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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Summertime NO_x measurements during the CHABLIS campaign: can source and sink estimates unravel observed diurnal cycles?" *by* S. J.-B. Bauguitte et al.

Anonymous Referee #1

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General comments.

This is an interesting, careful, and well-written paper that combines excellent NO and NO2 measurements, characterized by usefully small uncertainties that are clearly articulated, with a good application of box modeling to demonstrate nicely the effects of halogen radical chemistry on NOx lifetime, the NO/NO2 ratio, and thus O3 production, in the coastal Antarctic environment in the summertime. This MS reviewed very well for each of the 15 different evaluation points highlighted by the ACPD instructions to reviewers. Minor comments appear below.

Specific comments.

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p. 20374 line 18: "... our confidence in the ubiquitous impact of halogen chemistry, despite the scarcity of halogens [sic] ground-based measurements, has been greatly improved by satellite observations of BrO and IO...". A comment: recent results from the NASA ARCTAS and NOAA ARCPAC airborne campaigns have suggested possible unresolved issues with BrO retrievals from satellites, and these results have been presented at several workshops and will be highlighted at the upcoming Fall AGU meeting in San Francisco. Despite the publication record cited, the authors may want to soften or qualify this statement a bit here.

p. 20376 line 2: "This yielded a threefold increase in the NO2 conversion efficiency." Presumably this comparison is for identical sample illumination times? Please clarify.

p. 20376 line 28: "This was achieved by quantitative gas-phase titration of the NO/N2 mixture to NO2 by O3 generated from a pen-ray Hg lamp, and monitoring the un-titrated NO mole fraction (typically 5%)." As written, 'quantitative titration' seems to imply all the NO was converted to NO2, which was not the case.

p. 20377 line 12: "For all summer data reported here, we subtracted a 2 pptv artefact for NO, and 6 pptv artefact for NO2." How well known are these values? Can the authors provide an estimate of uncertainty for these values? Does the NO2 artefact refer to the detector artefact (NO artefact in the NO2 channel detector) only, or does it only refer to the contribution from any photolytic artefact in the illuminated NO2 sample cell, or does it combine the two?

p. 20378 line 15: "Ambient air was drawn back to the CASLab ... The residence time of the ambient air matrix in the PFA transfer lines was measured to be ~14 s...". This long residence time would certainly perturb the NO-NO2 equilibrium, but my reading suggests the manuscript only uses total NOx from this part of the experiment, which is fine. It would be good for the authors to note, and verify, that no analyses of the NO/NO2 ratio from the flux inlet were used in the present analysis.

p. 20381 line 19: jNitrate photolysis rate a factor of 5 smaller than Summit – were the

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downwelling F(lambda) values similar for Halley and for Summit? What is the sensitivity in the following analysis to this apparent difference?

p. 20381 lines 26-27: Please clarify the ozone, met, OH, HO2, IO, BrO etc. measurements cited and used in this analysis were from Halley.

p. 20382 line 2: Please define Leighton here.

p. 20382 line 3: Are nonzero IO and BrO values plausible for SZA>90? Could the authors speculate briefly on the source? What were the corresponding downwelling F(lambda) values for SZA>90?

p. 20384 line 16: Perhaps elaborate on the derived NOx lifetime dependence on the assumed mixed layer height?

p. 20393 lines 15-17: Here, and in the abstract, are assertions of halogen oxidation influencing the isotopic nitrate signature in the snowpack. The development of this reasoning is entirely lacking in the manuscript, however, so it might be good to either add some explanatory text or remove these comments; they seem out of place in an otherwise very coherent report.

p. 20399 (Table 1): Please add a value of the photolysis converter artefact for NO2, which is different than the detector artefact listed for the NO2 channel.

p. 20403 (Fig. 3): The random errors are shown, but it would also be appropriate to show the total uncertainty for each data point somehow, and these are likely not better than a few pptv for NO2 and perhaps 1-2 pptv absolute for NO. Is there a corresponding model uncertainty that could be shown?

p. 20404 (Fig. 4): Would a panel with wind speed be useful here? Further, it is likely that derived gradients in NOx lower than some value are not significant, and are determined by detector noise – however, once this is multiplied by a high diffusivity value in b), the derived NOx flux blows up, e.g., zero detectable NOx gradient in panel a) after 04/02/2005 appears as some of the highest values of NOx flux in panel c).

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Since it appears that the only non-zero NOx gradient above the noise was observed for dNOx/dz values in a) exceeding about 2 pptv per meter, I would suggest filtering the product shown in panel c) by this value. In that way, the only significant flux would be limited to a single day, but it would be defensible.

Technical corrections.

p. 20377 line 8: palladium is mis-spelled

p. 20384 line 16: clarify that the assumed 100 m boundary layer is for the summertime?

p. 20386 line 9: would 'mixing ratio' be better than 'sensitivity level' here? Clarify the Saiz-Lopez DOAS measurements were taken at Halley, or elsewhere?

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 20371, 2009.