

Interactive comment on “In situ measurements of molecular iodine in the marine boundary layer: the link to macroalgae and the implications for O₃, IO, OIO and NO_x” by R.-J. Huang et al.

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What a pity that the daytime OIO signals were not unambiguous, as removal of OIO by photolysis (or not) is a hot topic at the moment. Such observations from the field, where most experimental work is done these days, may hopefully help to resolve the conflicting laboratory measurements of I-atom quantum yields from OIO: QY < 0.05 (Tucceri et al., 2006) or QY = 1 (Gómez-Martín et al., 2009).

With regard to OIO detection limits, are the values of 12.5 and 3.3 ppt reported on page 373 still valid? Are these two different values a result of different path lengths, or are ambient I₂ levels important?

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The correlations presented in Fig 7 are certainly informative, and give further credence to the laboratory results of (Chambers et al., 1992), who incidentally, were the first to propose I₂ + NO₃ as a source of active iodine at night. The more recent calculations from (Kaltsayannis and Plane 2008) certainly back-up this hypothesis.

The discussion of OIO formation processes on page 374 is a bit vague: "The night-time OIO could be formed via the reactions of either IO + IO or IO + NO₃ (Saiz-Lopez et al., 2006a). However, the formation mechanism of daytime OIO is not clear so far, and the observations of daytime OIO are still very scarce (Stutz et al., 2007)." Efficient conversion of IO to OIO by NO₃ has been demonstrated in our laboratory (Dillon et al., 2008), and the implications for night-time MBL chemistry discussed. Given the mixing ratios of IO and NO₃ presented in Fig 7, and published rate coefficients, the reactions IO + NO₃ and IO + IO would be of approximately equal importance for OIO formation at night. By day surely one formation mechanism for OIO is clear, with the larger measured IO mixing ratios accounting for any OIO via IO + IO. Was BrO present at the site? As far as I am aware, uncertainties regarding the daytime OIO budget are mostly concerned with loss processes, principally photolysis (see above).

I wholeheartedly agree with your closing statement, "more laboratory-based studies and field measurements are required to clarify the importance of the nighttime atmospheric chemistry of iodine.", and would encourage authors to take note when increasingly rare lab studies do become available.

Chambers, R.M., Heard, A.C., and Wayne, R.P.: Inorganic Gas-phase reactions of the nitrate radical: I₂ + NO₃ and I + NO₃, J. Phys. Chem., 96, 3321-3331, 1992.

Dillon, T.J., Tucceri, M.E., Sander, S., and Crowley, J.N.: LIF studies of iodine oxide chemistry, part 3. Reactions IO + NO₃ = OIO + NO₂, I + NO₃ = IO + NO₂, and CH₂I + O₂ = (products): Implications for the chemistry of the marine atmosphere at night., Phys. Chem. Chem. Phys., 10, 1540-1554, 2008.

Gómez-Martín, J.C.G., Ashworth, S.H., Mahajan, A.S., and Plane, J.M.C.: Photochem-

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istry of OIO: Laboratory study and atmospheric implications, *Geophys. Res. Lett.*, 36, 2009.

Kaltsoyannis, N. and Plane, J. M. C.: Quantum chemical calculations on a selection of iodine containing species (IO, OIO, INO₃, (IO)₂, I₂O₃, I₂O₄ and I₂O₅) of importance in the atmosphere, *Phys. Chem. Chem. Phys.*, 10, 1723–1733, 2008.

Stutz, J., Pikelnaya, O., Hurlock, S.C., Trick, S., Pechtl, S., and von Glasow, R.: Daytime OIO in the gulf of Maine, *Geophys. Res. Lett.*, 34, 2007.

Tucceri, M.E., Hölscher, D., Dillon, T.J., Rodriguez, A., and Crowley, J.N.: Absorption cross section and photolysis of OIO, *Phys. Chem. Chem. Phys.*, 8, 834-846, 2006.

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