

Dear Editor:

Thank you for recommending our paper for publication in ACPD. We have carefully considered the reviewer comments and modified our manuscript accordingly.

We agree with Reviewer 2 that the issue of an ozone-induced bias in gaseous oxidized mercury concentrations measured by KCl denuders merits much more research than that contained in this manuscript, and we hope that our work spurs others to more completely investigate this phenomenon. While our results are preliminary, we feel they clearly show that an ozone-induced bias does exist, even if they are not able to quantify the extent of the bias for the full range of possible field conditions. Investigation of this bias in real field conditions is obviously an important next step, but our laboratory studies were also necessary, particularly since they eliminated many of the myriad confounding factors inherent in field studies and isolated ozone as a specific compound of interest.

Though there is certainly more work to be done, we feel the results in our current manuscript are sufficient to convincingly support our hypothesis, even considering the weighty implications of that hypothesis. The following responses and revisions support this contention:

1. We have attempted in the revised manuscript to more explicitly rule out and discuss alternative causes for our observed results. See page 4 lines 6-13, page 7 line 26-page 8 line 17.
2. In response to *Concern 1*: Indeed there is a correlation between  $\text{HgCl}_2$  and ozone in the dataset shown in Figure 3 (we assume the reviewer is referring to Figure 3, since Figure 1 is a diagram). The  $r$  value has been added to the manuscript on page 7 line 10. The short-term variability in  $\text{HgCl}_2$  concentration in the figure is the result of random instrument noise. Though it also appears in the body of the manuscript, we have noted in the figure caption that the detection limit for the oxidized Hg concentration is  $76 \text{ pg m}^{-3}$ . It is important to keep this in mind when viewing the figure. The reviewer is right to wonder whether something other than ozone could have been the cause of the change in  $\text{HgCl}_2$  concentration shown in Figure 3. We also puzzled over this same question extensively, and we designed the laboratory experiments to help answer this question by removing as many uncontrolled variables as possible. We have added discussion of possible alternative explanations on page 4 lines 6-13, page 7 line 26-page 8 line 17.
3. In response to *Concern 2*: We were also surprised by the variability in the amount of mercury removed from field denuders by ozone. Even the results of "Experimental Design 3," wherein we ozonated denuders during collection at  $10 \text{ L min}^{-1}$  in our controlled lab setup, were variable. In spite of this, the results for the different samples and different experiments were remarkably consistent in that loss of mercury from denuders was observed each time we added ozone. We have modified our discussion of these results on page 8 lines 9-17, and page 9 lines 17-22.
  - a. While it is possible that trace compounds in the carbon-scrubbed air used for laboratory denuder sampling produced some variability in the results, we feel this possibility is small, since most reactive compounds should be removed by the carbon scrubber.

- b. While it is possible that the ozone generator used produced reactive compounds other than ozone that influenced our results, it is likely that ozone was the dominant reactive compound in air during these experiments. A literature search and inquiries to manufacturers were unable to produce evidence for the production of significant amounts of non-ozone reactive compounds by UV lamp-based ozone generators. We have stated this on page 7 lines 26-29.
  - c. We have modified the discussion of the possibility of changes in ambient GOM speciation on page 8 lines 11-14, including extending this hypothesis to our laboratory results.
  - d. We have removed the last sentence of this paragraph.
  - e. Unfortunately, conditions during the different field sampling periods were not sufficiently different to allow statistical analyses of the ambient meteorological data.
4. In response to *Concern 3*: Our "Experimental Design 1" was intentionally different from normal field denuder methodology. This design showed 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 other experimental designs add to "Experimental Design 1" and make the case that the phenomenon is relevant for ambient ozone (Figure 3), ambient GOM (Table 2) and under more traditional sampling conditions (Table 3). We have tried to make this more clear on page 3 lines 20-25 and page 9 lines 17-22. We have also added a statement on page 7 line 30-page 8 line 5 that underscores the differences between typical field denuder sampling and our analytical setup.
5. In 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. We have added a statement to this end on page 9 lines 17-22.
6. We have re-crafted the statement that was formerly on page 9 lines 1-5. It is now on page 10 lines 13-17.
7. We were not able to study the effects of the age of KCl denuder coatings in a rigorous way. 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. However, recoating our denuders did not eliminate the effect. Also, in the field denuder experiments, the first denuders released less mercury in the presence of ozone, and the amount released increased with subsequent samplings. However, we tested the field denuders in the laboratory immediately after the first field denuder sampling, and they performed identically to our lab denuders when we loaded them with HgCl<sub>2</sub> in the lab and then ozonated them. Thus, we have some confidence that the variability in the field results was not due to differences among the denuders or the coatings.

8. We have added a statement on page 4 lines 6-13 to justify our use of 100°C sample lines and discuss the implications of this.
9. We have added a statement to the caption of Figure 1 about the source of air supplied to the Dasibi ozone generator.
10. We have added information about the purity of the Hg halides used as permeation sources on page 3 line 29.
11. We have modified the abstract according to the reviewer's request.