999 and  $0.14 \text{ cm s}^{-1}$  higher than the multiyear mean (Figure 1a), suggesting that the response of  $v_{d,O_3}$  to changes in LAI of this magnitude may be weaker than suggested by previous studies [Charusombat et al., 2010; Schwede et al., 2011; Fu and Tai, 2015; Ran et al., 2016].

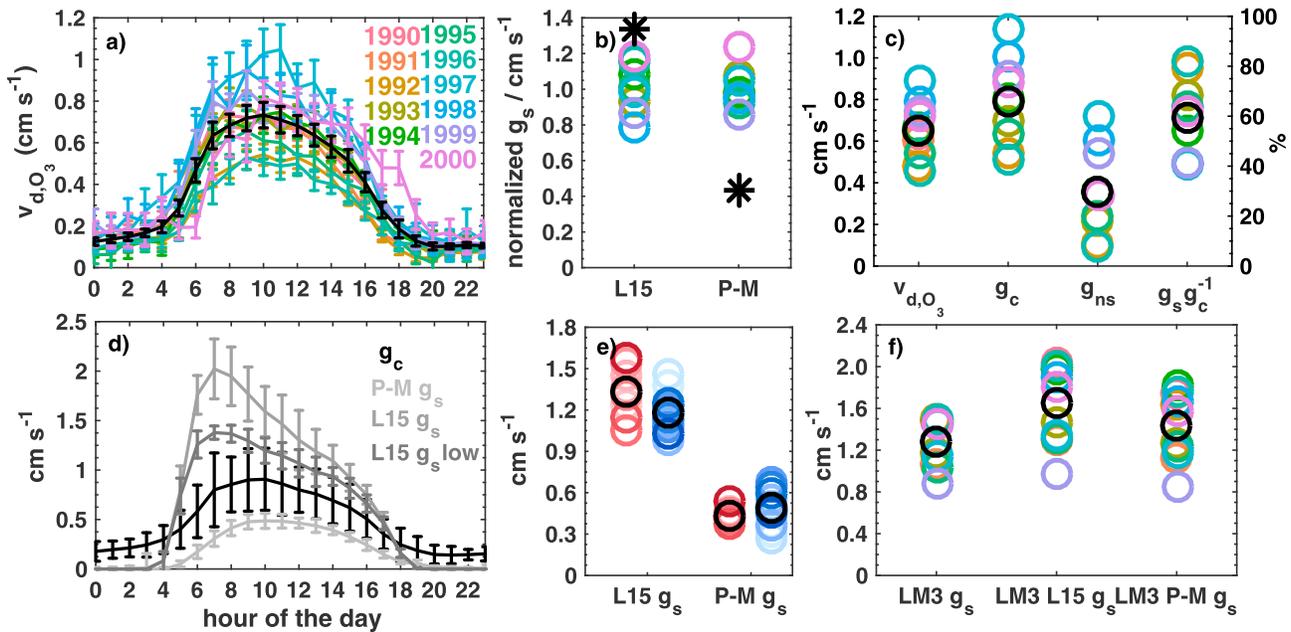
#### 4. Interannual Variability (IAV) in Stomatal Versus Nonstomatal $O_3$ Deposition

We now examine IAV in 1 June to 15 September (JJAS15) daytime mean  $O_3$  deposition velocities ( $v_{d,O_3}$ ). We also examine diurnal cycles to probe the mechanisms that control  $v_{d,O_3}$ . We find IAV in the shape of the JJAS15 mean diurnal cycle (Figure 2a): some years have a broad daytime maximum (1992 and 1996), while others have a morning or afternoon peak (1993 and 1995 versus 1997 and 2000).

JJAS15 daytime mean canopy resistance ( $R_c$ ) exceeds both the aerodynamic and quasi-laminar resistances by roughly an order of magnitude (Figure S2), confirming that  $R_c$  controls IAV in JJAS15 daytime  $v_{d,O_3}$ . We investigate how stomatal and nonstomatal conductances ( $g_s$  and  $g_{ns}$ ) impact IAV in  $R_c$  using two process-level  $g_s$  models driven by Harvard Forest observations and derived parameters (e.g., GPP; section 2.2 and Text S3). During 1992–2000, JJAS15 daytime mean  $g_s$  spans  $1.1\text{--}1.6 \text{ cm s}^{-1}$  for the Lin et al. [2015] model (L15) and  $0.37\text{--}0.54 \text{ cm s}^{-1}$  for the Shuttleworth et al. [1984] inversion of the Penman-Monteith (P-M) equation. Figure 2b shows the JJAS15 daytime mean  $g_s$  for 1992–2000 (values for each year are normalized by the respective multiyear means, which are shown in  $\text{cm s}^{-1}$  in black asterisks). Despite the discrepancies in magnitude, both estimates consistently show little IAV: the relative interannual spread of daytime mean  $g_s$  for 1992–2000 is 10.9% for P-M and 13.8% for L15. Neither approach to estimating  $g_s$  yields a ranking of low to high years that matches the  $v_{d,O_3}$  ranking (e.g., high  $g_s$  years are not high  $v_{d,O_3}$  years; Figures 2b and 2c). The similarities in IAV between P-M and L15 suggest that  $g_s$  does not control IAV in JJAS15 daytime mean  $v_{d,O_3}$  with the caveat that these models may not be sufficiently sensitive to low-frequency environmental controls.

For each  $g_s$  estimate, the shape of the mean diurnal cycle for most years deviates little from the shape of the multiyear mean diurnal cycle (Figures 2d, S3b, and S3d). Assuming that existing  $g_s$  models can adequately represent IAV in the  $g_s$  diurnal cycle, we conclude that deviations from the shape of the climatological  $v_{d,O_3}$  diurnal cycle (Figure 2a) are largely controlled by  $g_{ns}$ .

