Response to interactive comments by reviewer 1 on

"Passive air sampling of gaseous elemental mercury: a critical review"

REFEREE'S COMMENT:

This manuscript reviews the "state" of passive sampling for monitoring of gaseous elemental mercury in air. It suggests that development of passive air samplers (PASs) for gaseous elemental mercury is needed and that PASs in the foreseeable future may be useful as a complementary technique in remote regions and in developing countries. Many previous studies have reported different PASs for GEM, but there is still a lack of researches regarding the levels of accuracy and precision sufficient for requirements of PASs. Meanwhile, studies on atmospheric mercury source identification and the recording of personal exposure to GEM would be improved. These issues are extra necessary and in good application to the network of global mercury monitoring. I feel there is full contribution, including the contents and perspectives, from this manuscript to the authors. Therefore, I suggest that this paper should be published in the journal of Atmospheric Chemistry and Physics in case of the comments are addressed by the authors.

AUTHORS' RESPONSE:

The positive sentiments are greatly appreciated.

REFEREE'S COMMENT:

1) Summarize and simplify the contents. Introduction There are a lot of references cited in the first three paragraphs.

AUTHORS' RESPONSE:

The introduction has been adjusted to reduce the number of references cited in each point. A maximum of 3 references per referable item has been used in the introduction (the one exception being the range of background concentrations reported in each hemisphere).

AUTHOR'S CHANGES:

The introduction is now as follows:

1. Introduction

Mercury (Hg) is a contaminant of global concern, undergoing long-range atmospheric transport (LRAT) and deposition in remote ecosystems (Driscoll et al., 2013; Selin, 2009; Selin et al., 2007). Once deposited, inorganic Hg can be transformed to methylmercury (MeHg) through the activity of certain anaerobic microbes (Driscoll et al., 2013; Schroeder and Munthe, 1998; Selin, 2009). In both humans and wildlife MeHg is bioaccumulative and a potent neurotoxin (Driscoll et al., 2013; Scheuhammer et al., 2007; Wolfe et al., 1998), and at lower, chronic exposure has also been associated with reproductive impairments (Scheuhammer et al., 2007; Selin, 2009) and geno- and immunotoxicity (Wolfe et al., 1998). The major uptake pathway of MeHg for humans is through the consumption of fish and seafood (Driscoll et al., 2013; Selin, 2009; Pirrone et al., 2013). Hence, elevated Hg exposure is prevalent among human populations with high fish consumption (Driscoll et al., 2013; Johansen et al., 2007; Selin, 2009). Although MeHg is the most bioaccumulative form of Hg, all forms exhibit toxic effects on mammals, the degree of which depends on species, dose, time and route of exposure (Harari et al., 2012).

Within the global biogeochemical cycle of Hg, natural sources to the atmosphere include geological processes and evasion from surfaces, with the ultimate sink being burial in deep ocean sediment (Driscoll et al., 2013; Schroeder and Munthe, 1998; Selin, 2009). The Hg cycle is being disrupted by primary anthropogenic emissions, estimated to range from 1900 to 4000 Mgyr^{-1} *(AMAP, 2011; AMAP/UNEP, 2013; Selin, 2009 and references therein). Primary anthropogenic sources of Hg can be from both the direct use of Hg or its emission as a by-product and include coal combustion, waste disposal, artisanal gold mining, cremation of deceased bodies containing Hg-based dental fillings, and the* *production of cement, nonferrous metals, iron, steel, caustic soda, gold, and Hg itself (Driscoll et al., 2013; Selin, 2009; Zielonka et al., 2012).*

There are three forms of atmospheric Hg: gaseous elemental mercury (GEM), gaseous oxidised mercury (GOM) and particle bound mercury (PBM). The mean ambient concentration of total gaseous mercury (TGM) (made up of GEM and GOM) is approximately 1.3-1.7 and 1.1-1.3 ngm^{-3} *in the Northern and Southern Hemispheres, respectively (Dommergue et al., 2010; Sprovieri et al., 2010; Driscoll et al., 2013; Gustin et al., 2011; Luo et al., 2010; Selin, 2009; Selin et al., 2007), with higher levels in urban areas and close to sources (Cheng et al., 2014; Carpi, 1997; Zhang and Wong, 2007). GEM's relatively high vapour pressure and inertness to atmospheric oxidation leads to a long atmospheric residence time of approximately 1 year (Lin et al., 2006; Pirrone, 2010; Skov et al., 2004). GOM and PBM have much shorter atmospheric residence times and are deposited closer to their source locations (Lin et al., 2006; Pandey et al., 2011; Skov et al., 2007). Thus GEM is typically the dominant species of atmospheric Hg globally (Ebinghaus et al., 2002; Gustin and Jaffe, 2010; Pandey et al., 2011), and the only species subject to significant LRAT (Driscoll et al., 2013; Nguyen et al., 2009; Selin, 2009). The exact proportional make-up of TGM is dependent on proximity to Hg sources and the concentration of atmospheric oxidants (Selin et al., 2007; Skov et al., 2004; Sprovieri et al., 2010).*

