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Atmospheric Chemistry and Physics
Discussions

Interactive comment on “A smart nanofibrous material for adsorbing and real-time detecting elemental mercury in air” *by* Antonella Macagnano et al.

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AUTHORS REPLY TO REVIEWER COMMENTS R=Reviewer comment A=Authors answer

R.General comments. The task of the atmospheric mercury monitoring network developing is very important for understanding the scale of emission, regional and global transfer, deposition of this environmental pollutant. Existing system of background monitoring is based on AFS and AAS instrumental observations requiring high investments for set up of any new monitoring point. That’s why creation of new low-cost, hands off measurement systems is an imperative topical issue. The manuscript presents the results of the development of a novel sensor for air mercury measure-

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ments based on original manufacturing technology. The title reflects the contents of the paper, the main results are outlined in the Abstract. Introduction gives a comprehensive, 3.5 pages, review of the atmospheric mercury, speciation, mercury transfer, existing publications on the mercury sensors development. Principal part of the manuscript is devoted to description of a new sensor design and manufacturing technology, study of the absorptivity of the new material exposed to mercury vapour. Sensitivity of the new sensors is far not sufficient for the task of mercury monitoring declared in Introduction (see Specific comments, 1). No data on mercury measurement in ambient air, selectivity, and possible interferences are presented.

Specific comments 1) Commonly, in regulatory and scientific literature, the weight concentration units are used (ng/m3, pg/m3) for atmospheric mercury and mercury speciation. The authors use these units in Introduction, but different units: ppm, ppb, ppt in parts describing sensors. It is not explained what these units are related to: volume, mass, or number of molecules?

A1) Authors agree to the Reviewer comments: scientists involved in monitoring mercury in atmosphere are used to adopt mass/volume as units. On the other hands, in scientific literature scientists involved in developing and characterizing the features of sensors or more complex devices are also used to employ units as ppm, ppb, ppt. In fact the scientific literature reported in this manuscript and related to sensors for mercury detection, reports mercury concentration in part per billion/trillion/million etc. Since the authors are describing the parameters of the proposed sensor as potential subject for atmospheric monitoring, units as parts per. . ..were preferred. We suppose the volume units are used. It is inconvenient, because a comparison with conventional concentration units requires recalculation to the normal condition (P, T).

A1a) Authors agree to the Reviewer about the necessity to clarify which kind of ppb (volume, mass, number of molecule). As described within the manuscript, a permeation tube was used as Hg generator and Tekran instrument as analyzer of the Hg0 concentration. Thus a gas-tight syringe picked up defined microliters of air containing

Hg° delivered in the measuring chamber and then injected into the analyser. When concentration was expected extremely high (800 ppb), the gas withdrawal was carried out upon a further dilution with the gas carrier. Tekran reported the results in ng/m3, thus the final concentration was calculated taking into account the final volume (the dilutions) (5L/min - x5min) and then properly converted in ppm/ppb from the formula commonly used in environmental sampling and analysis (C(ppbv)=concentration (μg m-3) x Vmol (L/mol))/Molar Mass(gmol-1)). This is a conventional and common method to calculate the Hg concentration in laboratory, therefore was not described. Vice versa units as ppb will be marked with the subscript vol. Besides, the “tiny” ppb values can create a false impression of enabling background Hg concentration measurements. For example, mercury concentration of 1 ng/m3 is about 0.1 ppt (vol). It turns the achieved “low”detection limit (LOD) and measurement range of “20 -100 ppb (LOD 1,5 ppb)” (see lines 23-24) to a quite high figures in conventional units: 200,000 – 1,000,000 ng/m3 (LOD = 15,000 ng/m3). For comparison, the concentration of saturated Hg vapour is 12,000,000 ng/m3 at 18 oC. Such sensitivity gives no possibility to monitor mercury in ambient air, as the LOD is 10,000 times larger than the average background mercury concentration of 1.5 ng/m3 (see line 75).