We place more confidence in P-M than L15 for the following reasons. First, a recent finding using isotopic methods suggests that standard partitioning between daytime ecosystem respiration and GPP overestimates GPP by 25% during June–July at Harvard Forest [Wehr et al., 2016]. This finding challenges the assumptions inherent in photosynthesis-based approaches to estimate  $g_s$  (e.g., L15). Second, the magnitude of P-M  $g_s$  is less than  $g_c$  (Figure 2d), so P-M  $g_s$  can be accommodated in our resistance-in-series framework for  $O_3$  deposition,



**Figure 2.** (a) The 1 June to 15 September (JJAS15) hourly mean  $O_3$  deposition velocities ( $v_{d,O_3}$ ) from observations at Harvard Forest. Black indicates the multiyear mean. The error bars indicate the two standard errors. JJAS15 daytime (09:00 A.M. to 03:00 P.M.) mean (b) L15 and P-M stomatal conductance ( $g_s$ ) for each year, normalized to the respective multiyear means, which are shown in asterisks in  $cm\ s^{-1}$ , and (c)  $v_{d,O_3}$ , canopy conductance ( $g_c$ ), and nonstomatal conductance ( $g_{ns}$ ;  $cm\ s^{-1}$ ) and the percentage stomatal contribution to  $g_c$  ( $g_s\ g_c^{-1}$ ; %); the latter two are inferred using P-M  $g_s$ . (d) JJAS15 multiyear hourly mean  $g_c$  and  $g_s$  from P-M, L15, and L15 without hourly values greater than  $3\ cm\ s^{-1}$  (“L15  $g_s$  low”;  $cm\ s^{-1}$ ). The error bars indicate 2 standard deviations (interannual spread). These quantities are calculated using observations during 1992–2000 (section 2.2 and Text S3). (e) JJAS15 daytime mean P-M and L15  $g_s$  ( $cm\ s^{-1}$ ) driven by Harvard Forest observations for 1992–2014. The shades of red indicate the years when Harvard Forest  $O_3$  EC observations are available (1992–2000); other years are in shades of blue. Black indicates the multiyear means for 1992–2000 and 2001–2014. (f) JJAS15 daytime mean  $g_s$  simulated by GFDL LM3 at Harvard Forest for 1990–2000 and L15 and P-M  $g_s$  calculated with LM3-archived fields (Text S5). For all quantities, the seasonal mean by hour has at least 25 days of nonmissing data.

whereas L15  $g_s$  yields an unphysical, negative  $g_{ns}$ . We thus use P-M to examine IAV in the relative stomatal contribution to canopy conductance ( $g_s\ g_c^{-1}$  or “stomatal fraction”) and  $g_{ns}$  (Figures 2c, S3c, and S3e).

From year to year, the JJAS15 daytime mean P-M-derived stomatal fraction spans 41–82% (multiyear mean is 59%) at Harvard Forest (Figure 2c). The summertime stomatal fraction over Kane Experimental Forest is 55% for 1997 [Zhang et al., 2006]. Estimates for mixed temperate forests are 34% for 2002 [Hogg et al., 2007], 28% for 2000–2010 [Neiryck et al., 2012], 50% for 1998 [Zhang et al., 2006], and 47% for 2007 [Nunn et al., 2010]. JJAS15 mean  $g_s$  accounts for a substantial fraction of  $g_c$  each year at Harvard Forest, but the variance in P-M  $g_s$  across years is 5% of the variance in daytime mean  $g_c$ , in contrast to 106% for P-M-derived  $g_{ns}$ . The ranking across years of  $v_{d,O_3}$  and  $g_c$  is similar to that of  $g_{ns}$  (and the inverse that of the stomatal fraction; Figure 2c), implying that  $g_{ns}$  drives IAV in  $v_{d,O_3}$ .

Meteorological and carbon and energy eddy covariance (EC) measurements have continued after  $O_3$  EC was discontinued at Harvard Forest, allowing us to compute P-M and L15 for more recent years (Figures 2e and S4). The relative interannual spreads in P-M and L15  $g_s$  estimates are 26.9% and 11.6% for 2001–2014. While the relative spread in L15 slightly decreases, the P-M relative spread for 2001–2014 is 2.5 times that for 1992–2000. This finding raises the possibility of decadal variability in the contribution of  $g_s$  to IAV in  $g_c$ . Our conclusion that  $g_{ns}$  drives IAV in JJAS15 mean  $v_{d,O_3}$  thus may be limited to 1992–2000.  $O_3$  deposition and coincident meteorological observations are needed for several decades to elucidate more clearly the impact of IAV in  $g_s$  on  $g_c$ .

We return to 1990–2000 to examine  $g_s$  as simulated by GFDL LM3 at Harvard Forest. The relative interannual spread of JJAS15 daytime mean LM3-simulated  $g_s$  is 18.3%, slightly higher but similar to that for the 1990–2000 observation-driven estimates. The ranking of years for LM3-simulated  $g_s$  does not follow that for  $v_{d,O_3}$  from  $O_3$  EC (Figures 2c and 2f), consistent with our conclusion from the observation-driven  $g_s$  estimates that IAV in  $g_s$  does not control IAV in  $v_{d,O_3}$  at Harvard Forest during the 1990s. Similar to the

observation-driven L15  $g_s$ , we find that the LM3-simulated  $g_s$  is greater than  $g_c$ , indicating unphysical, negative  $g_{ns}$  (Figures 2c and 2f). Even if we scale the LM3-simulated  $g_s$  to the magnitude of the observation-driven P-M 1992–2000 JJAS15 daytime mean  $g_s$  (Figure 2b), the variance only explains 14% of the variance in  $g_c$  across years, implying a dominant role for IAV in  $g_{ns}$  on  $g_c$ .

We use LM3 to test how well the P-M and L15 approaches capture the IAV in LM3-simulated  $g_s$  (Figures 2f and S5). P-M and L15  $g_s$  are calculated from archived fields (Text S5). Relative interannual spreads are similar but slightly higher for LM3-driven L15 and P-M estimates (22.5% and 21.9%) than for LM3-simulated  $g_s$ . The LM3-driven P-M and L15 approaches emulate the ranking across years in LM3-simulated  $g_s$  (Figure 2f), indicating that both methods are capable of capturing IAV in LM3-simulated  $g_s$ . This consistency across independent approaches lends confidence to constraining  $g_s$  IAV using observation-driven P-M and L15.

