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Source–receptor relationships for atmospheric mercury in urban Detroit, Michigan

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Abstract

Speciated hourly mercury measurements were made in Detroit, Michigan during four sampling campaigns from 2000 to 2002. In addition, other chemical and meteorological parameters were measured concurrently. These data were analyzed using principal components analysis (PCA) in order to develop source receptor relationships for mercury species in urban Detroit. Reactive gaseous mercury (RGM) was found to cluster on two main factors; photochemistry and a coal combustion factor. Particulate phase mercury, Hg_p, tended to cluster with RGM on the same factor. The photochemistry factor corroborates previous observations of the presence of RGM in highly oxidizing atmospheres and does not point to a specific source emission type. Instead, it likely represents local emissions and regional transport of photochemically processed air masses. The coal combustion factor is indicative of emissions from coal-fired power plants near the receptor site. Elemental mercury was found on a factor for combustion from automobiles and points to the influence these emissions have on the receptor site, which was located proximate to two major interstate highways and the largest border crossing in the United States. This analysis reveals that the receptor site which is located in an industrialized sector of the city of Detroit experienced impacts from both stationary and point sources of mercury that are both local and regional in nature.

Keywords: Gaseous elemental mercury (GEM); Reactive gaseous mercury (RGM); Particulate phase mercury (Hg_p); Source–receptor relationships; Photochemistry; Coal burning; Automobile emissions

1. Introduction

Mercury is now classified by the United States Environmental Protection Agency (USEPA) as a persistent bioaccumulative and toxic (PBT) chemical (USEPA, 1998). In the past 20 years much research has been performed to help understand the biogeochemical cycling of mercury. It is now apparent that man's intentional (or unintentional) use of mercury has resulted in great perturbation of the natural mercury cycle. This has manifested itself in the bioaccumulation of mercury in fish (Hakanson et al., 1990). In fact, this perturbation is so serious that fish advisories are on the increase. If one focuses on the Great Lakes region alone, there are now statewide freshwater advisories (USEPA, 2003). In response to this situation, the USEPA has developed a strategy against the threat from PBTs so that risks should be reduced through regulation

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of mercury emissions. It is currently believed that emissions from coal burning utilities are the largest source within the US. Hence, new rules have just been issued by the agency in an effort to control these emissions (USEPA, 2005a). In addition, more research is required in order to reduce scientific uncertainty and to manage the risk from mercury to humans and vulnerable ecosystems. One approach is the development of source receptor relationships that can be utilized to assess contributions from various Hg sources based on observations made at sampling or receptor sites (Han et al., 2004). An advantage to this approach is that quantitative emissions data from sources, which are likely to affect the receptor site, are not required. This approach can result in considerable savings since source testing in general and for mercury in particular can be very costly, e.g. in the case of power plant emissions, testing requires that heavy sampling equipment be placed on a stack, working at high elevation is more challenging and requires highly trained personnel.

Source receptor relationships have been developed for mercury in precipitation (Dvonch et al., 1995) and for particulate phase mercury (Gildemeister, 2001). Results from both these studies reveal that mercury in precipitation and the particulate phase exhibit well-defined source receptor relationships. This manuscript describes results from field intensive studies which measured speciated mercury in Detroit, MI at selected times between 2000 and 2002. In addition to the speciated mercury measurements, ancillary measurements of several major criteria pollutants (ozone, carbon monoxide, sulfur dioxide, nitrogen oxides) and meteorological parameters were also made. The data were analyzed using principal components analysis (PCA) and used to develop source-receptor relationships. Specifically, correlations between elemental mercury (GEM), reactive gaseous mercury (RGM), and particulate phase mercury (Hg_p), and chemical and meteorological variables were enumerated using PCA in an effort to apportion the sources of mercury received at the Detroit monitoring site.

2. Methods

2.1. Mercury speciation measurements

Mercury speciation measurements were conducted during field intensive sampling in July and September 2000, July 2001 and July 2002 at a receptor site in the southwest section of the city of Detroit. This site is located in close proximity to the Rouge Industrial complex comprising iron–steel manufacturing, coke ovens, chemical plants, oil refineries, sewage sludge incineration and coal-fired utilities (Keeler et al., 2002). Adjacent to the receptor site is the Ambassador Bridge, which is the largest border crossing between Canada and the United States. The Tekran® 1130 and 1135 mercury speciation units were utilized to measure the concentrations of Hg^0, RGM, and Hg_p (Landis et al., 2002). The speciation unit was operated at a flow rate of $10\,L\,min^{-1}$ and programmed to sample ambient air at 1-h intervals. During sampling, ambient air was drawn through an impactor inlet through a potassium chloride (KCl) denuder that removed RGM, and then through a particulate filter, which captured Hg_p, and subsequently passed the air into the Tekran 2537 A mercury analyzer. Elemental mercury, Hg^0, was sampled onto gold traps at 5-min intervals and subsequently detected: this resulted in twelve 5-min determinations per hour of sampling time. After 1 h of sampling, the lines were flushed with zero air in preparation for desorption and detection of Hg_p and RGM as elemental mercury. The particulate unit was heated to 800 °C to desorb Hg_p, which was detected as elemental mercury. Finally, the KCl-coated denuder was heated to 500 °C to desorb the RGM, which was also detected as elemental mercury. After a 10-min cool down period, another 1-h sampling period was initiated. Thus after a 2-h interval (1 h of sampling and 1 h of desorption), a 1-h averaged Hg^0 concentration and 1-h integrated RGM and Hg_p concentrations were obtained. Freshly coated denuders were replaced on a weekly basis. The instrument was calibrated daily by means of an internal permeation source. The permeation source was calibrated prior to each intensive campaign. The detection limit for both RGM and Hg_p was calculated to be $4\,pg\,m^{-3}$ (2.4 pg absolute) based on $3\,\sigma$ where σ is the standard deviation for a blank value. The precision of the 2537 A analyzer determined by measuring the relative standard deviation of five replicate injections of vapor-phase mercury at two different concentrations averaged 0.4–1.0%. The accuracy of this instrument was not determined owing to a lack of certified vapor standards. However, the accuracy of gold amalgamation has been assessed to be in the 3–5% range (Kim and Kim, 2001).