

- (1981) Evidence for chamber-dependent radical sources: impact on kinetic computer models for air pollution. *Int. J. Chem. Kinet.* **13**, 735.
- Carter W. P. L., Atkinson R., Winer A. M. and Pitts J. N., Jr. (1982) Reply to "Comments on a smog chamber and modeling study of the gas phase  $\text{NO}_x$ -air photooxidation of toluene and the cresols". *Int. J. Chem. Kinet.* **14**, 813.
- Joshi S. B., Dodge M. C. and Bulfalini J. J. (1982) Reactivities of selected organic compounds and contamination effects. *Atmospheric Environment* **16**, 1301.
- Killus J. P. and Whitten G. Z. (1981) Comments on "a smog chamber and modeling study of the gas phase  $\text{NO}_x$ -air photooxidation of toluene and the cresols". *Int. J. Chem. Kinet.* **13**, 1101.
- Kyle E. and Orchard S. W. (1977) The photolysis of methylglyoxal vapour at 436 nm. *J. Photochemistry* **7**, 305.
- Nieboer H. and Duyzer J. H. (1978) Experimental and mathematical simulation of photochemical air pollution. In *Photochemical Smog Formation in the Netherlands* (Edited by R. Guicherit), p. 89, TNO-'s-Gravenhage.
- Parmenter C. S. (1964) Primary photochemical processes in glyoxal at 4358 Å. *J. Chem. Phys.* **41**, 658.

### AN EDDY-CORRELATION MEASUREMENT OF $\text{NO}_2$ FLUX TO VEGETATION AND COMPARISON TO $\text{O}_3$ FLUX\*

This paper is potentially very misleading, because the title suggests that they specifically measured the flux of  $\text{NO}_2$ . Indeed, their hot molybdenum converter also has an efficiency of unity for  $\text{HNO}_3$  (D. H. Stedman, private communication), so the measured flux was at least  $(\text{NO}_2 + \text{HNO}_3)$ , and may have included other compounds as well.

In Champaign, Illinois, over grass, I measured  $\text{HNO}_3$  fluxes by a profile method, and found them to be of the same magnitude as the  $\text{NO}_2$  fluxes measured by Wesely *et al.*  $\text{HNO}_3$  concentrations were frequently around 2 ppbv in the daytime. Therefore, it seems likely to me that a substantial fraction of the flux measured by Wesely *et al.*, was really  $\text{HNO}_3$ , and that their published  $V_d$  for  $\text{NO}_2$  ( $0.6 \text{ cm s}^{-1}$ ) is significantly larger than the actual  $V_d$  for  $\text{NO}_2$ .

Thank you for bringing this to the attention of potential users of this data. My own measurements will be submitted for publication in the very near future.

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### AUTHORS' REPLY

Huebert correctly identifies one of the flaws concerning interpretation by Wesely *et al.* (1982) of their data. As stated by Huebert, nitric acid vapor  $\text{HNO}_3$  was indeed measured with an efficiency of unity and the resulting possible contribution to  $\text{NO}_x$  flux was not noted in the paper. The possibility that concentrations of  $\text{HNO}_3$  can be rather high where the experiment was performed was brought to our attention only very recently. All values of  $\text{NO}_2$  flux, deposition velocity and surface resistance estimated by Wesely *et al.* should be considered as those for  $\text{NO}_x$  rather than  $\text{NO}_2$ . For future eddy-correlation experiments, fast-response  $\text{NO}_x$  measuring system could be easily modified to allow determination of the

flux both with and without  $\text{HNO}_3$ , perhaps on alternate half hours, so that the effects of  $\text{HNO}_3$  could be determined.

Another difficulty is the statement by Wesely *et al.* that  $\text{NO}_2$  is removed efficiently by water due to rapid reactions that form nitrous and nitric acid. These reactions are actually very slow for pure water and the typically small values of  $[\text{NO}_2]$  found in ambient atmospheric conditions (Lee and Schwartz, 1981). Thus for  $\text{NO}_2$  to be taken up quickly by vegetation, some rapid reactions with plant materials are needed. Atmospheric ozone is subject to similar constraints but still has a large deposition velocity over lush vegetation during the daytime, apparently because of access via leaf stomatal opening to reactive substances in solution inside plant leaves. It is possible that  $\text{NO}_2$  is also taken up rather rapidly when stomatal apertures are open but the most likely chemical reactions are not known with certainty.

Finally, it has been pointed out (O. T. Denmead, private communication) that the daytime fluxes and deposition velocities for  $\text{NO}_x$  and  $\text{O}_3$  are slightly overestimated by Wesely *et al.* because of the neglect of small corrections to the eddy-correlation estimates needed for density effects due to heat and water vapor transfer (Webb *et al.*, 1980). Such corrections would increase the surface resistance by about 10% during the daytime but leave the main conclusion of Wesely *et al.* unaffected.

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### REFERENCES

- Lee Y.-N. and Schwartz S. E. (1981) Evaluation of the rate of uptake of nitrogen dioxide by atmospheric and surface liquid water. *J. geophys. Res.* **86**, 11, 971-11, 983.
- Webb E. K., Pearman G. I. and Luenig R. (1980) Correction of flux measurements for density effects due to heat and water vapor. *Q. Jl R. met. Soc.* **106**, 85-100.
- Wesely M. L., Eastman J. A., Stedman D. H. and Yalvac E. D. (1982) An eddy-correlation measurement of  $\text{NO}_2$  flux to vegetation and comparison to  $\text{O}_3$  flux. *Atmospheric Environment* **16**, 815-820.

### BACKGROUND POLLUTANT MEASUREMENTS IN AIR MASSES AFFECTING THE EASTERN HALF OF THE UNITED STATES—I. AIR MASSES ARRIVING FROM THE NORTHWEST

Measurements of background concentrations of particulate and gaseous species in the atmosphere, such as those recently reported by Kelly *et al.* (1982), provide an important reference point for understanding anthropogenic pollutants. For this reason, several points in this paper, with respect to particulate organic carbon, require comment.

Kelly *et al.* (1982) compared organic carbon data for a U.S. continental rural site in South Dakota with extractable particulate organic matter measured at a remote site in Barrow, Alaska, in March 1979 (Daisey *et al.*, 1981). In comparing the South Dakota measurements to the Barrow

\* Wesely M. L., Eastman J. A., Stedman D. H. and Yalvac E. D. (1982) *Atmospheric Environment* **16**, 815-820.