The diurnal course of summertime mean  $g_s$  remains uncertain. The 1992–2000 multiyear mean diurnal cycle calculated via P-M has a broad daytime maximum, whereas L15 simulates  $g_s$  with an early-morning peak declining into the afternoon (Figures 2d, S3b, and S3d). This early-morning peak in observation-driven L15  $g_s$  also occurs in LM3-driven L15 (Figure S5) but is produced neither by LM3 (Figure S5) nor by P-M estimates (Figures 2d, S5, and S3b). Leaf-level  $g_s$  measurements during summers 1991–1992 [Bassow and Bazzaz, 1999] offer little constraint on the summertime mean diurnal cycle (Figure S6). Differences (IAV, magnitude, diurnal-cycle shape) between observation-driven L15 and P-M for 1992–2000 lessen when we omit hourly  $g_s$  greater than  $3 \text{ cm s}^{-1}$  from L15 (Figure 2d). For 84% of times that  $g_s$  is greater than  $3 \text{ cm s}^{-1}$  during JJAS15 for 05:00 A.M. to 06:00 P.M., atmospheric vapor pressure deficit (VPD) is less than 0.02 kPa, suggesting that some of the differences between P-M and L15 are from the sensitivity of  $g_s$  to low VPD in L15. Note that when L15  $g_s$  is greater than  $3 \text{ cm s}^{-1}$  during JJAS15 05:00 A.M. to 06:00 P.M., mean GPP is  $1.3 \text{ mol m}^{-2} \text{ s}^{-1}$  lower when VPD is less than 0.02 kPa. If stomatal and nonstomatal processes operate most strongly at different times of the day, constraining the stomatal contribution to the summertime mean diurnal cycle of  $v_{d,O_3}$  should provide insight into driving nonstomatal mechanisms.

## 5. Discussion and Conclusion

The understanding of  $O_3$  removal by temperate deciduous forests, prevalent over the eastern USA, is largely based on short-term observations, with interannual variability (IAV) in  $O_3$  deposition receiving little attention. However, source attribution and top-down approaches using observations (e.g., satellite data) to infer precursor emissions and their IAV rely on accurate estimates of sinks such as  $O_3$  dry deposition. Our analysis using 11 years (1990–2000) of  $O_3$  eddy covariance (EC) at Harvard Forest, a broadleaf deciduous forest in the northeastern USA, reveals substantial IAV in  $O_3$  deposition velocities ( $v_{d,O_3}$ ). This IAV is not captured by a chemistry-transport model with a modified Wesely [1989] dry deposition scheme that is frequently applied for source attribution, despite a known model sensitivity of surface  $O_3$  over the eastern USA to  $O_3$  deposition [Walker, 2014].

Examining  $O_3$  dry deposition in the traditional resistance-in-series framework with two independent stomatal conductance ( $g_s$ ) models driven by Harvard Forest observations, we conclude that IAV in summertime  $v_{d,O_3}$  during 1992–2000 mainly reflects nonstomatal processes. During other periods (e.g., 2001–2014), stomatal uptake may contribute substantially to IAV in  $v_{d,O_3}$  at Harvard Forest, as suggested by a factor of 2 increase in IAV in  $g_s$  estimated from  $H_2O$  EC during 2001–2014 (when  $O_3$  EC are unavailable) versus 1992–2000. Constraining stomatal  $O_3$  uptake is necessary to quantify the impacts of  $O_3$ -induced damage on long-term trends and variability in GPP [e.g., Sitch et al., 2007; Fares et al., 2013; Yue et al., 2016] and water use efficiency [e.g., Keenan et al., 2013, 2014; Holmes, 2014; Hoshika et al., 2015; Lombardozzi et al., 2015].

Summertime daytime mean nonstomatal conductance as inferred from the  $g_s$  estimate based on  $H_2O$  EC at Harvard Forest varies from 20 to 58% of canopy conductance during 1992–2000 (41% on a multiyear basis). Similarly, the range of the summertime daytime mean nonstomatal contribution is 43–65% during 2001–2006 (multiyear mean is 52%) at a ponderosa pine plantation [Fares et al., 2010]. The nonstomatal contribution to total deposition during a growing season or on a multiyear basis is also substantial (greater than 25%) at other temperate deciduous and mixed forests [Zhang et al., 2006; Hogg et al., 2007; Nunn et al., 2010; Neiryck et al., 2012] and over other land cover types [Zeller and Nikolov, 2000; Fowler

et al., 2001; Mikkelsen et al., 2004; Altimir et al., 2006; Cieslik, 2009; Gerosa et al., 2009; Rannik et al., 2012; Fares et al., 2012, 2014; Zona et al., 2014].

Pinpointing the role of climatic drivers of IAV in  $O_3$  dry deposition will improve projected changes of this process with climate. The persistent IAV in the magnitude of monthly mean  $v_{d,O_3}$  at Harvard Forest during summer 1990–2000 suggests that longer-term (several weeks to months) environmental conditions determine the magnitude of nonstomatal conductance and subsequently low versus high  $v_{d,O_3}$  years. Earlier studies [Bauer et al., 2000; Gerosa et al., 2009; Rannik et al., 2012] also suggest that there are longer-term controls on  $O_3$  dry deposition. We find that the environmental variables (e.g., relative humidity, friction velocity, temperature, solar radiation, and NO concentration [Fowler et al., 2001; Zhang et al., 2002; Altimir et al., 2006; Hogg et al., 2007; Lamaud et al., 2009; Coyle et al., 2009; Rannik et al., 2012; Neiryck et al., 2012]) shown to influence daytime nonstomatal deposition on various time scales during summer at other monitoring sites do not emerge as controls on summertime mean IAV at Harvard Forest. However, the generalizability of  $O_3$  deposition observations at Harvard Forest and other sites needs to be established. Combining long-term ecosystem-scale measurements over different land cover types is necessary for reliable scaling for global  $O_3$  dry deposition estimates.

In-canopy  $O_3$  destruction by terpenoids may contribute to nonstomatal deposition at Harvard Forest even though the forest is not considered to emit high terpene levels [McKinney et al., 2011]. We speculate that IAV in  $v_{d,O_3}$  at Harvard Forest is controlled by multiple nonstomatal depositional pathways, such as thermal decomposition and aqueous reactions on water films and light-mediated reactions on leaf waxes and soil and in-canopy chemistry [Fowler et al., 2009; Fumagalli et al., 2016], that vary in complex ways with environmental parameters. We emphasize the need for multidecadal observations over temperate deciduous forests to quantify nonstomatal versus stomatal  $O_3$  deposition and attribute variability to meteorological and biophysical drivers.

