Response to Comments by Anonymous Referee #1

This paper describes tests of 3 different passive samplers for gaseous elemental mercury. These samplers are typically deployed for 8 to 12 weeks. I disagree with the first sentence in the abstract. They will tell us little to nothing. These samplers are only useful in contaminated areas and are not appropriate for monitoring. Gradients in air concentrations between the Northern and Southern hemisphere have been well documented. They are not highly variable. Thus, as for these helping meet assessment needs these samplers, because of the long sampling time will tell us nothing about the "presence and movement of mercury and mercury compounds in the environment." We know gaseous elemental mercury is ubiquitous in the air. These sampling systems will tell us little about transport and deposition or mercury compounds. The authors need to be honest about these methods and what information will be gained, for in my mind this is little.

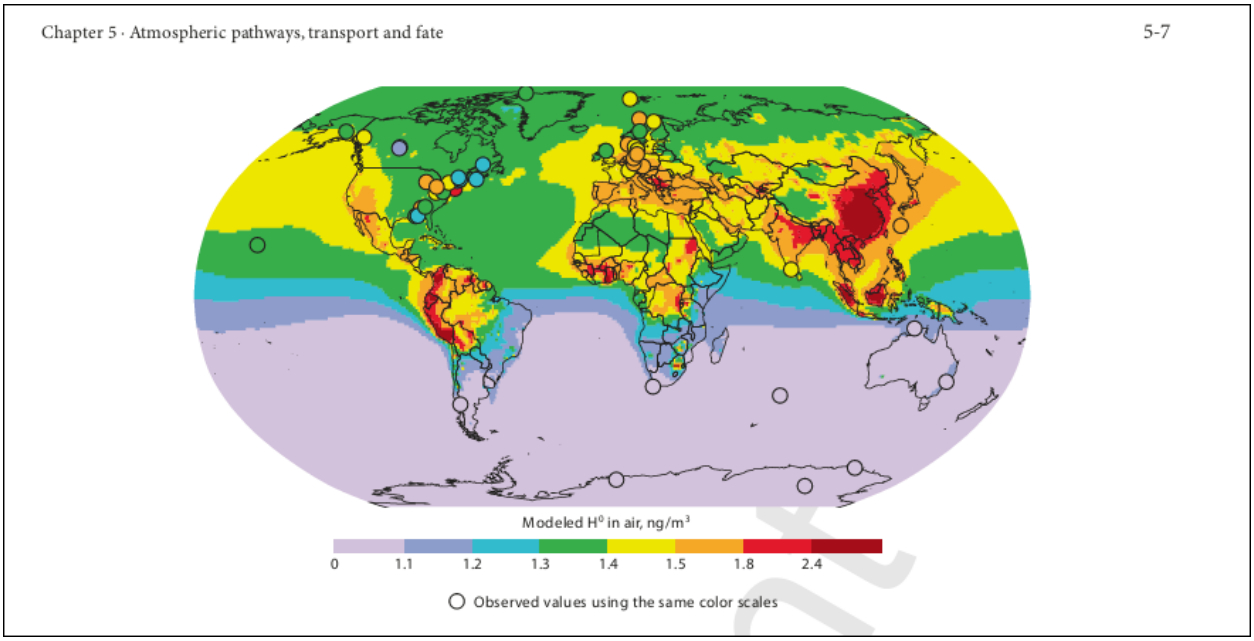
Considering that most of the authors of the paper expended considerable effort, time, and resources on the development of passive air samplers (PASs) for gaseous mercury, it probably comes not as a surprise that we assess the usefulness of those samplers profoundly differently from the reviewer and do not share the opinion that "they will tell us little to nothing". Reviewing the merits of PASs for gaseous elemental mercury (GEM), McLagan et al. (2016) identified primarily three areas where such samplers complement existing active sampling systems: "(1) long-term monitoring of atmospheric GEM levels in remote regions and developing countries, (2) atmospheric mercury source identification and characterization through finely resolved spatial mapping, and (3) the recording of personal exposure to GEM." Since the writing of this review five years ago, PASs for GEM have already proven their usefulness in all three of these application areas.