Ambient levels of the various forms of atmospheric Hg are most often measured using active or automated air samplers that draw a known volume of air over a Hg sorbent trap, which is desorbed periodically, and quantified (Lynam and Keeler, 2002). While commercially available active samplers are capable of measurements at relatively fine temporal resolution (Gustin and Jaffe, 2010), the spatial range of their application is limited to populated and generally affluent regions due to the high cost of the *instruments, their energy requirements and technical training necessary in their operation (Gustin and Jaffe, 2010; Gustin et al., 2011; Skov et al., 2007). Accordingly, the spatial resolution of atmospheric Hg measurements has been limited.*

Our purpose is to comprehensively review the existing literature on passive air samplers (PASs) for atmospheric Hg, focusing on GEM. Some of the samplers we review here are unable to distinguish between GOM and GEM (Gustin and Jaffe, 2010; Pandey et al., 2011; Skov et al., 2007). GEM generally makes up >98-99% of TGM at most sampling locations (Pandey et al., 2011; Gustin and Jaffe, 2010; Gustin et al., 2011) and thus GOM is expected to contribute a relatively minor proportion to the overall uncertainty of a GEM measurement (Pandey et al., 2011). For the sake of simplicity, we will therefore refer to the sorbate as GEM in this review. Starting with a summary of the rationale for passive air sampling of GEM, we then discuss the basic elements of PASs. Features and specific requirements of effective PASs for GEM are discussed vis-a-vis existing designs. We conclude by outlining future perspectives in GEM passive air sampling research. This review differs from the recent review by Huang et al., which had a much wider scope and discussed man-made and naturally occurring (e.g. moss and lichen) PASs for Hg, as well as wet and dry Hg deposition samplers (Huang et al., 2014). Furthermore, Huang et al. (2014) reviewed samplers for GEM, GOM and PBM; whereas we focus this review on PASs for GEM only.

REFEREE'S COMMENT:

6.3 "Do existing gaseous elemental mercury…" The last two paragraphs (Line 27 of page 34625 to line 3 of page 34627) mention the memory effects on sampler accuracy. All of them derive from the same reference, Brown et al. (2011). Also, the whole paragraph in 7.2, "Lessons from active monitoring".

AUTHORS’ RESPONSE:

It is true that the majority of references in the last two paragraphs refer to Brown et al. (2011). While we do cite several other references including Luo et al. (2010), Skov et al. (2007), Morris et al. (2002), etc., it is simply that Brown et al. (2011) have completed the most extensive testing of this concept to date. To our knowledge this is the only study that specifically addresses the topics of memory effects, and physical degradation of noble metal sorbents directly. Other studies that discuss these phenomena simply suggest that they may be the cause of problems that have arisen using these sorbents. Thus the Brown et al. reference dominates these sections. To quote the paper by Brown et al. (2011):

> *A couple of studies have identified the presence of a possible memory effect*[12,13] *and proposed that short and long-term effects exist; there has been no work to quantify this effect, its dependence on input variables, or its potential to bias measurement results. This paper now addresses that deficiency.*

AUTHOR’S CHANGE:

No Change

REFEREE’S COMMENT:

2) The same capitalization applies to table titles. For example, “Diffusive barrier” should replace with “Diffusive Barrier”.

AUTHORS’ RESPONSE:

This will be updated in a revised manuscript.

AUTHOR’S CHANGES:

Capitalisation of the first row of Table 1. is now only the first letter of the first word of each column heading as can be seen below:

Author(s)	**PAS type & dimensions** [*A:* cm^2; *d:* cm]	**Diffusive barrier**	**Sorbent material**	**Analytical method**	**Sampling rate** [m^{3}day^{-1}]	**Observed concentration** [ngm^{-3}]	***MDL* / *DT* for *MDL*** [ngm^{-3}] / [days]	***DT* tested** [days]	**Uncertainty** [%]

REFEREE’S COMMENT:

3) This paper was well organized, but I still find many confusing or complex sentences. In Figure 1, headings titles of page 34641, "Initially the SR is constant and analyte uptake will be linear (or near linear) and the sampler can be described as being in the effective deployment period."

