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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Estimation of Reactive Inorganic Iodine Fluxes in the Indian and Southern Ocean Marine Boundary Layer" *by* Swaleha Inamdar et al.

Anonymous Referee #1

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The paper uses concurrent observations of sea surface iodide (SSI), ozone (O3), and iodine monoxide (IO) along with several other parameters to assess different methods of estimating iodine fluxes to the marine boundary layer. Region-specific forms of these methods for the Indian Ocean and Southern Ocean are derived and further assessed against the observations. The results are substantially different in the Indian Ocean and Southern Ocean and on either side of the polar front. Furthermore, the results are often contrary to previous findings, highlighting the need for further studies. The fundamental finding of the paper that existing methods fail to reproduce observations and that consistent improvements applicable to the full data set are not forthcoming is worthy of publication; however, the authors must better demonstrate and communicate this with robust statistical tests. Toward this point I have the following specific major comments:

1) As the title states the observational region encompasses the Indian Ocean and Southern Ocean, however, analysis of (SSI) in the Indian Ocean alone fails to obtain a significant result. As the authors state this is likely due to the limited statistics (N=18). This finding calls into question whether the application of the combined fitted result should be applicable to the Indian Ocean. ANOVA or similar methods should be applied to determine whether the Indian Ocean is statistically different. In particular, an F-test should be conducted. The presented results suggest that spatial and temporal differences between the measurement campaigns, and other effects may present confounding variables to such methods. Despite this, even "failed" statistical tests with inconclusive results are needed for proper framing of the results in the Indian Ocean.

2) Similar statistical analysis is also needed for the different analyses north and south of the polar front. Pearson coefficients for the correlation of observed IO with various parameters divided and combined data set are shown in Fig. 8. These help give some idea of the differences between the correlations on either side of the front, but the picture is incomplete. Two particular results highlighted in the text are demonstrative: GEOS-Chem modeled IO is significantly correlated with observed IO in the data subsets but not in the complete data set. Fig. 8 shows this also the case for CAM-Chem at ∼94% confidence as well. The reason for this, as stated by the authors, is that the variability in both models across the polar front is significantly different than observed. Further, the reader can see this for themselves in Figs. 4 and 10. In contrast, correlations with chl-a are much more difficult to interpret. Most data occupy a limited dynamic range in Fig. 4 and the correlation plots in Fig. 9 indicate individual points may be driving the correlation but this is not clear. In both instances systematic statistical assessment of the data subsets would be helpful.

In addition I have the following additional two major comments. 3) As the authors state in the abstract their results start from "the first concomitant observations of iodine oxide

(IO), O3 in the gas phase, and sea surface iodide concentrations." The choice of "concomitant" implies some intrinsic link between the set of parameters, and theoretically these parameters are expected to correlate via the mechanism outlined by Eqs. 7 and 8. However, the authors ultimately find that the correlations are the opposite of those in the equations as shown in Fig. 8 and discussed in the text. Keeping close to the underlying data these correlations should be shown in full similar to Chl-a in Fig. 9.

4) The underlying measurements are contained in four other papers (Chance et al., 2019a,b and Mahajan et al., 2019 a,b) are fundamental to assessing these findings. These are sufficiently critical to the results presented that I would recommend linking them as companion papers. I cannot locate Chance et al. (2019b) and do not believe it is published. The measurements are described in part in Chance et al. (2019a) nonetheless it is troubling that such critical measurements are neither published nor described more fully. If the measurements are not yet published the description in this paper should be expanded. Notably, MAX-DOAS data (which are published elsewhere) appear in the supplement while the SSI data do not.