Re (1): Long-term monitoring of atmospheric GEM levels in remote regions and in developing countries. There are a number of site categories where measurements of GEM with existing active sampling techniques are logistically extremely challenging, prohibitively expensive or outright impossible. The reasons include:

- An electrical power supply is non-existent, intermittent or unreliable.
- Site access is difficult or only possible sporadically (e.g. research stations in remote areas, which are only serviced by vessels once or a few times in a year).
- The likelihood of loss of, or damage to, sampling equipment by natural forces or human intervention is high (e.g. sampling on volcanoes (Si et al., 2020), on sea ice, or in locations with illicit mercury use (Snow et al., 2021b)).

The simplicity, low cost, and limited site requirements (with respect to electrical power, etc.) often make it feasible to use PASs under such circumstances and will greatly expand the number of sites where GEM concentrations can be recorded.

In the map below, taken from the Global Mercury Assessment 2018 (AMAP/Un Environment 2019), the global distribution of model ensemble median gaseous elemental mercury concentration in surface air for 2015 are shown and compared with observed values. The places where GEM has been measured in the atmosphere (shown with circles using the same colour scale) show glaring spatial bias. There are large swathes of the global atmosphere where no such measurements have been conducted. Passive air samplers are poised to fill many of those data gaps.



We further point out, that PASs are not just suited to record the long-term average concentration of GEM in the atmosphere, but can also be used to record the isotopic composition of that mercury (Szponar et al., 2020).

Re (2): Atmospheric mercury source identification and characterization through finely resolved spatial mapping. One of the primary capabilities of PASs is the ability to measure simultaneously at numerous locations. This is again feasible, because of the low cost and limited site requirements relative to those of most active air sampling techniques. As a result, PASs have for the first time allowed for the mapping of the spatial concentration variability of GEM. While there are portable active sampling systems that have been used for mapping before, they typically make sequential short-term measurements at multiple locations and therefore cannot clearly discriminate temporal from spatial concentration variability. PASs for GEM have already been used to map spatial GEM concentration variability within a large urban area (McLagan et al. 2018a), in the vicinity of an abandoned mercury mine (McLagan et al., 2019), in geothermally active areas (Si et al., 2020), in artisanal gold-mining communities (Snow et al., 2021b) and in occupational environments (Snow et al., 2021b).

Monitoring for GEM does not have to be focussed on atmospheric background concentrations, but in fact is often called for in “contaminated areas”. The objective of such monitoring then could be (i) the identification or confirmation of atmospheric GEM emission sources (McLagan et al., 2018a), (ii) the quantification of atmospheric GEM emissions, whether they are anthropogenic (McLagan et al., 2019) or geogenic (Si et al., 2020), or (iii) the characterisation of human inhalation exposure (Snow et al. 2021b).

Re (3): Recording of personal exposure to GEM. If worn in the breathing zone of an individual, PASs can record the personal inhalation exposure to GEM (Snow et al., 2021a). This has been demonstrated e.g. for the exposure of the acute and chronic exposure of people in artisanal and small-scale gold mining (Snow et al. 2021b, Black et al., 2017, de Barros Santos et al., 2017).

In summary, the reviewer appears to have a very limited imagination as to what "monitoring of atmospheric mercury worldwide" could possibly comprise. We are looking forward to proving the reviewer wrong in predicting that little of merit will be gained from the type of sampler evaluated in our study.

Abstract and throughout the paper what has been done should be described in the past tense.
Line 28 remove both
Line 46 remove highly

These are largely suggestions on writing style rather than required corrections in grammar and thus we do not see the need for adopting these changes. Just as an example, every compound is "toxic" depending on dose, so to characterize mercury as "highly toxic" seems hardly inappropriate.