AUTHORS' RESPONSE:

For clarification purposes we have updated this line and several other sentences that may have been confusing have also been updated and alterations indicated below.

AUTHOR'S CHANGES:

Figure 1 heading, page 34641 (second sentence):

> *Initially the SR is constant and the amount of sorbed analyte will increase linearly with time. During this phase the sampler can be described as being in the effective deployment period.*

Lines 15-17, page 34609:

> *PASs quantify the amount of a target compound that is taken up by the sorbent of the sampler from the atmosphere over a given period of time.*

Lines 15-18, page 34614:

> *While SR has an upper limit, because of the requirement for keep it tightly controlled (see Section 4.2), the length of deployment is limited by both the desired temporal resolution and the equilibrium uptake capacity, i.e. the need to remain in the linear uptake phase (Fig. 1).*

Line 2, page 34617

> *Passive sampling of GEM in air has been documented in the literature for over 35 years (McCammon and Woodfin, 1977).*

REFEREE'S COMMENT:

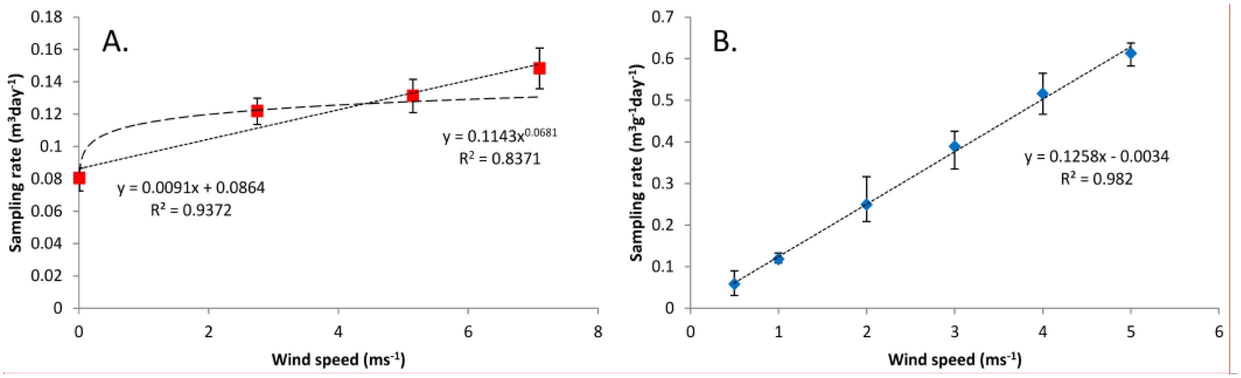
4) Error bars should be added in Figure 3.

AUTHORS' RESPONSE:

These will be added to Figure 3 in the final manuscript

AUTHOR'S CHANGES:

The figure now appears as follows with error bars included. Additionally, the equation for the power trendline in Panel A. of Figure 3. was updated. A conversion needed to be performed on the data as it was reported in ml min^{-1} in Skov et al. (2007), yet here we want m^{3}day^{-1}. Previously this conversion was not applied, but now reflects the correct, converted relationship: $y = 0.1143x^{0.0681}$.



Response to interactive comments by reviewer 2 on

"Passive air sampling of gaseous elemental mercury: a critical review"

REFEREE'S COMMENT:

Mercury is a pollutant of global concern and is distributed worldwide mainly via atmospheric transport. Therefore, monitoring of mercury concentration in the atmosphere is important. However, because of the issues associated with the commonly used active sampling devices, such as high cost, electricity requirement, and well-trained personnel for operation, monitoring activities of atmospheric mercury are mainly limited to developed countries or affluent regions. Passive air samplers of atmospheric mercury are gaining popularity recently because of their lower cost and simplicity to operate, and no need for electricity. These advantages of passive air samplers can extend ambient mercury monitoring to developing countries and remote regions and thus enhanced the spatial resolution of measurements. This manuscript, instead of giving a detail review of the existing passive air samplers for gaseous elemental mercury (GEM), focuses mainly on the developments of passive air samplers of GEM and discusses whether existing samplers meet these requirements. In general, this manuscript is well written and organized, and is timely for an important topic. Therefore, I think this manuscript can be accepted for publication in Atmospheric Chemistry and Physics by addressing the following comments.

