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Atmospheric
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Discussions

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

S. N. Lyman et al.

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Thank you for bringing up several very important points. We have striven to respond to each one thoroughly and openly.

Response to item 3: Indeed, the results of our study appear chemically counterintuitive at first, but the process may in fact be thermodynamically favorable. We don't know the mechanism by which the reaction of mercury halides with ozone is occuring, but a first guess might be the following:

$HgCl_2 + 2O_3 => Hg^0 + 2O_2 + 2ClO$

The free energies of formation ($\Delta G^0{}_f$) for these compounds are as follows (in kJ/mol):

$HgCl_2$: -173

O_3: +163

Hg^0: 0

O_2: 0

ClO: 34 (calculated from the enthalpy of formation and entropy, as found at
http://webbook.nist.gov/cgi/cbook.cgi?Source=1972BRI13&Units=SI&Mask=1E9F)

$\Delta G^0{}_R$ for the reaction can be calculated as $\sum(\Delta G^0{}_f$ of products) - $\sum(\Delta G^0{}_f$ of reactants). This gives a $\Delta G^0{}_R$ of -85 kJ/mol, indicating that the reaction could occur. Note that while Hg is reduced by O_3 in this reaction, Cl is oxidized.

We did not include this in the manuscript because it seemed to us too speculative, since we have no experimental evidence to indicate the mechanism of the reaction, and we cannot rule out much more complex, heterogeneous processes.

Response to item 4: We agree that this is an important topic that merits much more research than we have been able to present in this study. However, we feel that it is vital to publish our results at this point to alert the atmospheric mercury community to a potential problem with a common technique, and to provide impetus for further research in this area.

The reviewer states that the "burden of proof… should be high." We submit that this same logic should be applied to the existing KCl denuder method. Very little is known about the chemistry, interferences, and/or biases of the KCl denuder method, yet it continues to be applied by a growing body of research scientists and government agencies. Research into the efficacy of this method is vital to the atmospheric mercury community, and is long overdue.

We hope that other groups replicate our research and carry it further to the more difficult task of in-field validations of automated KCl denuder systems. We have discussed this need in the Implications section of the manuscript, page 12574, lines 13-21.

We have made every attempt to control for potential interferences and consider alternative hypotheses in the process of this research. If the reviewer has alternative hypotheses that are not considered in the manuscript or the review, please notify us and we will gladly include a discussion of them in the revised manuscript.

Response to item 6: We agree that field experiments with automated KCl denuder systems sampling ambient air are needed to confirm our experimental results. We do show that the HgX_2-ozone reaction is relevant in ambient air with ambient ozone (Figure 3), at flow rates typical of field KCl denuder sampling (Table 3), and with oxidized mercury compounds collected from the ambient atmosphere (Table 2).

Unfortunately, a rigorous test of field KCl denuders will likely require the development of field-deployable standards for gaseous oxidized mercury compounds. We feel that this is an essential next step in understanding this method. We have discussed this in the Implications section of the manuscript, page 12574, lines 13-21.

It may be possible to deploy two denuder systems side-by-side, and add ozone to one system to see the difference between the two, but the poor precision of denuder measurements, and the fact that ozone is already abundant in gaseous oxidized mercury-rich ambient air, makes it unlikely that the difference would be statistically significant.

As mentioned before, we have tried to address any alternative hypotheses that could explain our results. Please alert us to any we have overlooked.

Response to Concern 1: The original concentration of $HgCl_2$ was about twice the 2.5 minute detection limit, and the detection limit is lower if integrated over a longer period. The detection limit of our system is ˜30 pg m^{-3} if 30 minute average samples are used. Using 30 minute averages, the difference in $HgCl_2$ concentration before and after ambient ozone concentrations rose above zero ppb is about three times the magnitude of the detection limit.

We disagree that the figure shows the $HgCl_2$ concentration decreasing before the ozone concentration begins to rise. The initial rise in ozone concentration is small, but it precisely corresponds with the drop in $HgCl_2$.

The manuscript addresses the issue of field studies that show positive correlation between ambient ozone and ambient gaseous oxidized mercury. It appears on lines 4-8 on page 12574.

Response to Concern 2: When interpreting these results, it is important to note that the precision of KCl denuder measurements is at best 15%, and more commonly closer to 30%. This alone could explain the observed variability.

