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Atmospheric Measurement Techniques Discussions

# *Interactive comment on* "A field intercomparison of three passive air samplers for gaseous mercury in ambient air" *by* Attilio Naccarato et al.

**Anonymous Referee #4**

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The paper is well written and as the title suggests relates to an inter-comparison of 3 passive samplers for gaseous mercury in ambient air. Throughout the paper the analyte is referred to as gaseous mercury which by definition would normally include both elemental Hg (GEM) and reactive gaseous Hg species (RGM). There are no validation studies to my knowledge that report that passive samplers will determine RGM and therefore it would be more appropriate to refer the analyte as GEM and also provide additional discussion on this point.

The use of passive samplers has limited value to fully understanding the cycling of Hg in the atmosphere as they only provide an average concentration over the deployment period. Generally, the legislation for ambient air only considers annual averages as representative of long term exposure. In this respect, passive samplers add additional



value to monitoring networks especially if they are deployed in remote locations. There is no discussion in the paper regarding manual sampling methods that use gold traps with a vacuum pump which is more comparable to passive samplers than an automated ambient air monitor such as the Tekran 2537. Manually sampling does require a power supply to operate the vacuum pump but they can also be used with rechargeable battery packs which for several weeks and they also offer total gaseous mercury (TGM) and much larger sample volumes. There are several aspects of the analytical performance evaluation of the passive samplers in this paper that are questionable and therefore need revising.

The detection limit calculations are based solely on the variability of the field blanks and currently ignore the actual blank values which are significant in relation to the mass of mercury collected on the passive samplers studied. Reporting detection limits less than the blank valve is questionable as it is not possible to quantify a mass of mercury less than the blank. The authors should recalculate the detection limits according the following IUPAC expression (LOD = Blank + 3$\sigma$n-1). This is far more appropriate way to report LODs for techniques that employ pre-concentration.

It is well known that sampling rates for passive samplers are affected by temperature, pressure, humidity and wind speeds. In this study these parameters are ignored even-though the metrological conditions at the sampling location have been measured and are available. The automated Tekran analyzers are based on a standardized volume measurement and the passive samplers are not. If the authors ignore the metrological conditions then the comparison is not valid. At both sites the metrological conditions were highly variable and in addition to this no pressure correction has been made for barometric pressure and elevation on each site. The impact of metrological conditions on sampling rates is discussed later on in the paper as an explanation for the higher variability at the Canadian site so why was the volumetric correction not applied? I would prefer that all passive sampler results are reported using a standardized volume based on the average metrological conditions on site for the deployment period. It

would also be good to know how the uncertainty of the sampling rate is affected by the metrological conditions. Whilst the overall correction might be small it is still important when performing and report the comparison. Humidity is unlikely to have an impact. Wind speed could have an impact but since the samplers are housed in a shelter then one could argue that this could also be ignored. The correction should therefore focus on temperature and pressure. for the Accuracy assessment was performed by comparing the result the Tekran analyzers operating on each site. The paper explains that two Tekran instruments were operated but it seems that results from only one analyzer was used for the comparison? Surely, the comparison should be done on the average of the two Tekran results? If there are periods of known downtime for one of the two analyzers or technical justifications for ignoring a period of time then that is understandable but to ignore one analyzer and assume that the second analyzer is accurate does not seem correct. It seems that the authors have adopted a strategy of running analyzers in parallel but only using the second analyzer as reassurance them that the other analyzer was performing well. It would be nice to see the trend for both analyzers especially when so called spike events are experienced. Other concerns relate to the online analyzer reporting GEM even though the description of the analyzer suggests that TGM was determined because sampling was performed directly onto gold traps? The authors need to focus on what they are actually measuring with each technique applied. As mentioned above the Tekran measurements are based on a standardized volume whereas the passive samplers are not. It would be acceptable in the paper to discuss this in more detail and refer to comparability rather than accuracy. Having a passive sampler offering good agreement to the automated measurement is a very reassuring but to define the accuracy on this basis is not acceptable.

Overall this is very interesting study and the publication will be interest to many readers conducting mercury research in the field of atmospheric measurements. If passive samplers are deployed at more sites in the future then it is important to standardize the sample rate volumes especially when performing comparisons with automatic measurement systems.



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