#### Acknowledgments

We acknowledge support from NOAA grant NA14OAR4310133 and an NSF Graduate Research Fellowship (DGE-16-44869) to O.E.C. Harvard Forest observations were supported in part by the U.S. Department of Energy, Office of Science (BER), and NSF Long-Term Ecological Research. O.E.C. acknowledges a useful conversation with Harald Rieder. Please contact O.E.C. for the data used here. This is Lamont-Doherty Earth Observatory contribution 8077. We acknowledge the useful comments and feedback from two anonymous reviewers.

#### References

- Ainsworth, E. A., C. R. Yendrek, S. Sitch, W. J. Collins, and L. D. Emberson (2012), The effects of tropospheric ozone on net primary productivity and implications for climate change, *Annu. Rev. Plant Physiol. Plant Mol. Biol.*, doi:10.1146/annurev-arplant-042110-103829.
- Altimir, N., P. Kolari, J.-P. Tuovinen, T. Vesala, J. Bäck, T. Suni, M. Kulmala, and P. Hari (2006), Foliage surface ozone deposition: A role for surface moisture?, *Biogeosciences*, *3*, 209–228.
- Baldocchi, D. D., B. B. Hicks, and P. Camara (1987), A canopy stomatal resistance model for gaseous deposition to vegetated surfaces, *Atmos. Environ.*, *21*(1), 91–101.
- Bassow, S., and F. Bazzaz (1999), Canopy photosynthesis study at Harvard Forest 1991–1992, HF059, Harvard Forest Data Archive, Harvard Forest, Petersham, Mass.
- Bauer, M. R., N. E. Hultman, J. A. Panek, and A. H. Goldstein (2000), Ozone deposition to a ponderosa pine plantation in the Sierra Nevada Mountains (CA): A comparison of two different climatic years, *J. Geophys. Res.*, *105*, 22,123–22,136, doi:10.1029/2000JD900168.
- Bey, I., D. J. Jacob, R. M. Yantosca, J. A. Logan, B. D. Field, A. M. Fiore, Q. Li, H. Y. Liu, L. J. Mickley, and M. G. Schultz (2001), Global modeling of tropospheric chemistry with assimilated meteorology: Model description and evaluation, *J. Geophys. Res.*, *106*, 23,073–23,095, doi:10.1029/2001JD000807.
- Boose, E., and E. Gould (1999), *Shaler Meteorological Station at Harvard Forest 1964–2002, HF000*, Harvard Forest Data Archive, Harvard Forest, Petersham, Mass.
- Businger, J. A., J. C. Wyngaard, Y. Izumi, and E. F. Bradley (1971), Flux-profile relationships in the atmospheric surface layer, *J. Atmos. Sci.*, *28*, 181–189.
- Charusombat, U., D. Niyogi, A. Kumar, X. Wang, F. Chen, A. Guenther, A. Turnipseed, and K. Alapathy (2010), Evaluating a new deposition velocity module in the Noah land-surface model, *Boundary-Layer Meteorol.*, *137*, 271–290, doi:10.1007/s10546-010-9531-y.
- Cieslik, S. (2009), Ozone fluxes over various plant ecosystems in Italy, *Environ. Pollution*, *157*, 1487–1496, doi:10.1016/j.envpol.2008.09.050.
- Cowan, I. R., and G. D. Farquhar (1977), Stomatal function in relation to leaf metabolism and environment, in *Integration of Activity in the Higher Plant*, edited by D. H. Jennings, pp. 471–505, Cambridge Univ. Press, Cambridge, U. K.
- Coyle, M., E. Nemitz, R. Storeton-West, D. Fowler, and J. N. Cape (2009), Measurements of ozone deposition to a potato canopy, *Agric. For. Meteorol.*, *149*, 655–666, doi:10.1016/j.agrformet.2008.10.020.
- Emmons, L. K., et al. (2010), Description and evaluation of the Model for Ozone and Related chemical Tracers, version 4 (MOZART-4), *Geosci. Model Dev.*, *3*, 43–67, doi:10.5194/gmd-3-43-2010.
- Erisman, J. W., A. Van Pul, and P. Wyers (1994), Parameterization of surface resistance for the quantification of atmospheric deposition of acidifying pollutants and ozone, *Atmos. Environ.*, *28*(16), 2595–2607, doi:10.1016/1352-2310(94)90433-2.
- Fares, S., M. McKay, R. Holzinger, and A. H. Goldstein (2010), Ozone fluxes in a *Pinus ponderosa* ecosystem are dominated by non-stomatal processes: Evidence from long-term continuous measurements, *Agric. For. Meteorol.*, *150*(3), 420–431, doi:10.1016/j.agrformet.2010.01.007.
- Fares, S., R. Weber, J. H. Park, D. Gentner, J. Karlik, and A. H. Goldstein (2012), Ozone deposition to an orange orchard: Partitioning between stomatal and non-stomatal sinks, *Environ. Pollut.*, *169*, 258–266, doi:10.1016/j.envpol.2012.01.030.
- Fares, S., R. Vargas, M. Detto, A. H. Goldstein, J. Karlik, E. Paoletti, and M. Vitale (2013), Tropospheric ozone reduces carbon assimilation in trees: Estimates from analysis of continuous flux measurements, *Global Change Biol.*, *19*, 2427–2443, doi:10.1111/gcb.12222.

