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Artifacts associated with the measurement of particulate mercury in an urban environment: The influence of elevated ozone concentrations

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Abstract

The potential for ozone to cause an artifact during sampling of fine particulate mercury was investigated in southwest Detroit in July 2001 and July 2002. During the July 2001 sampling period, the use of KI and KCl denuders placed upstream to remove ozone and reactive gaseous mercury, $Hg^{2+}_{(g)}$, resulted in *more* particulate mercury (maximum 33 pg m^{-3}) on a *denuded* filter when compared to an undenuded one. Additionally, a KCl *denuded* quartz filter also showed *more* particulate mercury (maximum 12 pg m^{-3}) compared to an undenuded filter when ozone concentrations were most elevated. Further sampling in July 2002 used a repeated sampling design and resulted in *more* particulate mercury on *undenuded* filters when compared to denuded ones. Conditions in July 2001 were characterized by elevated concentrations of ozone during which there were three ozone action days declared by the State of Michigan whereas ozone concentrations in July 2002 were 22% lower. One possible explanation for the observations may be that elemental mercury, $Hg^{0}_{(g)}$, is oxidized to reactive gaseous mercury, $Hg^{2+}_{(g)}$, during sampling leading to an artifact. The potential for this type of artifact may be greater during periods of high photochemical activity and this must be considered when sampling during the warmer seasons when high levels of oxidants are likely to be present in an urban atmosphere.

Keywords: Atmospheric mercury; Annular denuders; Measurement challenges; Urban aerosol

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1. Introduction

Particulate-phase mercury is considered an important player in the atmospheric deposition of mercury to the aquatic and terrestrial environment. The atmospheric concentrations of this species are usually low (pg m^{-3}), making accurate and precise measurement an arduous task. There have been some suggestions that measurement of this species might actually be the most difficult to perform (Lu and Schroeder, 1999). This has significant consequences for studies, which assess deposition because measurement deficiencies can produce misleading conclusions with regard to the nature and extent of deposition.

Measurement of particulate-phase mercury has been ongoing for the past 20 years. Although present in ultra-trace amounts it can be collected and analyzed using a combination of ultra-clean sampling techniques (Keeler et al., 1995) and analytical techniques such as cold vapor

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Table 1
Particulate-phase mercury measurements in the United States with number of samples N, given in parentheses

Location	Particulate mercury ($pg\,m^{-3}$)	Reference
Chicago, IL	22–518 (16)	Keeler et al. (1994)
	1–494 (393)	Landis et al. (2002b)
Lake Michigan	9–54 (9)	Keeler et al. (1994)
Detroit, MI	57–1230 (20)	Keeler et al. (1994)
	2–160 (540)	Gildemeister et al. (2004)
Vermont	1–43 (103)	Burke et al. (1995)
Rural Great Lakes	1–103 (1133)	Burke (1998)
South Florida	4–462 (268)	Dvonch et al. (1995)
Toronto, ON	3–91 (28)	Lu et al. (1998)

atomic fluorescence spectroscopy (CVAFS), and instrumental neutron activation analysis (INAA) (Olmez et al., 1998).

Table 1 provides a summary of particulate mercury measurements made in several locations in the United States. These sites were chosen because they were known to be proximate to mercury sources and were expected to be impacted by emissions from these sources. International field comparisons have also been carried out and measured levels of particulate-phase mercury were found to be in the range 4.5–26 $pg\,m^{-3}$ at Mace Head, Ireland (Ebinghaus et al., 1999) and 13–314 $pg\,m^{-3}$ in Tuscany, Italy (Munthe et al., 2001).

Spatial variability in particulate mercury levels was observed in Michigan where concentrations at the more industrialized southern sites were higher by a factor of two in comparison to northern sites (Keeler et al., 1995). Temporal variability associated with particulate mercury has also been observed with higher concentrations typically found in the winter time (Iverfeldt, 1991; Keeler et al., 1995). It is surmised that colder ambient temperatures in the winter result in less acidic and oxidative gas phase species present, less sunlight available for photochemical reactions, and perhaps a stronger partitioning towards the condensed phase.

By definition, particulate-phase mercury is likely to encompass solid or liquid materials, which may be either homogeneous or heterogeneous with respect to physical and/or chemical composition and shape. Typically, this phase is sampled by filtration, a widely used technique for aerosol sampling owing to its simplicity and economy. Furthermore, the filter samples occupy a relatively small volume and may be stored for later analysis without rapid deterioration. However, there are numerous potential sources of error, which may lead to imprecise and inaccurate determination of this important phase in the atmosphere. For example, since particulate-phase mercury is present in the atmosphere at low concentrations long sampling times are required. This may be problematic when particles, which are trapped on a filter, impart a large contact area to the airstream, which may enhance volatilization of semi-volatile species when the corresponding gas–phase concentrations in the airstream fall below equilibrium levels. This leads to negative bias or error which results in underestimation of the particulate-phase concentration and overestimation of the gas–phase concentration. Positive bias or error may occur because the high specific surface area on the filter permits less volatile gaseous species present in the sampling stream to sorb to or react with the deposited solid phase and/or the sampling medium (Xiao et al., 1991; Lu et al., 1998). Diurnal variations in aerosol concentrations and other parameters, e.g. temperature and relative humidity, may promote positive or negative errors during aerosol measurement (Volckens and Leith, 2002). The presence of errors due to gaseous species during particulate sampling are well documented during atmospheric sampling for nitrates (Appel et al., 1984; Shaw et al., 1982), sulfates (Pierson et al., 1976) and organic carbon (McDow and Hutzincker, 1990; Kirchstetter et al., 2001) and may result in a change in the composition of the deposited phase.

Knowledge of the existence of error during the measurement of atmospheric aerosols has prompted the use of denuders during sampling in an attempt to circumvent problems. Annular denuders have been used in a variety of atmospheric studies to collect gaseous atmospheric pollutants since the 1980s (Koutrakis et al., 1988; Spicer et al., 1982; Kloskowski et al., 2002). More recently, denuders have found an application in gas-phase atmospheric mercury sampling. Denuders whose inner walls have been coated with silver (Kvietkus et al., 1995) or gold (Munthe et al., 1990; Xiao et al., 1991) have been used and found to give comparable results (Kvietkus et al., 1995) when sampling for elemental mercury, $Hg^0_{(g)}$. Potassium chloride (KCl)-coated denuders have been used to sample for reactive gaseous mercury, $Hg^{2+}_{(g)}$, and found to have greater than 96% efficiency (Xiao et al., 1997; Somnar et al., 1999; Feng et al., 2000; Landis et al., 2002a). In spite of the abundant measurements of particulate-phase mercury,