A1b) Authors knew that the range in which measurements were carried out could be related only to very polluted scenarios: this concept has been reported within the manuscript and in the Conclusion paragraph. The concentration range was selected in order to describe some sensing performances such as the response time and its relationships with the concentration, and the calibration curve that allows to determine the range of concentration where the sensor responses have a linear curve shape (up to about 40 ppb). The limit of detection here reported has been measured taking into account the sensor response changes (shift of current after Hg exposure) after 10 min (response time was clearly reported). Thus it was the minimum value at which the analyte can be reliably detected in a 10 min-measure. It was calculated according to the literature as 3xStandard Deviation of the electrical signal (signal-to-noise ratio) multiplied by the response/concentration ratio (the slope of the response curve). In fact, in a previous work (Macagnano et al., submitted, Macagnano et al., 2015a) the authors reported a higher sensor sensitivity, with the possibility to detect up to dozens ppt, despite of a longer time necessary to reveal the analyte at these concentrations, in air. In this work the chance to apply the sensor in polluted sites and in real time has been presented and described (r145-149). Depending on the strategy of sampling and the coverage of the fibres, the limit of detection could be improved, about 2 ppt when slowly flowed within the measuring chamber (1 h measurement). However, despite the high sensitivity of the chemosensors to Hg0 vapour, the responses appeared to be slow. What the present manuscript would like stress? It describes the properties of a versatile sensor (ease of preparation, low cost apparatus) conductive at room temperature (low power) and sensitive to mercury vapours: this feature is depending on the time of exposure, due to the time necessary to entrap Hg enough to be detected as current variation. No carrier gas are required (it works in air). Sensor is robust: titania and gold are chemical compounds considered among the most robust materials. Thermal drift effects are expected to be lowered (only a 3min-heating process for desorption). Depending on the strategy of sampling and fibres treatments, the limit of detection could be improved. Potentials to be industrially fabricated (low cost of the process and the raw materials, electrospinning technology is commonly used in companies involved in textile, filtering and biomedicine) and used for large area monitoring (low dimension, low consumption, no gas carrier, no skilled operators). Their features make them promising candidates for sensor platforms (wired or WiFi connected).

R2) How the LOD value was determined and at what exposure time? There is no description in the text. Different figures of LOD are presented in Abstract and Conclusion (compare lines 23-24 and 390-391).

A2) Authors described the way they calculated LOD within previous answer

R3) Lines 69- 70 “Since automated measurement methods of Hg require power, argon gas, and significant operator training, they are difficult to apply: : :” Argon is not required for AAS systems.

A3) The Authors sentence collected the several drawbacks related to the conventional equipment for mercury detection. Obviously these instruments are extremely performing for mercury detection, and they generally need gold traps to work. The mercury analysers based on gold amalgamation and Atomic Absorption Spectrometry (AAS) detection are able to operate with ambient air as carrier gas. One or two pure gold traps are installed in series to run the dual amalgamation procedure and the sampling is run at about 1 L min-1 with sampling times of at least 10 minutes. Under these conditions, a detection limit of about 0.1 ng m-3 is achieved. On the other hand, some VOCs contained in ambient air may be adsorbed at the surface of the gold trap, and then can cause interferences (broad bands) to UV light spectral absorption of mercury at 253.7 nm.

R4) Lines 105-107 " decorated with gold nanoparticles (AuNPs) to obtain nanostructured materials capable of adsorbing GEM as a useful alternative system for making regional and global estimates of air Hg concentrations". Gold adsorbs not only GEM.

A4) The sensor is expected to be robust such as the commercial sensors based on metal-oxides are. The sensor is composed of TiO2 and gold, two chemical compounds considered among the most robust materials since resistant to common solvents and VOCs as well as microorganisms attacks. Specifically titanium dioxide is insoluble in water, hydrochloric acid, dilute sulfuric acid, and organic solvents and almost insoluble in aqueous alkaline media. It could be dissolved slowly in hydrofluoric acid and hot concentrated sulfuric acid. Additionally gold is the most non-reactive of all metals, never reacts with oxygen (one of the most active elements) and water, which means it is not subjected to corrosion. Both the compounds are thermally stable also in extreme environmental condition. Additionally, the sensor is designed to work at room temperature (decreasing thermal drift effects are expected), being thermally treated only for a few minutes (up to desorb mercury from AuNPs (450°C). On the other hand, gold metal reacts with chlorine or bromine, iodine and it dissolves in aqua regia but doesn't react with aqueous bases. Therefore, contaminated environments by halides and sul-

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phides should affect the adsorption of mercury, thus cartridges or traps or coatings (as suggested in literature) for these interfering compounds should be used or gold nanoparticles should be properly functionalized (e.g. alkanethiols).

R5) Lines 116-118 This is true that: “sampling rates (SRs) using the same passive samplers may depend on environmental conditions and atmospheric chemistry at each site. Moreover, it has been also highlighted that the performance of passive samplers may be influenced by meteorological factors (e.g., T _C, RH, wind speed) therefore inducing bias for the result of passive sampling (Plaisance et al.,. 2004; Sderstrm et al., 2004).” However, there is no evidence that the developed samplers are independent of meteorological factors (e.g. humidity) and interference of trace gases and aerosols, especially under long exposure time.

A5) In a cocktail of other chemicals, this sensor has been designed as a pretty selective sensor, being able to greatly decrease the environmental disturbances allowing the investigator/manufacturer to design/fabricate easier strategies to prevent contaminations from environment (selective filtering systems or coatings). Among common potential contaminants authors investigated water vapour influence (%RH) reporting no-effects on the electrical signals [Zampetti et al., Procedia Engineering 120 (2015) 422 – 426], but obviously, experimental data concerning the effects of further interfering gas (as halides and sulphides), as well as other physical parameters will be subject of further investigation (as specified in Conclusions paragraph).