Line 84 remove for the first time

We believe to have presented in the manuscript the first blind inter-comparison of passive air samplers for mercury and therefore this statement to be factual. If the reviewer can provide a reference to other such studies and we will reference them and alter the text.

Lines 95, 189, 344, and 534 remove ", which" and replace with "that"

All four of these clauses starting with "which" are not defining clauses and therefore the use of "which" is grammatically correct. As it is possible to remove the clause without destroying the meaning of the sentence, the clause is non-essential and "which" can be used. We, therefore, think that no change to the grammar for those sentences is required.

Line 221 put a comma before because

We could add a comma during the revision.

Comment on sampling rate calculation- this will depend on wind and possibly temperature and RH, and I am not sure how this is accounted for since this will vary by each location

On line 219 we indicated that constant sampling rates for all the samplers were applied. We could include the phrase "these rates were not adjusted for deployment-specific meteorological conditions" in a revised version.

Furthermore, on lines 115 to 117, we had written: "Results for the *Mer*PAS® with temperature-adjusted sampling rates, that had also been submitted were disregarded, as they were the only set of results seeking to take into account this effect. Temperature adjustment did not improve the accuracy of the *Mer*PAS® results."

Lines 485-492 include a discussion of the possibility that the sampling rates are affected by wind speed and temperature and whether those influences could explain the observed discrepancies between active and passive sampling results.

Finally, we also had written on line 539: "A promising result of this study is that the SRs of the CNR-PAS at the two locations are more similar than for the other two PAS, which may hint at an SR that has a relatively small dependence on meteorological factors."

Line 264 you should put the value for each sampler and the standard deviation

The concentration values given in this line refer to the measurements obtained by active sampling. On lines 263 and 271, we already report the standard deviation of the actively recorded air concentrations.

Paragraph that starts line 265. Were values measured by the two Tekrans the same? Typically they are systematically different.

This information is provided on lines 384-389: "the "0075" instrument yielded values averaged over the deployment periods that were consistently lower than those measured by the "5037" instrument that was chosen as the reference. This bias was on average 3.2 % for the 11 sampling periods and ranged from a low of 1.0 % for the third 2-week period to a high of 6.5 % for the last 4-week period." Although concentrations were consistently lower on the "0075", it was not a systematic difference that could be corrected and this resulted in data not meeting QC criteria. This is addressed on lines 267-269: "The secondary co-located 2537a analyzer experienced an 8% shift in the mass-flow meter calibration during the study. Since it was not possible to determine when the shift occurred, data from this analyzer were not used for comparison with the PAS."

As you can see regarding the discussion of the data the Tekrans measured the variability while the passive samplers only measure the average and tell us little about the presence and movement of mercury or the compounds.

While it is often useful to know the variability of the GEM concentration at fine temporal resolution, there are many instances where the average of that concentration is of primary interest. In fact, when analyzing spatial and temporal variation in GEM concentrations, data measured at high resolution are regularly aggregated into monthly, seasonal and annual concentration bins (see e.g. Cole et al., 2014, Weiss-Penzias et al., 2016), indicating that those time periods of analysis convey valuable information on the presence and movement of mercury in the environment. These time periods are very well served with a PAS.

Also please put the standard deviations in for each sampler. Are the values statistically significantly different between Italy and Canada using these samplers? I would expect Toronto to be a bit higher due to the fact it is a big city.

The average concentration values as measured by each PAS were reported in Table S8 as mean ± sd. We do not see any merit in testing whether those two concentrations are statistically significantly different between the two locations. As is appropriate for a study that is comparing different sampling techniques, statistical analysis is focussed on the differences between samplers and not between locations. The average GEM concentration with standard deviation as measured by the Tekran systems over the twelve weeks of the entire study was 1.72 ± 0.25 ng m^{-3} in Italy (as given on line 262) and 1.57 ± 0.45 ng/m^{-3} in Canada (as provided on line 270), i.e. the opposite of the reviewer's expectations. Note that the Toronto location is in the north end of the city next to a large park and not in downtown metropolitan Toronto, while in Rende the sampling was carried out at a site potentially affected by vehicular traffic from a highway, a nearby urban area, and also by the presence of a small manufacturing area a few kilometers away.

