

Atmos. Meas. Tech. Discuss., author comment AC2
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Reply on RC2

Jan Gačnik et al.

Author comment on "Behavior of KCl sorbent traps and KCl trapping solutions used for atmospheric mercury speciation: stability and specificity" by Jan Gačnik et al., Atmos. Meas. Tech. Discuss., <https://doi.org/10.5194/amt-2021-153-AC2>, 2021

Dear reviewer,

thank you for the comments. Your comments are marked with bullets.

- Line 16-18: the stability test of Hg(II) showed a highest loss of 5.5 % (mostly around 1-2 %), this is overall small relative to the analytical uncertainty of atmospheric GOM (could be biased by several times). I do not think a correction of such a small loss would improve the analysis of atmospheric GOM. I agree that a much lower loading of Hg(II) (e.g., 5-100 pg) may have caused higher loss of Hg(II), but this was not done in this study. Therefore, based on the findings of this study, it is not practicable to draw a conclusion that the GOM measurements should be corrected by the loss of Hg(II) (e.g., 5 %).

I agree with the comment, there are biases of much higher orders than 5 % for GOM. We have therefore excluded the sentence "GOM losses should be taken into account when using KCl sorbent traps for atmospheric Hg speciation, especially at low ambient GOM concentrations."

- Line 156: why a KCl solution with a concentration of 1 mol L⁻¹ was used to soak the quartz wool? Have the authors tried other concentrations? Would a higher concentration improve the sampling of GOM or cause a higher retention of GEM?

We have only tried 1 mol L⁻¹ concentration. We have tested a variety of other conditions in the stability test (trap type, loading type, species loaded, high/low airflow, high/low species concentration). Solubility of KCl is the delimiting factor for increasing the concentration, highest being 4.5 mol L⁻¹ at 20 °C. This would not be a major increase from 1 mol L⁻¹ therefore we think that it would not change the outcome of the experiment.

- Line 157-158: these KCl sorbent traps were reused by heating to a temperature of 600 °C. This temperature is relatively higher than the traditional temperature setting (e.g., 500-550 °C) for the desorption of GOM from KCl coated denuders. I think this may change the morphology of KCl, as suggested by the authors.

Though 500-550 °C is used for denuders, KCl sorbent traps are mostly heated at temperatures around 700 °C - i.e. Lumex speciation traps and their pyrolysis with AAS detection. In literature, there are instances of even higher temperatures being used with KCl coated materials and sorbent traps for Hg(II) pyrolysis.

- Line 159-160: the authors used a mixed acid solution to leach the Hg(0) collected on the KCl sorbent traps, I think these treatments would also change the chemical properties of KCl traps, which may increase the retention of GEM by the sorbent traps.

This is a misunderstanding: once traps were leached with acid, they were not reused again. They were "reused" before the start of experiment by heating to ≈ 600 °C three times prior to the experiment (as described in line 158).

- Line 182-183: The authors should explain why these two experiments would precisely generate HgCl₂ or HgBr₂. Have the authors determined the Hg(II) compounds in these two solutions?

The concentration of HgCl₂ or HgBr₂ compounds was measured by CV-AAS as described in section 2.2. We were aware of the exact composition of Hg_xCl_x and Hg_xBr_x species in the solution by calculating the species abundance from the equilibrium constants. We have added a reference to the exact calculation which is described in our previous work. The added sentence goes as following: "By equilibrium calculations described in the work of Gačnik et al. we confirmed that the spiking solutions contained only HgCl₂ and HgBr₂ without other Hg_xCl_x or Hg_xBr_x species (Gačnik et al., 2021)".

- Line 276-280: In my opinion, an over interpretation of the results is not of significant scientific values. As mentioned above, the leaching and reuse processes of the KCl sorbent traps would probably change the morphology of KCl traps (especially for the KCl crystal and KCl crystal + Al₂O₃ catalyst), and they are quite different from the processes for the reuse of KCl denuders.

We have excluded this interpretation to your suggestion.

- Line 324-325: A comparison of the absolute losses between the low and high loading of Hg(II) is meaningless.

We have excluded this comparison to your suggestion.

- Line 331-336: I agree with the authors that loss of Hg(II) could occur during the sampling. However, the losses could be associated with many factors, such as quantity of Hg(II) on the sorbent traps, sampling and flushing flow rate, ozone, humidity, etc.. In this study, the loading of Hg(II) is much higher than the real atmospheric conditions, and the air flow was also lower than the GOM sampling flow rate (e.g., 10 LPM) and flushing flow rate during desorption processes (e.g., 1.0 LPM). Therefore, using the loss rate determined from this study to correct GOM measurement is not expected.

We changed the paragraph to the following: "Longer sampling times are often used for low concentrations of Hg²⁺ (the amount of Hg²⁺ collected from the ambient atmospheric samples is in the order of picograms), therefore some losses of GOM will be observed most of the time. Losses depend not only on the parameters tested in our work, but also on meteorological conditions (e. g. humidity, presence of ozone, temperature...)."

- Section 3.6: A GOM bias of 3500 % for the using the KCl solution trap is extremely higher. The authors should specify that the KCl solution trap should be not relevant for field GOM sampling. Note that KCl solution trap is generally used for the sampling of GOM in flue gas.

We have added a sentence to your suggestion: "The calculated biases show that KCl trapping solutions are not appropriate for ambient GOM sampling, while they are still a valid choice for flue gas sampling (high GOM concentrations)."

The fact that these solutions are generally used for sampling of GOM in flue gas is already

stated in the introduction (lines 77-79).