- Fares, S., F. Savi, J. Muller, G. Matteucci, and E. Paoletti (2014), Simultaneous measurements of above and below canopy ozone fluxes help partitioning ozone deposition between its various sinks in a Mediterranean oak forest, *Agric. For. Meteorol.*, *198*, 181–191, doi:10.1016/j.agrformet.2014.08.014.
- Finkelstein, P. L., T. G. Ellestad, J. F. Clarke, T. P. Meyers, D. B. Schwede, E. O. Hebert, and J. A. Neal (2000), Ozone and sulfur dioxide dry deposition to forests: Observations and model evaluation, *J. Geophys. Res.*, *105*, 15,365–15,377, doi:10.1029/2000JD900185.
- Finkelstein, P. L. (2001), Deposition velocities of SO<sub>2</sub> and O<sub>3</sub> over agricultural and forest ecosystems, *Water Air Soil Pollut.: Focus*, *1*, 49–57.
- Foken, T. (2006), 50 years of the Monin-Obukhov similarity theory, *Boundary Layer Meteorol.*, doi:10.1107/s10546-006-9048-6.
- Foken, T. (2008), *Micrometeorology*, Springer, Berlin.
- Fowler, D., C. Flechard, J. N. Cape, R. L. Storeton-West, and M. Coyle (2001), Measurements of ozone deposition to vegetation quantifying the flux, the stomatal and the non-stomatal components, *Water Air Soil Pollut.*, *130*, 63–74, doi:10.1023/A:1012243317471.
- Fowler, D., et al. (2009), Atmospheric composition change: Ecosystems–atmosphere interactions, *Atmos. Environ.*, doi:10.1016/j.atmosenv.2009.07.068.
- Fu, Y., and A. P. Tai (2015), Impact of climate and land cover changes on tropospheric ozone air quality and public health in East Asia between 1980 and 2010, *Atmos. Chem. Phys.*, *15*, 10,093–10,106, doi:10.5194/acp-15-10093-2015.
- Fuentes, J. D., T. J. Gillespie, G. den Hartog, and H. H. Neumann (1992), Ozone deposition onto a deciduous forest during dry and wet conditions, *Agric. For. Meteorol.*, *62*, 1–18.
- Fumagalli, I., C. Gruening, R. Marzuoli, S. Cieslik, and G. Gerosa (2016), Long-term measurements of NO<sub>x</sub> and O<sub>3</sub> soil fluxes in a temperate deciduous forest, *Agric. For. Meteorol.*, *228*, 205–216, doi:10.1016/j.agrformet/2016.07.011.
- Ganzeveld, L., and J. Lelieveld (1995), Dry deposition parameterization in a chemistry general circulation model and its influence on the distribution of reactive trace gases, *J. Geophys. Res.*, *100*, 20,999–21,012.
- Ganzeveld, L., L. Bouwman, E. Stehfest, D. P. van Vuuren, B. Eickhout, and J. Lelieveld (2010), Impact of future land use and land cover changes on atmospheric chemistry–climate interactions, *J. Geophys. Res.*, *115*, D23301, doi:10.1029/2010JD014041.
- Ganzeveld, L., C. Ammann, and B. Loubet (2015), Modelling atmosphere–biosphere exchange of ozone and nitrogen oxides, in *Review and Integration of Biosphere–Atmosphere Modelling of Reactive Trace Gases and Volatile Aerosols*, edited by: R.-S. Massad and B. Loubet, pp. 85–105, Springer, Netherlands.
- Gao, W., and M. L. Wesely (1995), Modeling gaseous dry deposition over regional scales with satellite observations—I. Model development, *Atmos. Environ.*, *29*(6), 727–737, doi:10.1016/1352-2310(94)00284-R.
- Gerosa, G., A. Finco, S. Mereu, M. Vitale, F. Manes, and A. B. Denti (2009), Comparison of seasonal variations of ozone exposure and fluxes in a Mediterranean Holm oak forest between the exceptionally dry 2003 and the following year, *Environ. Pollution*, *157*(5), 1737–1744, doi:10.1016/j.envpol.2007.11.025.
- Goldstein, A. H., M. McKay, M. R. Kurpius, G. W. Schade, A. Lee, R. Holzinger, and R. A. Rasmussen (2004), Forest thinning experiment confirms ozone deposition to forest canopy is dominated by reaction with biogenic VOCs, *Geophys. Res. Lett.*, *31*, L22106, doi:10.1029/2004GL021259.
- Goulden, M. L., J. W. Munger, S. M. Fan, B. C. Daube, and S. C. Wofsy (1996), Measurements of carbon sequestration by long term eddy covariance: Methods and a critical evaluation of accuracy, *Global Change Biol.*, *2*(3), 169–182.
- Hardacre, C., O. Wild, and L. Emberson (2015), An evaluation of ozone dry deposition in global scale chemistry climate models, *Atmos. Chem. Phys.*, *15*(11), 6419–6436, doi:10.5194/acp-15-6419-2015.
- Hallquist, M., et al. (2009), The formation, properties and impact of secondary organic aerosol: Current and emerging issues, *Atmos. Chem. Phys.*, *9*(14), 5155–5236, doi:10.5194/acp-9-5155-2009.
- Hogg, A., J. Uddling, D. Ellsworth, M. A. Carroll, S. Pressley, B. Lamb, and C. Vogel (2007), Stomatal and non stomatal fluxes of ozone to a northern mixed hardwood forest, *Tellus B*, *59*(3), 514–525, doi:10.1111/j.1600-0889.2007.00269.x.
- Holmes, C. D. (2014), Air pollution and forest water use, *Nature*, *507*(7491), E1–E2, doi:10.1038/nature13113.
- Horii, C. V., J. W. Munger, S. C. Wofsy, M. Zahniser, D. Nelson, and J. B. McManus (2004), Fluxes of nitrogen oxides over a temperate deciduous forest, *J. Geophys. Res.*, *109*, D08305, doi:10.1029/2003JD004326.
- Hoshika, Y., G. Katata, M. Deushi, M. Watanabe, T. Koike, and E. Paoletti (2015), Ozone-induced stomatal sluggishness changes carbon and water balance of temperate deciduous forests, *Sci. Rep.*, *5*, doi:10.1038/srep09871.
- Högström, U. (1988), Non-dimensional wind and temperature profiles in the atmospheric surface layer: A re-evaluation, *Boundary-Layer Meteorol.*, *42*, 55–78.
- Jensen, N. O., and P. Hummelshøj (1995), Derivation of canopy resistance for water vapour fluxes over a spruce forest, using a new technique for the viscous sublayer resistance, *Agric. For. Meteorol.*, *73*, 339–352.
- Jensen, N. O., and P. Hummelshøj (1997), Erratum to “Derivation of canopy resistance for water vapour fluxes over a spruce forest, using a new technique for the viscous sublayer resistance”, *Agric. For. Meteorol.*, *85*, 289.
- Jeong, S.-J., D. Medvigy, E. Shevliakova, and S. Malyshev (2012), Uncertainties in terrestrial carbon budgets related to spring phenology, *J. Geophys. Res.*, *117*, G01030, doi:10.1029/2011JG001868.
- Keenan, T. F., D. Y. Hollinger, G. Bohrer, D. Dragoni, J. W. Munger, H. P. Schmid, and A. D. Richardson (2013), Increase in forest water-use efficiency as atmospheric carbon dioxide concentrations rise, *Nature*, *499*(7458), 324–327, doi:10.1038/nature12291.
- Keenan, T. F., D. Y. Hollinger, G. Bohrer, D. Dragoni, J. W. Munger, H. P. Schmid, and A. D. Richardson (2014), Keenan et al. reply, *Nature*, *507*(7491), E2–E3, doi:10.1038/nature13114.
- Kurpius, M. R., and A. H. Goldstein (2003), Gas-phase chemistry dominates O<sub>3</sub> loss to a forest, implying a source of aerosols and hydroxyl radicals to the atmosphere, *Geophys. Res. Lett.*, *30*(7), 1371, doi:10.1029/2002GL016785.
- Lamaud, E., B. Loubet, M. Irgine, P. Stella, E. Personne, and P. Cellier (2009), Partitioning of ozone deposition over a developed maize crop between stomatal and non-stomatal uptakes, using eddy-covariance flux measurements and modelling, *Agric. For. Meteorol.*, *149*, 1385–1396, doi:10.1016/j.agrformet.2009.03.017.
- Launiainen, S., G. G. Katul, T. Grönholm, and T. Vesala (2013), Partitioning ozone fluxes between canopy and forest floor by measurements and a multi-layer model, *Agric. For. Meteorol.*, *173*, 85–99, doi:10.1016/j.agrformet.2012.12.009.
- Lelieveld, J., and F. J. Dentener (2000), What controls tropospheric ozone?, *J. Geophys. Res.*, *105*, 3531–3551, doi:10.1029/1999JD901011.
- Leuning, R. (1995), A critical appraisal of a combined stomatal photosynthesis model for C<sub>3</sub> plants, *Plant Cell Environ.*, *18*(4), 339–355, doi:10.1111/j.1365-3040.1995.tb00370.x.
- Lin, Y. S., et al. (2015), Optimal stomatal behaviour around the world, *Nat. Clim. Change*, *5*(5), 459–464, doi:10.1038/nclimate2550.
- Lombardozi, D., J. P. Sparks, and G. Bonan (2013), Integrating O<sub>3</sub> influences on terrestrial processes: Photosynthetic and stomatal response data available for regional and global modeling, *Biogeosciences*, *10*, 6815–6831, doi:10.5194/bg-10-6815-2013.

