Atmos. Chem. Phys. Discuss., 10, C5040–C5044, 2010
www.atmos-chem-phys-discuss.net/10/C5040/2010/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Release of mercury halides from KCl denuders in the presence of ozone" *by* S. N. Lyman et al.

Anonymous Referee #2

Received and published: 9 July 2010

Referee Comments

Title: Technical Note: Release of Mercury Halides from KCl Denuders in the Presence of Ozone

Authors: S.N. Lyman, D.A. Jaffe, M.S. Gustin

Overview The "discussion paper" is a conundrum for this atmospheric mercury scientist because:

1) The authors are highly competent analytical scientists undertaking the highly relevant and important topic concerning the performance of KCl-coated annular denuders for collecting gaseous oxidized mercury (GOM) species.

2) Based on my personal research experience, this type of work, with a complex sampling system, ozone generator, Hg species generation, transfer and surface adsorption/desorption effects at the part per quadrillion level is very difficult.

3) The results are counter-intuitive and difficult to understand chemically, since it suggests that a strong oxidant, ozone, results in the reduction of oxidized mercury to elemental mercury.

4) Because of the authors stated implications, it seems that the burden of proof for a cause and effect should be high. Publishing as a technical note with a limited number of lab-based experiments seems impatient, considering the complexity and importance of the topic.

5) The authors display an appropriate amount of cautiousness making it clear that the results are initial lab-based experiments and do not predict the quantitative extent of the bias to field GOM measurements.

6) More definitive experiments focused on the widely used field method of KCl-denuder sampling and analysis method for GOM should have been done. Also the experiments could have been more expansive to include or rule out possible alternative causes or effects to explain the results.

7) The final recommendations are excellent (page 12574, lines 26 to 29 and page 12575 lines 1 to 6).

Concerns with the data interpretation

I found the discussion or reconciliation of the variable results within each experiment or between different experiments to be somewhat skeletal. It does not appear that the data from the various experiments is entirely coherent with the author's key chemistry conclusions.

Concern 1: In Figure 3, the reported statistically significant anti-correlation of HgCl2 and O3 is reported for HgCl2 data that is at or below the stated detection limit. Also,

it appears that the HgCl2 concentration was decreasing significantly even before O3 was added. If Figure 3 is accurate and there is a strong anti-correlation of 03 and HgCl2 using KCl-denuders, how can we reconcile published reports showing strong, positively correlated GOM and O3 in the atmospheric using KCl-denuders? How does this impact the interpretation? What other possible causes could explain the data or have been considered and ruled out?

Concern 2: In Table 2 there are results than span the scale of essentially no loss (3%), some loss (14%) and highest loss (37%). If anything, these contrasting results suggest that the experiment was not under control. In addition, the author's interpretation is cautious enough, but still challenging to fully support. First the authors suggest that other air compounds present during sampling could explain the differences, but this explanation is surprisingly not extended to the other experimental results. Why did the authors dismiss the possibility that trace amounts of non-ozone, highly reactive compounds produced by the Daisibi 1008-PC ozone generator, contributed to the observed lab results (Page 12571, lines 20 to 24)? Second, the authors speculate that differences in GOM species could explain the results. It is difficult for me to support a large change in GOM species composition for a single location without any supporting evidence. In addition, no statistical analysis is done on this data, comparing differences in ambient humidity and ambient O3 concentration, unlike the analysis presented in Table 1. Most importantly, this experiment did not consider the limitations on sample collection time and sample storage on KCl denuders as reported in Landis et al., (2002) ES&T and Risch et al., (2007) WASP. Considering these two papers, the salient question one might ask is whether the highly variable results are just due to variability of the low humidity sample location, long-sample times (6 hours) combined with shipping and storage of a limited number of samples?

Concern 3: The statistical analysis and discussion focuses primarily on the results in Table 1, based on Experimental Design 1 "Ozonation after loading with HgX2 in the laboratory". In Experimental Design 1 ozone made from zero air is exposed to KCl

denuders at low flow rates for 30 minutes after HgCl2 sample loading is done in zero air. Experimental Design 1 is an extreme test and one can argue that it does not address the general theme of the paper to evaluate the KCl denuder method. One could argue that it has no relevance to field data. The KCl denuder method is the collection of GOM species in ambient air at high flow rates and desorption to GEM immediately in zero air at low flow rates without ozone present. In my opinion, the manuscript would be more relevant had it focused on data presented in Table 3, based on Experimental Design 3 "Ozonation during collection of HgCl2". However, the data set in Table 3 is very limited, so would not be enough to be at the heart of a full scientific manuscript for publication. In any case, it is good that the authors included important explanatory statements about the limitations of extrapolating the results beyond the lab-based experiments (page 12571, lines 20 to 29).

Concern 4: Does the %Hg lost reported in the 3 different tables and 2 figures form a coherent and somewhat predictable pattern – or not?

Other issues

1) The statement made on page 12574, lines 22 to 23 seem to be in conflict with the statement made on page 12574, lines 13 to 15. I believe the statement made on page 12574, lines 22 to 23 is over reaching and should be re-crafted to be in line with 12574, lines 13 to 15.

2) Under standard conditions, KCl-denuder surfaces are conditioned over time due to exposure to ambient air, sample collection and repeated desorption at 500 degrees C. Was the age or condition of the denuders studied?

3) In Figure 1, it does not show the source or quality of the air supplied to the Dasibi 1008-PC O3 generator/analyzer. The source and quality of the air supplied to this instrument should be clearly described in the text.

Please also note the supplement to this comment:

http://www.atmos-chem-phys-discuss.net/10/C5040/2010/acpd-10-C5040-2010-supplement.pdf

---

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 12563, 2010.