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Atmos. Chem. Phys., 9, 3697-3707, 2009

www.atmos-chem-phys.net/9/3697/2009/

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## Inferring ozone production in an urban atmosphere using measurements of peroxyacetic acid

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**Abstract.** Observations of peroxyacetic acid ( $\text{HO}_2\text{NO}_2$ ) obtained simultaneously with those of  $\text{NO}$  and  $\text{NO}_2$  provide a sensitive measure of the ozone photochemical production rate. We illustrate this technique for constraining the ozone production rate with observations obtained from the NCAR C-130 aircraft platform during the Megacity Initiative: Local and Global Research Observations (MILAGRO) intensive in Mexico during the spring of 2006. Sensitive and selective measurements of  $\text{HO}_2\text{NO}_2$  were made in situ using chemical ionization mass spectrometry (CIMS). Observations were compared to modeled  $\text{HO}_2\text{NO}_2$  concentrations obtained from the NASA Langley highly-constrained photochemical time-dependent box model. The median observed-to-calculated ratio of  $\text{HO}_2\text{NO}_2$  is 1.18. At  $\text{NO}_x$  levels greater than 15 ppbv, the photochemical box model underpredicts observations with an observed-to-calculated ratio of  $\text{HO}_2\text{NO}_2$  of 1.57. As a result, we find that at high  $\text{NO}_x$ , the ozone production rate calculated using measured  $\text{HO}_2\text{NO}_2$  is faster than predicted using accepted photochemistry. Inclusion of an additional  $\text{HO}_x$  source from the reaction of excited state  $\text{NO}_2$  with  $\text{H}_2\text{O}$  or reduction in the rate constant of the reaction of  $\text{OH}$  with  $\text{NO}_2$  improves the agreement.

Final Revised Paper (PDF, 519 KB) Discussion Paper (ACPD)

Citation: Spencer, K. M., McCabe, D. C., Crouse, J. D., Olson, J. R., Crawford, J. H., Weinheimer, A. J., Knapp, D. J., Montzka, D. D., Cantrell, C. A., Hornbrook, R. S., Mauldin III, R. L., and Wennberg, P. O.: Inferring ozone production in an urban atmosphere using measurements of peroxyacetic acid, Atmos. Chem. Phys., 9, 3697-3707, 2009. Bibtext EndNote Reference Manager



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