- Lombardozi, D., S. Levis, G. Bonan, P. G. Hess, and J. P. Sparks (2015), The influence of chronic ozone exposure on global carbon and water cycles, *J. Clim.*, *28*, 292–305, doi:10.1175/JCLI-D-14-00223.1.
- Massman, W. J., J. Pederson, A. Delany, D. Grantz, G. Den Hartog, H. H. Neumann, S. P. Oncley, R. Pearson, and R. H. Shaw (1994), An evaluation of the regional acid deposition model surface module for ozone uptake at three sites in the San Joaquin Valley of California, *J. Geophys. Res.*, *99*, 8281–8294, doi:10.1029/93JD03267.
- Massman, W. J. (1999), A model study of  $\text{KB H}^{-1}$  for vegetated surfaces using 'localized near-field' Lagrangian theory, *J. Hydrol.*, *223*(1), 27–43, doi:10.1016/S0022-1694(99)00104-3.
- McKinney, K. A., B. H. Lee, A. Vasta, T. V. Pho, and J. W. Munger (2011), Emissions of isoprenoids and oxygenated biogenic volatile organic compounds from a New England mixed forest, *Atmos. Chem. Phys.*, *11*, 4807–4831, doi:10.5194/acp-11-4807-2011.
- Medlyn, B. E., R. A. Duursma, D. Eamus, D. S. Ellsworth, I. C. Prentice, C. V. Barton, K. Y. Crous, P. de Angelis, M. Freeman, and L. Wingate (2011), Reconciling the optimal and empirical approaches to modelling stomatal conductance, *Global Change Biol.*, *17*(6), 2134–2144, doi:10.1111/j.1365-2486.2010.02375.x.
- Meyers, T. P., P. Finkelstein, J. Clarke, T. G. Ellestad, and P. F. Sims (1998), A multilayer model for inferring dry deposition using standard meteorological measurements, *J. Geophys. Res.*, *103*(D17), 22,645–22,661, doi:10.1029/98JD01564.
- Mikkelsen, T. N., H. Ro-Poulsen, K. Pilegaard, M. F. Hovmand, N. O. Jensen, C. S. Christensen, and P. Hummelshøj (2000), Ozone uptake by an evergreen forest canopy: Temporal variation and possible mechanisms, *Environ. Pollut.*, *109*, 423–429.
- Mikkelsen, T. N., H. Ro-Poulsen, M. F. Hovmand, N. O. Jensen, K. Pilegaard, and A. H. Egeløv (2004), Five-year measurements of ozone fluxes to a Danish Norway spruce canopy, *Atmos. Environ.*, *38*, 2361–2371, doi:10.1016/j.atmosenv.2003.12.036.
- Milly, P. C. D., S. L. Malyshev, E. Shevliakova, K. A. Dunne, K. L. Findell, T. Gleeson, Z. Liang, P. Phillippis, R. J. Stouffer, and S. Swenson (2014), An enhanced model of land water and energy for global hydrologic and earth-system studies, *J. Hydrometeorol.*, 1739–1961, doi:10.1175/JHM-D-13-0162.1.
- Moore, K. E., D. R. Fitzjarrald, R. K. Sakai, M. J. Goulden, J. W. Munger, and S. C. Wofsy (1996), Seasonal variation in radiative and turbulent exchange at a deciduous forest in central Massachusetts, *J. Appl. Meteorol.*, *35*, 122–134.
- Munger, J. W., S. C. Wofsy, P. S. Bakwin, S.-M. Fan, M. L. Goulden, B. C. Daube, A. H. Goldstein, K. E. Moore, and D. R. Fitzjarrald (1996), Atmospheric deposition of reactive nitrogen oxides and ozone in a temperate deciduous forest and a subarctic woodland 1. Measurements and mechanisms, *J. Geophys. Res.*, *101*(D7), 12,639–12,657, doi:10.1029/96JD00230.
- Munger, J. W., and S. Wofsy (1999a), *Biomass Inventories at Harvard Forest EMS Tower Since 1993, HF069*, Harvard Forest Data Archive, Harvard Forest, Petersham, MA, USA.
- Munger, J. W., and S. Wofsy (1999b), *Canopy-Atmosphere Exchange of Carbon, Water and Energy at Harvard Forest EMS Tower Since 1991, HF004*, Harvard Forest Data Archive, Harvard Forest, Petersham, MA, USA.
- Neirynek, J., B. Gielen, I. A. Janssens, and R. Ceulemans (2012), Insights into ozone deposition patterns from decade-long ozone flux measurements over a mixed temperate forest, *J. Environ. Monit.*, *14*(6), 1684–1695, doi:10.1039/C2EM10937A.
- Nunn, A. J., S. Cieslik, U. Metzger, G. Wieser, and R. Matyssek (2010), Combining sap flow and eddy covariance approaches to derive stomatal and non-stomatal  $\text{O}_3$  fluxes in a forest stand, *Environ. Pollut.*, *158*, 2014–2022, doi:10.1016/j.envpol.2009.11.034.
- Padro, J. (1996), Summary of ozone dry deposition velocity measurements and model estimates over vineyard, cotton, grass and deciduous forest in summer, *Atmos. Environ.*, *30*(11), 2363–2369.