However, since the results of Table 2 are more variable than in the other experimental setups, the method precision argument may not be adequate in this case. It is possible, as the reviewer suggests, that some methodological failing caused this variability. However, note the small variability within each sample set in the amount of mercury lost from denuders in the presence of ozone (i.e. the standard deviation in the "% Hg lost in 2.5 min O_3" column of Table 2). This is an indicator that the sampling, storage, and analysis procedures were under tight control. This is why our discussion of Table 2 focuses on environmental variables that may have produced the variability among sample sets.

The lab experiments (except for Figure 3) involved air scrubbed with an activated carbon canister. We concede that a small amount of CO, NO_x and hydrocarbons may have been able to pass through this canister, but this should not have significant implications for our results, since our results still clearly show release of mercury from denuders when ozone is added. This outcome was consistent across all experiments.

If the reviewer is aware of any evidence that UV lamp-based ozone generators generate reactive compounds other than ozone, please provide it for us. We have not been able to find any, in spite of an exhaustive literature search. Mercury lamps like the one used in this study emit light with peaks at 184, 254, 365, 405, 436, 546, and 578 nm. O_2 is photolyzed by the 184 nm peak, and at that wavelength it produces only $O(^3P)$, not $O(^1D)$, eliminating the possibility of OH radical formation. Any NO_2 that passed through the activated carbon canister could be photolyzed to produce $O(^1D)$, which could have contributed to OH formation, but most of the experiments were carried out with extremely low water vapor (see tables), making it unlikely that this reaction was significant. SO_2 was probably trapped out by the carbon, as were other common reactive species.

Note also that all blank denuders were also ozonated, and no Hg peaks were found from them, showing that the ozone generator did not produce artifact mercury (see Figure 4).

Figure 3 is evidence that the ozone-denuder effect occurs with ambient ozone.

Our preliminary statistical analysis on the results presented in Table 2 was not enlightening, since there were only three sample periods, and the variability of ambient ozone, temperature, and humidity was quite low in these springtime samples. A continuation of these experiments is warranted, in different seasons and locations.

We are not sure what the reviewer refers to with regards to the Landis et al. and Risch et al. papers. Risch et al. show that KCl denuders held for five days did not lose any mercury relative to those analyzed immediately after sampling, giving credibility to our 2-4 day analysis time for field denuders. Note also that ambient humidity was not particularly low in these samples.

Response to Concern 3: Our "Experimental Design 1" was intentionally different from normal field denuder methodology. We intended it to show clearly that ozone, and not other reactants that exist in ambient air, resulted in the loss of oxidized mercury compounds from KCl denuders. We concede that on their own these experiments are insufficient to fully support the hypothesis that ozone releases oxidized mercury compounds from denuders under normal field conditions, but they did show in a definitive way that ozone removes mercury under some conditions.

The differences between "Experimental Design 1" and typical field denuder sampling are clearly stated on page 12571 line 25 to page 12572 line 4.

Also, on page 12573 lines 20-25 please see our discussion of how each of the experimental designs helps make the case for an ozone-induced bias on KCl denuders in field conditions.

Response to Concern 4: We believe that the results reported in this manuscript do present a coherent picture and create a strong case that ozone does affect the ability of KCl denuders to retain oxidized mercury compounds. While the different experiment types yielded different results, and while the ozonation of field denuders in particular yielded data with high variability, in all of the experiments KCl denuders lost mercury when exposed to ozone, and this is to us convincing evidence that the effect we observed was real. This is emphasized in the manuscript on page 12573 lines 20-25.

Response to Other Issue 1: The reviewer's comment here is puzzling. Is he/she suggesting we have a good understanding of GOM in the atmosphere? We stand by the statements made in the manuscript on these lines.

Response to Other Issue 2: We were not able to study the effects of the age of KCl denuder coatings in a comprehensive way. However, when we first discovered that our denuders suffered from a bias under some conditions, one of the first things we suspected was that the effect was due to the age of the KCl coating. Recoating our denuders did not eliminate or reduce the effect.

Response to Other Issue 3: The source of air to the Dasibi 1008-PC is included in the figure caption.

Many of these concerns, including those in the reviewer's supplemental document, were addressed prior to final manuscript submission to ACPD, as directed by the Editor. A copy of that response is attached.