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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Inorganic bromine in the marine boundary layer: a critical review" *by* R. Sander et al.

Anonymous Referee #2

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General Comment

This paper reviews the existing observations of "inorganic bromine" in the marine boundary layer and attempts to utilize them for insight into processes despite differences in sampling and an analysis techniques. A good job is done although inconsistencies in terminology and the failure to state the sampling and analysis techniques explicitly during key arguments in the text make the paper awkward to read at times. There are also some particularly weak sections that the authors may wish to improve or remove since they currently add little to the review.

Specific Comments:

1. P. 2968 L. 5-12. To quote the authors: "In this paper we use the term 'bromine' and the symbol Br to denote the total of all inorganic bromine compounds. We only

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use 'bromide' if the ion Br- is meant specifically". Strictly, speaking NAA, PIXE and XRF which are common techniques for much of the data in Table 2 measure "total Br including organic particulate Br". Furthermore for PIXE and XRF, samples are subject to high vacuum conditions and really measure "total in-volatile particulate Br including organic Br". Thus, the assumption implicit in the authors' definition above is that organic particulate matter comprises an insignificant fraction of the the non-bromide fraction of an aerosol. This may well be justified for coarse particulate bromine near a sea salt source but it not so clear that it holds true for fine particle Br in the accumulation or nucleation mode. Why not explicitly state this, drop 'inorganic' from the title and point out the scarcity of speciation studies of particulate bromine as a function of particle size in the atmosphere?

2. P. 2968 L. 29 The sentence warning of high blanks in Nucleopore is awkward detracting from the flow of the text. Furthermore in a critical review, other filter types should be discussed as well as Nucleopore. Either do this or delete the sentence.

3. P. 2969 L. 8-10 The use of one set of unpublished observations in Hawaii to prove the assertion that mixing chemically distinct particles on filters does not lead to volatilization artifacts is weak.

4. P. 2969 L. 22-24 A newer reference to add to this for sea salt is Gong, S.L., L.B. Barrie, and M. Lazare, 2002, CAM: A Size Segregated Simulation of Atmospheric Aerosol Processes for Climate and Air Quality Models 2. Global sea-salt aerosol and its budgets, J. Geophys. Res., 107, D24, 4779, doi:10.1029/2001JD002004.

5. P. 2980 L. 25-29 The statement that NAA or PIXE measures total inorganic Br is incorrect (see comment 1 above). NAA and PIXE measure total Br atoms in the sample including those in organic compounds. That organic Br contributed neglibly to total BR in particles is an assertion that needs to be proven with comparisons of INA and IC at many locations. The authors state that they are not aware of any such studies. However, this reviewer is aware of at least one study NAA and IC analysis on filters

ACPD

3, S1075–S1078, 2003

at Alert in the Arctic. In "Barrie, L.A., S.M. Li, D.L. Toom, S. Langsberger, W. Sturges, 1994, Lower tropospheric measurements of halogens, nitrates and sulphur oxides by denuder and filter systems during Polar Sunrise Experiment 1992, J. Geophys. Res. D., 99, 25,453-25,468" it was concluded that total bromine on particulate matter in Arctic winter spring on Teflon filters was mainly bromide (see Table 1).

6. P. 2981 L. 21-23 It is suggested that there is no known mechanism for obtaining enriched Br on sub-micrometer particles. The authors argue that external mixing of chemically distinct aerosol types could not lead to enriched fine particle Br and that there is no know mechanism that can lead to sub-micrometer particulate Br. The mechanism of mobilization of Br- from sea salt aerosol as a reactive gas by heterogeneous reactions is the most likely source of this fine particle Br. Until a complete simulation is conducted of gas-particle interactions that highly resolves particle size and includes realistic equilibrium and non-equilibrium gas-particle reactions and NH3 as well as the effects of transport, I am not convinced that current knowledge falls short in explaining enriched fine particle Br. In the lower Arctic troposphere at Alert in spring with very acidic sulphuric acid aerosols present in the fine particles, there is a dramatic shift of the partitioning of total bromide from the gas phase to the fine particle phase as ozone drops below 3 ppb(see reference in comment 5 above). This is explainable by the decrease of reactive gaseous Br compounds (BrO, HOBr and organic gaseous Br{see reference to Sturges et al in comment 7 below}) as ozone disappears leaving nothing to maintain the dynamic equilibrium between particlate and gas phase bromide. Also, the presence of halogenated dicarboxylic acids (Br-C3 and Br-C4) in the atmosphere particulate matter (Kawamura et al, 2003, JAC, 44 323-335) during active Arctic spring indicates that Br is involved in organic particulate formation through gas to particle conversion mechanisms. There is no reason to believe that this does not happen outside the polar regions.

7. P. 2983 L. 5 The reference here is to a ground breaking work but it does not support the general statement since the Arctic is much larger than Barrow Alaska. I suggest

ACPD

3, S1075–S1078, 2003

you add a few other references of measurements made elsewhere such as Alert and Spitsbergen. Also there is a follow-up study to Berg et al of Br gas-particle partitioning by Sturges et al 1993, Spring measurements of tropospheric bromine at Barrow Alaska GRL, 20, 201-203 that should not be missed in a critical review.

8. P. 2983 L. 6-7 This statement is incorrect. From latitude 53 to 58 which is NOT the polar region, there is significantly enriched particulate Br in Figure 2

9. P. 2983 Section 4.4 This section is very weak. In L.20 there is "limited" data. In L. 23 there is "unpublished data" and the analytical methodolgies of Moyers and Duce(1972) or Rancher and Kritz(1980) to determine gas-particle partitioning are not described and critiqued.

10. P. 2988. L. 4. I believe Gong has a new 2003 review paper that you might add to this critical review.

Technical comments

11. P. 2970 L.1 Delete Absolute

12. P. 2972 L.28 Arctic marine air

13. P. 2974 L. 6 to 8 IChange to "If the method..... below the DL is not specied, it is impossible...etc."

14. P. 2974 L. 12 add after unpublished "but from laboratories with methodologies published in the literature cited here"

15. P. 2977 L5 add after samples "except North Sea samples"

16. P. 2980 L. 2 delete "absolute" and add "for " after "compensate"

Interactive comment on Atmos. Chem. Phys. Discuss., 3, 2963, 2003.