I have following minor and technical comments. Line 28: As commented above, "concomitant" here may be misleading in the abstract. While the latter portion of the abstract (L 37-39) makes clear that "Sea-air fluxes ... calculated from the atmospheric ozone and seawater iodide ... failed to adequately explain the detected IO in this region" it does not make clear that the correlations are largely null or even contrary to expectations. Line 58-60: Saiz-Lopez et al. (2006b) included IO condensation onto particles in order to explain particle growth. However, I do not believe there is any claim of direct nucleation by IO. This sentence should be clarified. Line 73 and 74: Why are these reactions not labeled and numbered? Line 266: The detection limit and precision should match units to be more easily compared. Line 270-272: Consider simplifying description of wind flagging to inclusion of the forward hemisphere or the like. Presently mildly confusing. Line 302-30: Wind speed is first introduced here but discussed frequently hereafter. What is the wind speed referred to? e.g. is it U10 or some other standard? This is particularly relevant later when comparing with model treatment of wind parameters. Line 305 - 307: As is made clear later on line 317, neither of the activation energies determined in MacDonald et al. (2014) is significantly different from zero. While it does not examine the products separately, Magi et al. (1997) does find a significant activation energy for the first I- + O3 reaction. MacDonald et al. noted that the Arrhenius pre-exponential factor in Magi et al. is ten orders of magnitude greater than the diffusion limit to justify assuming an activation energy for the first step of zero. More recent work has also called the rates determined in Magi et al. into question (Moreno et al., 2018), however, the confounding factors (high iodide concentrations and iodide surface activity) cannot fundamentally dispel the observed positive temperature dependence. Notably, the values reported in MacDonald are predicated on an assumption that the activation energy of I- + O3 is zero and it is even more uncertain whether the overall activation energy to produce I2 is negative. The activation energies from MacDonald are better summarized as approximately zero (e.g. Moreno and Baeza-Romero 2019) as the overall temperature dependence remains unresolved. Line 401-405: While diurnal variation in O3 can be inferred, its reversal is not apparent in Fig. 5b as referred to. Line 645 - 646: How do the authors infer that photochemistry is responsible for the differences? This is not obvious to me. Line 654 – 655: From Fig. 7 it appears that the p-value for the HOI correlation is 0.04. Given that 5% significance is used as a standard elsewhere in the paper this would indicate that HOI does show significant correlation contrary to this statement. Line 771: VOI not previously introduced. Figure 3: The literature calculations are not readily compared with the observations as they are in separate panels. The observations should appear in both panels. Figure 9: It should be made clear that the IO here is observed as modeled IO is also presented elsewhere. The legends readily blend in with the scattered data and should be made more clearly separate. Table 2: The database location column should be moved left of the equations as it is otherwise unclear in isolation what the differences between Eq. 2, 3, and 5 are. Iodide and nitrate concentrations should be given with consistent (though not necessarily the same) units, i.e. M or mol L-1 but not both. Table 2 and Supplement: In addition to the expectation of higher R2 values for fitting to the same data set, equations having more degrees of freedom are expected to have better fits. The adjusted R2 values should be used for proper comparison of the overall parameterizations. If this is already the case it should be described as such in the supplement.

References: Chance, R., Tinel, L., Sherwen, T., Baker, A., Bell, T., Brindle, J., Campos, M. L. A. M., Croot, P., Ducklow, H., He, P., Hoogakker, B., Hopkins, F. E., Hughes, C., Jickells, T., Loades, D., Macaya, D. A., Mahajan, A. S., Malin, G., Phillips, D. P., Sinha, A. K., Sarkar, A., Roberts, I. J., Roy, R., Song, X., Winklebauer, H. A., Wuttig, K., Yang, M., Zhou, P. and Carpenter, L. J.: Global sea-surface iodide observations, 1967-2018, submitted, doi:10.5285/7e77d6b9-83fb-41e0-e053-6c86abc069d0, 2019a. Chance, R., Tinel, L., Carpenter, L. J., Sarkar, A., Sinha, A. K., Mahajan, A. S., Chacko, R., Sabu, P., Roy, R., Jickells, T. D., Stevens, D. and Wadley, M.: Surface inorganic iodine speciation in the Indian Ocean and Indian Ocean sector of the Southern Ocean, Manuscr. Prep., 2019b. MacDonald, S. M., Gómez Martín, J. C., Chance, R., Warriner, S., Saiz-Lopez, A., Carpenter, L. J. and Plane, J. M. C.: A laboratory characterisation of inorganic iodine emissions from the sea surface: Dependence on oceanic variables and parameterisation for global modelling, Atmos. Chem. Phys., 14(11), 5841–5852, doi:10.5194/acp-14-5841-2014, 2014. Magi, L., Schweitzer, F., Pallares, C., Cherif, S., Mirabel, P. and George, C.: Investigation of the Uptake Rate of Ozone and Methyl Hydroperoxide by Water Surfaces, J. Phys. Chem. A, 101(27), 4943–4949, doi:10.1021/JP970646M, 1997. Mahajan, A. S., Tinel, L., Hulswar, S., Cuevas, C. A., Wang, S., Ghude, S., Naik, R. K., Mishra, R. K., Sabu, P., Sarkar, A., Anilkumar, N. and Saiz Lopez, A.: Observations of iodine oxide in the Indian Ocean Marine Boundary Layer: a transect from the tropics to the high latitudes, Atmos. Environ. X, 1(January), 100016, doi:10.1016/j.aeaoa.2019.100016, 2019a Mahajan, A. S., Tinel, L., Sarkar, A., Chance, R., Carpenter, L. J., Hulswar, S., Mali, P., Prakash, S. and Vinayachandran, P. N.: Understanding Iodine Chemistry Over the Northern and Equatorial Indian Ocean, J. Geophys. Res. Atmos., (x), 2018JD029063, doi:10.1029/2018JD029063, 2019b. Moreno, C. G., Gálvez, O., López-Arza Moreno, V., Espildora-García, E. M. and Baeza-Romero, M. T.: A revisit of the interaction of gaseous ozone with aqueous iodide. Estimating the contributions of the surface and bulk reactions, Phys. Chem. Chem. Phys., 20(43), 27571–27584, doi:10.1039/c8cp04394a, 2018. Moreno, C. and Baeza-Romero, M. T.: A kinetic model for ozone uptake by solutions and aqueous particles containing I- and Br-, including seawater and sea-salt aerosol, Phys. Chem. Chem. Phys., 21(36), 19835–19856, doi:10.1039/c9cp03430g, 2019

Please also note the supplement to this comment:
https://www.atmos-chem-phys-discuss.net/acp-2019-1052/acp-2019-1052-RC1-supplement.pdf

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Discussion paper