Were the blank corrections subtracted for each sampling interval or just across the whole time? The former is the best way to do this and it is not clear in the text how this was done.

The amount quantified in each individual sampler was corrected for the average blank contamination obtained at a sampling site (see lines 115 and 218). To make this clearer, we can add the following information to section 2.7 in a revised version: "Because field blank levels were

not statistically significantly different between different deployment periods, but were different between Rende and Toronto, the average field blank contamination at one location was used for blank correction."

Line 385 –how do you know which Tekran concentrations were right?

There is no way of knowing which Tekran system measures the "right" concentration. However, the system labelled "5037" met the QC criteria, whereas the system labelled "0075" "experienced an 8 % shift in the mass-flow meter calibration during the study" and "since it was not possible to determine when the shift occurred" (line 268), we decided to use the system labelled "5037" for comparison with the passive sampling results. When there is a known issue with an instrument but we are not sure when the problem started to occur, we err on the side of caution and use the data in which we have the most confidence based on our QC protocols.

Discussion regarding sampling rate. This demonstrates how this will be variable depending on conditions and they need a way to adjust for this.

The reviewer is correct that the sampling rates can be somewhat influenced by local conditions during a deployment period, most importantly temperature and wind speed. In the case of the *Mer*PAS®, the dependence of the sampling rate on those conditions has been quantified in extensive laboratory experiments (McLagan et al. 2017) and a way to adjust for this influence during field deployment has also been presented (McLagan et al., 2018b). In the case of the CNR-PAS, the influence of meteorological parameters has not yet been fully investigated. However, laboratory experiments on the performance of the sorbent membrane at different temperature and humidity conditions have been conducted (Macagnano et al., 2018, Avossa et al., 2020).

If you are at a remote location and are not collecting meteorological data how can you calculate the SR?

As previously explained, the dependence of the sampling rates on meteorological variables is small. Because only the average conditions during the entire deployment period are relevant, it will often be possible to use temperature and wind speed conditions estimated from climate normal. An example of how this can be done for sampling sites around the world, see Herkert et al. (2018).

If sites have different meteorological conditions and you have no Tekran system how will you know how accurate your values are?

It is possible to assess the accuracy of a PAS-derived air concentration based on evaluation studies such as the one described in the current paper. In the case of the *Mer*PAS®, an earlier evaluation study assessed sampler accuracy at numerous sampling sites across the world with a wide range in climatic conditions (McLagan et al., 2018b). As for the more recently developed CNR-PASs, the effect of meteorological conditions is still under investigation. A study regarding the performance at different temperatures and humidities has recently been published (Avossa et al., 2020). The current paper about the accuracy of the sampler will contribute to the future evaluation of the CNR-PAS's performance.

Given the low concentrations what will this information tell us? Basically nothing useful. Again. . . these passive sampling systems did not capture spikes. So what is the utility of these methods?

We refer to the detailed response to similar sentiments expressed by the reviewer above. Again, while there can be situations when "spikes" in concentrations are important, there are also

numerous instances where temporally averaged concentrations (even if they happen to be low) are perfectly adequate for meeting monitoring objectives.

The authors should also look at the literature and discuss other passive sampling systems that have been tested for gaseous elemental mercury.

Some of us have reviewed earlier passive sampling systems for GEM in McLagan et al. (2016) and concluded that "none of the GEM PASs developed to date achieve levels of accuracy and precision sufficient for the reliable determination of background concentrations over extended deployments". Incidentally, this judgement was part of the driving force for developing the PASs comparatively assessed in this study. We don't see a need to repeat a discussion of these earlier systems here.

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