AUTHORS' RESPONSE:

The positive sentiments are greatly appreciated.

REFEREE'S COMMENT:

1. Switch the order of Section 2 (Basic elements of passive air sampling) and Section 3 (The rationale for a passive air sampler for gaseous elemental mercury). It seems more reasonable to first provide the rationale for passive air sampling of GEM in the beginning of the manuscript then followed by presenting the basic elements of passive air sampling, which is then followed by discussing the requirements of passive air samplers for GEM.

AUTHORS' RESPONSE:

Although Section 2 introduces many important terms and processes essential to GEM PASs, after re-reading section 3, none of the terms and processes referred to in the current section 2 are directly used in the current section 3. Considering the sentiment of Reviewer 2 it does therefore seem reasonable that we should introduce the rationale for the need for GEM PASs before describing their basic elements. As such in the revised manuscript we will switch these sections so that the rationale precedes the basic elements.

AUTHOR'S CHANGES:

Sections 2 and 3 have been reversed so that the rationale now precedes the basic elements section. Line 3-5 on page 34609 has also been update to the following to reflect this change:

> *Starting with a summary of the rationale for passive air sampling of GEM, we then discuss the basic elements of PASs*

REFEREE'S COMMENT:

2. The authors discussed potential problems with sorbents in existing samplers, such as passivation, memory effects, and physical degradation. However, in addition to those issues, how to assure that the adsorbed or absorbed GEM is not lost due to reactions with other constituents of the atmosphere, such as ozone and water vapor, because passive sampler is often used for longer sampling intervals (weeks or months)?

AUTHORS' RESPONSE:

Passivation specifically is the term used to describe how adsorbed GEM is affected by other constituents in the atmosphere. To quote ourselves (Page 34625; Lines 4-7): "Passivation occurs when GEM binding sites on a sorbent become obscured by interfering compounds or **when reactions between atmospheric constituents and sorbed Hg strip some of the analyte from the sorbent over time."** As such, we believe that the manuscript already does address the issues the reviewer identified.

AUTHOR'S CHANGES:

No change

REFEREE'S COMMENT:

3. This manuscript focuses on the discussion of passive air sampling of GEM, not on the review of existing devices, and thus the existing passive air samplers for GEM are only briefly presented and summarized in Section 5, Table 1 and Figure 2. This may be fine for those who are familiar with these devices. However, for those who are interested but do not have experience with these devices, it may not be easy to understand this information. Therefore, I would suggest the authors to expand Section 5 to include an introduction of existing PASs for GEM and the guidelines for the selection of proper PAS for various purposes.

AUTHORS' RESPONSE:

We do not agree that section 5 is too brief and we believe that more a elaborate description of each sampler is likely to only confuse people more. While Section 5 is relatively brief, it is accompanied by Table 1 and Figure 2 in order to reduce the word count. Moreover, we refer back to individual designs in multiple instances through the remainder of the review (e.g., relating to their functionality), making a more extensive description of individual passive sampler designs a repetitive addition here. Finally, we feel the shortcomings of the existing passive samplers for mercury that we have identified, support neither a more extensive description of those samplers nor the development of guidelines for selection among them.

AUTHOR'S CHANGES:

No change

REFEREE'S COMMENT:

4. The title of right-hand side y-axis should be Uptake Rate instead of Sampling Rate? According to the definitions in page 34610, it is the Uptake Rate that will change over time, not the Sampling Rate, right?

AUTHORS' RESPONSE:

We assume this is in reference to Figure 1, not Figure 3. The right hand axis of Figure 1 is correctly labelled as 'Sampling Rate'. The sampling rate should remain constant, but only while the sampler is operating in the linear uptake phase. Once the sampler begins to approach the equilibrium uptake capacity and moves into the curve-linear phase, the sorbent is no longer working at its peak efficiency in "stripping" the air of Hg. For this reason it is greatly advantageous to only sample in the linear uptake phase or what we refer to as the effective deployment period.

At the request of another reviewer we have offered to update the second sentence in the caption of Figure 2: "Initially the *SR* is constant and the amount of sorbed analyte will increase linearly with time. During this phase the sampler can be described as being in the effective deployment period." This may help reduce any further confusion in this area.

If this comment is indeed in relation to Figure 3, 'Sampling Rate' is again the correct axis title. This data was derived from literature values and shows the dependence of sampling rate on wind speed.

AUTHOR'S CHANGES:

No change to figure axes titles. Change to Figure caption mentioned previously.