

## ***Interactive comment on “Measurements of N<sub>2</sub>O<sub>5</sub>, NO<sub>2</sub>, and O<sub>3</sub> east of the San Francisco Bay” by E. C. Wood et al.***

**Anonymous Referee #1**

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General comments:

This is a brief manuscript describing a limited set of measurements of N<sub>2</sub>O<sub>5</sub> using a prototype instrument based on LIF. In spite of the brevity, there are some important conclusions about nitrogen oxide chemistry at night. The basic approach is the thermal dissociation of N<sub>2</sub>O<sub>5</sub> to NO<sub>3</sub>, followed by the detection of the latter by LIF. I can find no obvious errors in the experimental approach or in the general analysis of the data. There are clearly issues with the instrument sensitivity to a variety of factors, such as aerosol scattering and long term drifts in laser power, but the authors appear to have done a reasonable job of addressing these. The main scientific conclusion is that the lack of a large N<sub>2</sub>O<sub>5</sub> signal indicates fairly rapid loss of this intermediate over night.

As noted, this is a conclusion that has been reached by other studies in the past. In this case, however, the authors show that for winter conditions in the study region, the loss of NO<sub>x</sub> by the nocturnal reaction of NO<sub>2</sub> with O<sub>3</sub> should be nearly an order of magnitude more important than the daytime reaction of NO<sub>2</sub> with OH. This is an important result that highlights the seasonal variability of NO<sub>x</sub> chemistry.

Specific comments:

1. The authors should note that one reason for the dominance of the nighttime pathway is the small calculated OH concentration. In fact, the rate of both day and night loss processes for NO<sub>x</sub> are considerably smaller under these conditions than in summer. A quick estimate and contrast of the NO<sub>x</sub> lifetime in summer and winter would be an interesting addition to this discussion.
2. The interpretation of the signal, which is the sum of NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub>, exclusively as N<sub>2</sub>O<sub>5</sub> is reasonable under the conditions described. The authors should perhaps note more explicitly that the correction for the NO<sub>3</sub> contribution would range from roughly 1 - 10% for the stated range of conditions.
3. The height of the inlet above the ground surface was 1.2 m. Is it possible that deposition to the ground plays a role in the N<sub>2</sub>O<sub>5</sub> loss? If so, the lifetime of N<sub>2</sub>O<sub>5</sub> with respect to hydrolysis on aerosol may not be as short as inferred. Previous modeling studies of Geyer, Stutz and coworkers have showed that there may be significant vertical gradients in NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub>, especially within the last few meters above the ground surface.
4. Figure 3: Why is the NO<sub>2</sub> concentration only displayed when there is N<sub>2</sub>O<sub>5</sub> present? Is there a more complete time series in NO<sub>2</sub>, or was the NO<sub>2</sub> instrument only running simultaneously with the N<sub>2</sub>O<sub>5</sub> measurement?

Technical comments:

1. Page 8: At low NO and NO<sub>3</sub> concentrations, the quantity  $F(\text{NOSUM}) =$

$2[\text{N}_2\text{O}_5]/(2[\text{N}_2\text{O}_5] + [\text{NO}_2])$  rather than  $2[\text{N}_2\text{O}_5]/[\text{NO}_2]$ .

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Interactive comment on Atmos. Chem. Phys. Discuss., 4, 6645, 2004.

**ACPD**

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