

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 NO_x 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 NO_x 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 NO_x 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 NO_x 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 NO_x flux blows up, e.g., zero detectable NO_x gradient in panel a) after 04/02/2005 appears as some of the highest values of NO_x flux in panel c).

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Since it appears that the only non-zero NO_x gradient above the noise was observed for $d\text{NO}_x/dz$ 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.

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