- Park, R. J., S. K. Hong, H.-A. Kwon, S. Kim, A. Guenther, J.-H. Woo, and C. P. Loughner (2014), An evaluation of ozone dry deposition simulations in East Asia, *Atmos. Chem. Phys.*, *14*, 7929–7940, doi:10.5194/acp-14-7929-2014.
- Paulson, C. A. (1970), The mathematical representation of wind speed and temperature profiles in the unstable atmospheric surface layer, *J. Appl. Meteorol.*, *9*, 857–861.
- Pleim, J., and L. Ran (2011), Surface flux modeling for air quality applications, *Atmosphere*, *2*(3), 271–302, doi:10.3390/atmos2030271.
- O'Dowd, C. D., P. Aalto, K. Hmeri, M. Kulmala, and T. Hoffmann (2002), Aerosol formation: Atmospheric particles from organic vapours, *Nature*, *416*(6880), 497–498, doi:10.1038/416497a.
- Ran, L., J. Pleim, R. Gilliam, F. S. Binkowski, C. Hogrefe, and L. Band (2016), Improved meteorology from an updated WRF/CMAQ modeling system with MODIS vegetation and albedo, *J. Geophys. Res. Atmos.*, *121*, 2393–2415, doi:10.1002/2015JD024406.
- Rannik, Ü., N. Altimir, I. Mammarella, J. Bäck, J. Rinne, T. M. Ruuskanen, P. Hari, T. Vesala, and M. Kulmala (2012), Ozone deposition into a boreal forest over a decade of observations: Evaluating deposition partitioning and driving variables, *Atmos. Chem. Phys.*, *12*, doi:10.5194/acp-12-12165-2012.
- Richardson, A. D., et al. (2006), A multi-site analysis of random error in tower-based measurements of carbon and energy fluxes, *Agric. For. Meteorol.*, *136*(1), 1–18.
- Rienecker, M. M., et al. (2011), MERRA: NASA's modern-era retrospective analysis for research and applications, *J. Clim.*, *24*(14), 3624–3648.
- Savage, K. E., and E. A. Davidson (2001), Interannual variation of soil respiration in two New England forests, *Global Biogeochem. Cycles*, doi:10.1029/1999GB001248.
- Schwede, D., L. Zhang, R. Vet, and G. Lear (2011), An intercomparison of the deposition models used in the CASTNET and CAPMoN networks, *Atmos. Environ.*, *45*(6), 1337–1346, doi:10.1016/j.atmosenv.2010.11.050.
- Sheffield, J., G. Goteti, and E. F. Wood (2006), Development of a 50-year high-resolution global dataset of meteorological forcings for land surface modeling, *J. Clim.*, *19*(13), 3088–3111, doi:10.1175/JCLI3790.1.
- Shevliakova, E., S. W. Pacala, S. Malyshev, G. C. Hurtt, P. C. D. Milly, J. P. Caspersen, L. T. Sentman, J. P. Fisk, C. Wirth, and C. Crevoisier (2009), Carbon cycling under 300 years of land use change: Importance of the secondary vegetation sink, *Global Biogeochem. Cycles*, *23*, doi:10.1029/2007GB003176.
- Shuttleworth, W. J., et al. (1984), Eddy correlation measurements of energy partition for Amazonian forest, *Quart. J. Roy. Meteorol. Soc.*, doi:10.1002/qj.49711046622.
- Sitch, S., P. M. Cox, W. J. Collins, and C. Huntingford (2007), Indirect radiative forcing of climate change through ozone effects on the land-carbon sink, *Nature*, doi:10.1038/nature06059.
- Stevenson, D. S., et al. (2006), Multimodel ensemble simulations of present-day and near-future tropospheric ozone, *J. Geophys. Res.*, doi:10.1029/2005JD006338.
- Sun, G., S. B. McLaughlin, J. H. Porter, J. Uddling, P. J. Mulholland, M. B. Adams, and N. Pederson (2012), Interactive influences of ozone and climate on streamflow of forested watersheds, *Global Change Biol.*, *18*, 3395–3409, doi:10.1111/j.1365-2486.2012.02787.x.
- Turnipseed, A. A., S. P. Burns, D. J. Moore, J. Hu, A. B. Guenther, and R. K. Monson (2009), Controls over ozone deposition to a high elevation subalpine forest, *Agric. For. Meteorol.*, *149*(9), 1447–1459, doi:10.1016/j.agrformet.2009.04.001.
- Urbanski, S., C. Barford, S. Wofsy, C. Kucharik, E. Pyle, J. Budney, K. McKain, D. Fitzjarrald, M. Czikowsky, and J. W. Munger (2007), Factors controlling  $\text{CO}_2$  exchange on timescales from hourly to decadal at Harvard Forest, *J. Geophys. Res.*, *112*, G02020, doi:10.1029/2006JG000293.

