Environmental Science & Technology

Viewpoint

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Progress on Understanding Atmospheric Mercury Hampered by Uncertain Measurements

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Received: June 3, 2014
Published: June 18, 2014

dx.doi.org/10.1021/es5026432 | *Environ. Sci. Technol.* 2014, 48, 7204−7206

Mercury (Hg) is a potent neurotoxin and globally reducing environmental levels is seen as paramount for protecting human and wildlife health. In 2013, many countries finalized the negotiations on, and have now signed, the Minamata Convention on Mercury, which commits participating countries to reduce emissions and use of mercury. Successful implementation of the treaty will require adequate verification through global monitoring.

In the past decade, the number of atmospheric measurements of speciated Hg has rapidly multiplied. Mercury data are being collected by monitoring networks in Europe, Canada, East Asia, and the United States. These measurements are relatively expensive and mounting evidence suggests they suffer from significant biases. As a community, we are confronted with the question, "Are current analytical methods for Hg adequate to address policy requirements?" We conclude that better analytical techniques are urgently needed.

In the atmosphere Hg occurs as three operationally defined forms: gaseous elemental mercury (GEM), gaseous oxidized mercury (GOM) and particle-bound mercury (PBM). GOM and PBM are believed to consist of Hg(II) compounds. Oxidation of GEM to GOM and subsequent deposition is thought to be the major pathway to deliver Hg to ecosystems. Thus, GOM provides a critical link between human emissions and ecosystem exposure. A number of laboratory and theoretical chemical investigations have been performed, but at present there is no consensus on what the chemical form(s) of GOM is(are), nor any reliable method to identify the chemical form(s) in the atmosphere. It is likely that more than one form of Hg(II) exists in the atmosphere, depending on its source.

At present the primary method to identify GOM is use of a KCl coated denuder for concentration and collection, followed by thermal desorption and atomic fluorescence to quantify the desorbed GEM. PBM is collected on a regenerable quartz filter downstream of the denuder and is quantified similarly. This method has been adopted by the Canadian Atmospheric Mercury Network, the U.S. Atmospheric Mercury Network and the European Global Mercury Observation System for standard measurements. QA/QC protocols have been developed for these networks, but these protocols do not provide a way to calibrate for GOM or PBM, quantify collection efficiency or quantify measurement interferences.

A number of studies have been published that indicate there are significant problems with the existing methods for GOM and PBM. By using possible GOM compounds, such as $HgCl_2$ and $HgBr_2$, it has been shown that the KCl denuder method is subject to interferences from ozone, water vapor and possibly other compounds as well.[1,2] Other studies have found that KCl denuder measurements do not agree with measurements made with alternative collection surfaces. It is also not clear what is the true uncertainty in measurements of PBM, as comparisons with other methods have yielded large discrepancies between commercial, automated PBM measurements and manual methods with alternative samplers.[3] All of these point to substantial problems with our current methods to quantify GOM and PBM.

At present we are not able to quantify the uncertainty in GOM and PBM measurements. This is because (1) we do not know the chemical form being measured, (2) there is no accepted calibration method and (3) we have a limited understanding of interferences. It is not yet clear whether we will be able to correct GOM and PBM data collected with current methods to account for these biases. This will require a more detailed understanding of Hg chemistry and detailed interference tests with reliable field-deployable calibrators.

We acknowledge that some measurements of GOM made with the KCl denuder method have been successfully interpreted, at least qualitatively. Some studies have demonstrated an inverse relationship and approximate "mass conservation" between GOM and GEM. However, these studies do not provide definitive evidence that the KCl denuder method is free from bias. Work investigating ozone interference has found that the ratio of GOM to GEM can be biased low while the total gaseous Hg concentration (GOM + GEM) is approximately conserved.[1] In other words, GOM can decompose to GEM during sampling and be analyzed as GEM. It is also possible that the KCl denuder method works better in some environments than others.

At present, we believe unspeciated Hg measurements (i.e., measurements with no upstream processing prior to sample introduction into an atomic fluorescence analyzer) are well calibrated and the true uncertainty can be reasonably described. There is some uncertainty as to whether current unspeciated measurements capture total gaseous mercury (TGM) or GEM. If desired, total atmospheric mercury (TAM = GEM + GOM + PBM) can be measured using a pyrolyzing inlet. In principle, measurements of TAM should be more accurate than current methods to measure the individual species.

Working with Hg(II) compounds is challenging due to their toxicity, tendency to decompose, and stickiness in calibration systems. But without high quality calibrations it is not possible to validate measurements, quantify uncertainties or fully evaluate atmospheric models.[4] Calibration methods for oxidized Hg compounds are improving[5] and these will improve the quality of future interference studies as well as routine measurement studies for GOM and PBM.

In order to have confidence in atmospheric chemical measurements, we must be able to quantify their uncertainty. This includes routine calibration in realistic conditions and rigorous testing for interferences. At present, the existing and planned atmospheric mercury networks have inadequate attention to quality control for GOM and PBM measurements. To resolve these issues, the community needs to

1 Develop calibration methods for GOM and provide routine calibrations for field instrumentation;

dx.doi.org/10.1021/es5026432 | Environ. Sci. Technol. 2014, 48, 7204−7206

2 Conduct detailed investigations to quantify interferences in the existing GOM methods and develop new methodologies to measure it; and
3 Conduct fundamental research on the chemistry, reaction kinetics and chemical identity of the compounds that make up GOM and PBM in the atmosphere.

We believe these items should be given high priority by the mercury scientific community. To do otherwise impedes scientific progress and environmental monitoring efforts. Space limitations prevent us from including a complete set of relevant references. For a more complete list of relevant publications, please go to http://atmos.washington.edu/jaffegroup/modules/hg/

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Notes
The authors declare no competing financial interest.

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