Assessing the role of dry deposition in observed ozone-meteorology correlations

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Sarah Kavassalis and Jennifer G. Murphy

University of Toronto, Department of Chemistry, Toronto, Ontario, Canada

Background

Ozone, a potent greenhouse gas, phytotoxin, and human health hazard, is produced in the troposphere through complex, non-linear, meteorologically dependent chemistry. Our ability to successfully explain the observed ozone-meteorology correlations is important not only from a regulatory perspective, but also one of understanding fundamental ozone chemistry. Summertime ozone-relative humidity (RH) correlations, commonly seen in surface measurements, reflect a combination of meteorology, land-surface processes, and photochemistry, however, the relative significance of these factors in driving the humidity relationship is not yet clear.

Observations

Average summer (June, July, August) midday (12-4pm) O_3–meteorology correlations over the US are shown below for CASTNET stations with at least five years of data.

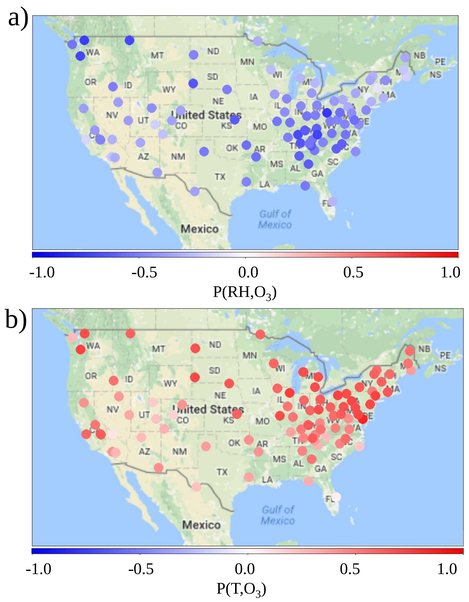

Fig. 1. observed, summer, midday (12-4pm) Pearson's correlation coefficient of ozone versus a) relative humidity and b) temperature from 1987 to 2015 at EPA-CASTNET stations.

$P(T,O_3)$ is strongest in the North East, while $T(RH,O_3)$ is strongest in the South East and North West, consistent with other studies (4).

Interpreting the O_3-RH Relationship

Numerous mechanisms have been suggested in the literature (1-4) to explain the strong negative correlation seen between summertime ozone and relative humidity. These include:

- Relationship to the ozone-temperature correlation
- The photolysis of ozone and subsequent loss of $O(^1D)$ to H_2O
- The association of humid days with enhanced cloud cover and thus reduced photochemistry
- Dry, ozone-rich air from stratospheric intrusions
- Precipitation leading to decreased precursor emissions and increased humidity

While the first two mechanisms are the most cited explanations, models that reproduce observed $p(T,O_3)$ and include known H_2O sensitive photochemistry, still fail to reproduce the strength and geographic dependence of $p(RH,O_3)$ (5).

A Role for Deposition?

Dry deposition is thought to be the dominant sink for ozone in the summertime planetary boundary layer over the continental US (6), with 30-90% of that dry deposition sink attributable to stomatal uptake (7-8). In non-drought stressed plants, stomatal resistance is controlled by response to sunlight , CO_2, temperature, and vapour pressure deficit (VPD). **VPD is the difference between ambient vapour pressure, vp_{air}, and saturated vapour pressure, vp_{sat}** and is thus coupled with humidity and temperature.

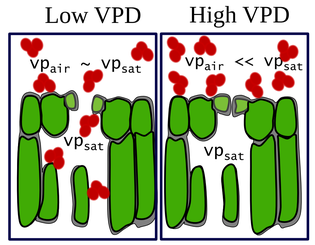

Fig. 2. representation of uptake of ozone by vegetation through stomata. High VPD means stomata close, removing a large ozone sink.

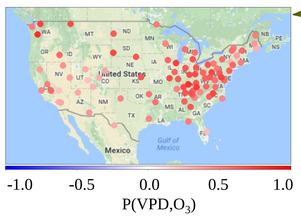

Fig. 3. observed, summer, midday (12-4pm) Pearson's correlation coefficient of ozone versus VPD (calculated from station temperature and RH) from 1987 to 2015 at EPA-CASTNET stations.

O_3-VPD Correlations

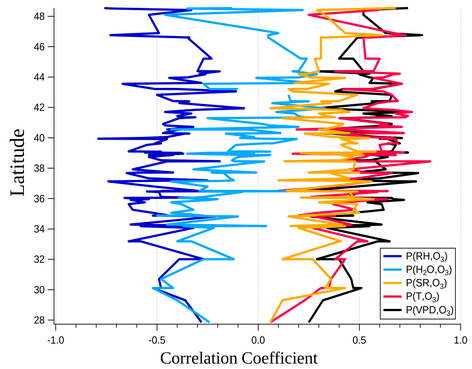

Fig 4. zonally averaged correlation coefficients of O_3 against all CASTNET measured meteorological parameters.