R6) Lines 121-124 “In this work we describe an alternative approach adopted in the place of conventional ones demonstrating that the combination of gold affinity for Hg with a nanoscale sized framework of titania provided the chance to create promising sensors for environmental monitoring in real time, characterised by high sensitivity to the analyte.” See note (1). Besides, the technology of real-time monitoring is not described.

A6) Authors disagree with the Reviewer about this question since Figs. 7 and 10 are transient responses (i.e. real time electrical signal changes under defined mercury concentrations).

R7) Lines 128-131. “The TGM/GEM sensor surface described here could be deployed in a global network such as GMOS; a permanent network of ground based monitoring sites and observations of Hg and/or related species on a global scale and with remote sensors would in fact be highly desirable”. Again, see note (1). The achieved sensitivity is insufficient for background measurement at the level of few ng/m3 provided by GMOS stations, and for speciation study at the level of pg/m3. 8) Lines 333-338. For better understanding of sensing measurements: “The sensor was exposed to a flow of Hg0 336 in air with a concentration of 800 ppb for 1 min (Fig. 7, right)” In terms of standard units, we see that the sensor was exposed to almost saturated Hg vapour at 8 mg/m3. Thereby it is not clear how such high concentration was measured? Earlier (line 234), it was mentioned, that “The Hg0 concentration was checked by Tekran®2537A analyser”. Tekran 2537 is not capable of measuring such high concentration.

A7) About those questions, authors clarified in a previous comment the sampling methods. Technical corrections 1) Numerous misprints: “fibers” instead of “vapour”: Lines 91-91: “cold-fiber atomic absorption spectroscopy : : :. cold-fiber atomic fluorescence spectroscopy” Line 141: ”Morphological, optical, electrical aspects and sensing measurements of fibers of GEM in air” Line 144: “adsorbing and removal Hg fiber”

A7a)Thanks to Reviewer: all the typos and misprints will be properly modified

The same mistakes in the Reference list: Lines 412-414 “Ferrua, N., Cerutti, S., Salonia, J. A., Olsina, R. A. and Martinez, L. D., 2007. On-line preconcentration and determination of mercury in biological and environmental samples by cold fiber-atomic absorption spectrometry. J. Hazard. Mater. 141 693–699” In the original Cold Vapour, see: http://www.sciencedirect.com/science/journal/03043894/150 Lines 412-414 “Determination by Cold Fiber Atomic Absorption Spectroscopy. Analytical Letters 39” In the original Cold Vapour, see:

http://www.tandfonline.com/doi/full/10.1080/00032710600622167 2) Lines 73 -76 The sentence “Previous research highlighted that Hg-concentration levels in air vary greatly across different environmental locations, remote as the Polar Regions, background or rural, and urban locations with an average range between 1.5 ngm-3 (GEM) and 1 pgm-3 (GOM and PBM), depending on the speciation” should be revised: probably just by replacing “between” with “of”.

A7b) A proper revision about typos will be provided.

R9) Conclusion. Obviously, an advanced comprehensive research has been done for the novel sensor design and manufacturing technology development. However, the sensitivity is far not sufficient to achieve the declared goal “to create promising sensors for environmental monitoring in real time, characterised by high sensitivity to the analyte” (lines 123-124). Probably, the new sensors can be used for other applications involving measurement of high mercury concentrations, such as technological or mercury exposure control. I would suggest that the manuscript No acp-2016-1077, after suggested corrections, can be redirected for publication in a journal dedicated to sensor technologies, which will be more suitable for this kind of research than Special Issue “Global Mercury Observation System – Atmosphere” (GMOS-A). The proposed novel Hg sensor may be made more suitable for the use in the GMOS project upon its further development and improvement. A9) The authors conclusions are related to the resulting and then promising features of the sensor to be used for global mercury monitoring (low cost fabrication, low power consumption, no gas carriers, no skilled operators, miniaturization, versatility and potentials to be improved). Sensors provided with high surface area and porosity are suitable for exceptional interaction with environment, which means that, with the appropriate functionalisation, they are able to react with their target substance with great sensitivity. Therefore a potential commercialisation is significant. As previously explained, preliminary results are here reported: further investigation is required in order to design a final set-up configuration (an integrated microheater for desorption, a micropump, a set of filtering membranes for interfering) as well as an improved geometry of the sensor and the Hg delivery system. In Authors opinion, based on the reported results within the manuscript, the proposed sensor sounds as one of the most promising sensors for mercury monitoring.

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