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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Observations of the diurnal and seasonal trends in nitrogen oxides in the western Sierra Nevada" *by* J. G. Murphy et al.

J. G. Murphy et al.

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The comments of Referee 2 have been addressed in the following way:

General/Specific Comments

This referee felt that the manuscript would benefit from some rearrangement and inclusion of text motivating the analysis and justifying comparison of data from different years at the sites.

- A paragraph has been added to the introduction to address this suggestion. Briefly, examination of meteorological and chemical measurements at sites in the region that do have long term records suggests that, on average, one summer is very similar to another and that interannual variability does not compromise our analysis.

Is the instrument response the same in dry air as it is in ambient air?

- A small humidity correction is required for the data due to the role of water in the quenching of NO2 fluorescence. The size of this correction was measured in lab and also confirmed by comparison of dry air calibrations and standard additions throughout the campaign. At a water vapour mixing ratio of 1 percent the correction is 18%. Text has been added in section 3 to describe this correction. The magnitude of the water correction depends on the fluorescence cell pressure and other experimental details which vary with the pumping and nozzle used for supersonic expansion. In previous configurations of the instrument that did not use supersonic expansion (e.g. (Thornton, et al., 2000)) the correction was 6% for 1 % water.

What is the fate of the organic nitrate compounds? What fraction are sticky and thus likely to deposit out in transit? Are any water soluble? Is it possible to include a table of suspected PNs and ANs, their fates, information on water solubility and deposition rates and atmospheric lifetimes?

- The fate of organic nitrates is highly uncertain. In the case of PNs, we can assume that PAN is a major contributor and some work has been done to quantify its water solubility and deposition rates. In the case of ANs, there are even more possible species than there are parent hydrocarbons and our technique does not give us any information about speciation. Organic nitrate species with a hydroxyl functional group can be expected to be sticky and behave in similar ways to nitric acid. Other multi-functional nitrates may undergo reaction and/or decomposition in the R group to generate different organic nitrates, which will not register as a loss since our technique measures the sum. The question of the identity and the tendency to dissolve/deposit of the individual organic nitrates is beyond the scope of this paper, however we hope that our measurements motivate further investigation.

P 4427 lines 6 - 8: why?

- High nitric acid but low ozone in the later airmass is suggestive of descending air, because reduced contact with the surface would prevent the emission of VOCs and

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the deposition of nitric acid, but the airmass origin is not conclusively known

Technical Corrections

What does semi-continuous mean for the UC-BFRS site?

- Measurements are made routinely but occasionally there are gaps of several months in the dataset.

In figures and text consistently, designate HNO3 as gas phase and semi-volatile aerosol nitrate (perhaps “GP+SVAN HNO3”??) so that readers do not mistake the HNO3 data presented.

- In Section 3 it is stated that what we call HNO3 refers to both the gas phase form and particulate nitrate. Recent measurements of ammonia on the western slopes of the Sierra Nevada (M. Fischer, personal communication) indicate that gas phase NH3 concentrations are very low and therefore we infer that semivolatile particulate nitrate is not a substantial contribution to our total ‘HNO3’ measurement. Therefore we believe that our terminology is not misleading to the readers.

Section 4 seems somewhat fragmented and could be improved with reorganization (e.g., significant portion of last paragraph seems better as an introductory paragraph).

- In our rewriting of the introduction we have attempted to rationalize the ordering of the manuscript and feel that Section 4 is crucial for giving context to the measurements described in Section 5.

In section 5.1 it states that data were obtained for the full annual cycle and then a few sentences later it states that electrical power outages prevented measurements during most of May. There is an inconsistency here.

- Language about annual cycle made more consistent in section 5.1

- Verbs used with ‘data’ have been corrected

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- Extraneous ‘which’s changed to ‘that’s

- 4435- Line 22, ‘the’ switched back to ‘to’

- “will be” has been changed to “are” and tenses corrected in the text

References

Thornton, J. A., Wooldridge, P. J. and Cohen, R. C.: Atmospheric NO2: In situ laser-induced fluorescence detection at parts per trillion mixing ratios, Analytical Chemistry, 72, 528-539, 2000.

Interactive comment on Atmos. Chem. Phys. Discuss., 6, 4415, 2006.