Strong O_3-VPD correlations are seen at most CASTNET stations (fig. 3) and VPD is, on average, the best meteorlogical predictor of midday ozone in the summer (fig. 4).

Model Framework

To investigate the meteorlogical sensitivity of ozone due to VPD-dependent deposition, we used a box model with the RACM chemical mechanism (9) and a resistence based deposition scheme (fig. 5).

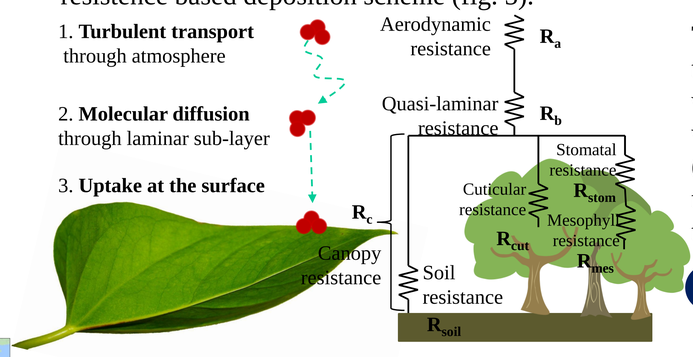

Fig. 5. schematic of Wesely-based deposition scheme (10).

Deposition velocity is then given by, $V_d = \frac{1}{R_a + R_b + R_c}$

where canopy resistance is, $R_c = \frac{1}{R_{stom} + R_{mes}} + \frac{1}{R_{cut}} + \frac{1}{R_{soil}}$

Multiple options in the literature exist for parameterizing R_{stom} and we investigate two common choices:

Wesely $$R_{stom} = R_{\min}\left\{1+\left(\frac{200}{SR+0.1}\right)^2\right\}\left\{\frac{400}{T(40-T)}\right\} \quad (10)$$

Jarvis $$R_{stom} = \frac{R_{\min}}{f_{phen}\, f_{light}\, f_{Temp}\, f_{VPD}\, f_{SWC}} \quad (11)$$

Box Model Results

Model runs aimed to simulate typical summer conditions at an average CASTNET site, where relative humidity was varied by varying absolute water vapour. R_{min} was chosen based on CASTNET values, and the Jarvis *f* terms were from the literature for a *Fagus sp.*, *Liquidambar styraciflua*, and *Picea abies* (12-14) forest with a total LAI of 2.2 (the CASTNET average).

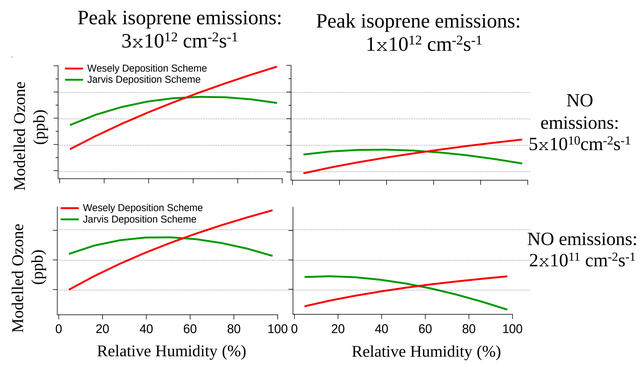

Fig. 6. RACM box model results showing simulated midday average O_3 concentrations under two different NO and isoprene emissions scenarios, with two different R_{stom} terms, with the same summertime meteorology in each.

The inclusion of a VPD sensitive R_{stom} (Jarvis) leads to decreasing midday ozone at high relative humidity, which is in agreement with observations. Model runs with the non-VPD dependent deposition scheme (Wesely) do not capture the observed O_3-RH trend, as the increase in PO_3 due to enchanced PHOx is greater than the chemical loss of $O(^1D)$ to H_2O.

Conclusions

VPD dependent deposition provides a plausible mechanism to explain the strength of the summertime ozone-relative humidity correlation seen at surface sites.

References

(1) Jacob et al., JGR, 1993. (2) Cox et al., Atmos. Environ., 1993. (3) Camalier., Atmos. Environ., 2007. (4) Tawfik et al., Atmos. Environ., 2013. (5) Davis et al., Atmos. Environ., 2011. (6) Racherla and Adams, ACP, 2008., (7) Fowler et al., Water Air Soil Poll., 2001. (8) Hardacre et al., ACP, 2015. (9) Stockwell et al., JGR: Atmos., 1997. (10) Wesely, Atmos. Environ., 1989 (11) Jarvis, Phil. Trans. R. Soc. B, 1976 (12) Buker et al., Environ Pollut., 2007. (13) Gunderson, Plant Cell and Env., 2012. (14) Karlsson et al., Environ Pollut., 2000.

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skavassa@chem.utoronto.ca