- Val Martin, M., C. L. Heald, and S. R. Arnold (2014), Coupling dry deposition to vegetation phenology in the Community Earth System Model: Implications for the simulation of surface O<sub>3</sub>, *Geophys. Res. Lett.*, *41*, 2988–2996, doi:10.1002/2014GL059651.
- van Donkelaar, A., et al. (2008), Analysis of aircraft and satellite measurements from the Intercontinental Chemical Transport Experiment (INTEX-B) to quantify long-range transport of East Asian sulfur to Canada, *Atmos. Chem. Phys.*, *8*, 2999–3014.
- Walker, T. W. (2014), Applications of adjoint modelling in chemical composition: Studies of tropospheric ozone at middle and high northern latitudes, PhD thesis, Univ. of Toronto, Toronto, Canada.
- Wang, Y., D. J. Jacob, and J. A. Logan (1998), Global simulation of tropospheric O<sub>3</sub>-NO<sub>x</sub>-hydrocarbon chemistry, 1. Model formulation, *J. Geophys. Res.*, *103*, 10,713–10,726, doi:10.1029/98JD00158.
- Wehr, R., J. W. Munger, J. B. McManus, D. D. Nelson, M. S. Zahniser, E. A. Davidson, S. C. Wofsy, and S. R. Saleska (2016), Seasonality of temperate forest photosynthesis and daytime respiration, *Nature*, *534*, 680–683, doi:10.1038/nature17966.
- Wesely, M. L., and B. B. Hicks (1977), Some factors that affect the deposition rates of sulfur dioxide and similar gases on vegetation, *J. Air Pollut. Control Assoc.*, *27*, 1110–1116, doi:10.1080/00022470.1977.10470534.
- Wesely, M. L. (1989), Parameterization of surface resistances to gaseous dry deposition in regional-scale numerical models, *Atmos. Environ.*, *23*(6), 1293–1304.
- Wesely, M. L., and B. B. Hicks (2000), A review of the current status of knowledge on dry deposition, *Atmos. Environ.*, *34*(12), 2261–2282, doi:10.1016/S1352-2310(99)00467-7.
- Wild, O. (2007), Modelling the tropospheric ozone budget: Exploring the variability in current models, *Atmos. Chem. Phys.*, *7*, 2643–2660.
- Wittig, V. E., E. A. Ainsworth, S. L. Naidu, D. S. Karnosky, and S. P. Long (2009), Quantifying the impact of current and future tropospheric ozone on tree biomass, growth, physiology and biochemistry: A quantitative meta analysis, *Global Change Biol.*, doi:10.1111/j.1365-2486.2008.01774.x.
- Wolfe, G. M., J. A. Thornton, M. McKay, and A. H. Goldstein (2011), Forest-atmosphere exchange of ozone: Sensitivity to very reactive biogenic VOC emissions and implications for in-canopy photochemistry, *Atmos. Chem. Phys.*, *11*(15), 7875–7891, doi:10.5194/acp-11-7875-2011.
- Wu, S., L. J. Mickley, J. O. Kaplan, and D. J. Jacob (2012), Impacts of changes in land use and land cover on atmospheric chemistry and air quality over the 21st century, *Atmos. Chem. Phys.*, *12*, 1597–1609, doi:10.5194/acp-12-1597-2012.
- Wu, Z., X. Wang, F. Chen, A. Turnipseed, A. Guenther, D. Niyogi, U. Charusombat, B. Xia, W. Munger, and K. Alapaty (2011), Evaluating the calculated dry deposition velocities of reactive nitrogen oxides and ozone from two community models over a temperate deciduous forest, *Atmos. Environ.*, *45*, doi:10.1016/j.atmosenv.2011.02.063.
- Wu, Z. Y., L. Zhang, X. M. Wang, and J. W. Munger (2015), A modified micrometeorological gradient method for estimating O<sub>3</sub> dry depositions over a forest canopy, *Atmos. Chem. Phys.*, doi:10.5194/acp-15-7487-2015.
- Young, P. J., et al. (2013), Pre-industrial to end 21st century projections of tropospheric ozone from the Atmospheric Chemistry and Climate Model Intercomparison Project (ACCMIP), *Atmos. Chem. Phys.*, doi:10.5194/acp-13-2063-2013.
- Yue, X., T. F. Keenan, W. Munger, and N. Unger (2016), Limited effect of ozone reductions on the 20 year photosynthesis trend at Harvard Forest, *Global Change Biol.*, doi:10.1111/gcb.13300.
- Zeller, K. F., and N. T. Nikolov (2000), Quantifying simultaneous fluxes of ozone, carbon dioxide and water vapor above a subalpine forest ecosystem, *Environmental Pollution*, *107*, 1–20.
- Zhang, L., J. R. Brook, R. Vet, M. Shaw, and P. L. Finkelstein (2001), Evaluation and improvement of a dry deposition model using SO<sub>2</sub> and O<sub>3</sub> measurements over a mixed forest, *Water, Air, Soil Pollut.: Focus*, *1*, 67–78.
- Zhang, L., J. R. Brook, and R. Vet (2002), On ozone dry deposition—With emphasis on non-stomatal uptake and wet canopies, *Atmos. Environ.*, *36*, 4787–4799.
- Zhang, L., J. R. Brook, and R. Vet (2003), A revised parameterization for gaseous dry deposition in air-quality models, *Atmos. Chem. Phys.*, *3*, 2067–2082.
- Zhang, L., R. Vet, J. R. Brook, and A. H. Legge (2006), Factors affecting stomatal uptake of ozone by different canopies and a comparison between dose and exposure, *Sci. Total Environ.*, *370*, 117–132.
- Zona, D., B. Gioli, S. Fares, T. De Groot, K. Pilegaard, A. Ibrom, and R. Ceulemans (2014), Environmental controls on ozone fluxes in a poplar plantation in western Europe, *Environ. Pollut.*, *184*, 201–210, doi:10.1016/j.envpol.2013.08.032.

## Erratum

In the originally published version of this article, the author incorrectly calculated the average of the wind direction (wdirc) in Table S1 of the supplementary information. It was calculated as an arithmetic mean, and the calculation was changed because wind direction is a circular variable. This version may be considered the version of record.