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Mercury, $PM_{2.5}$ and gaseous co-pollutants in the Ohio River Valley region: Preliminary results from the Athens supersite

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Abstract

This paper presents preliminary results from an ongoing air quality project at a rural super site in Athens, Ohio (39°18′N, 82°7′W). Athens is located in the heart of the Ohio River Valley region, which is characterized by a high number of coal-fired power plants, chemical plants, and manufacturing industries. Highly time-resolved gaseous elemental mercury (Hg^0), reactive gaseous mercury (RGM), and particulate mercury (Hg_p) data are reported in this paper. Mercury species are measured using an automated Tekran 2537A CVAFS analyzer and Tekran 1130 and 1135 speciation and particulate modules. Continuous mercury data are reported from 27 July 2004, to 30 July 2005. This study also measured wet deposited mercury; reported here are results from 3 May 2004, until 31 May 2005. The highest mercury deposition occurred during September 2004. This is due in part to a series of unusual weather events featuring transport predominantly from the north, northeast, and southeast. The effects of the remnants of hurricanes Frances and Ivan on air quality data are also apparent during this month. This paper also presents results of $PM_{2.5}$, gaseous co-pollutant, and meteorological measurements. Results are compiled into daily and monthly averages to display diurnal and seasonal patterns. Low background concentrations with frequent pollution episodes make this rural site an excellent location to capture transport events into and out of the Ohio River Valley.

Keywords: Hg^0; RGM; Hg_p; Ambient mercury measurements; Mercury deposition

1. Introduction

The Ohio River Valley is viewed as a major pollution source region in the United States because of its high number of coal-fired power plants, mining activities, and industrial plants including chemical, metal smelting, and manufacturing activities. The ambient air quality monitoring program at Ohio University is an ongoing research project to study air pollution in the Ohio River Valley. Current research is aimed at trying to better quantify the ambient and deposited concentrations of gaseous elemental mercury (Hg^0), reactive gaseous mercury (RGM) and particulate mercury (Hg_p, aerodynamic diameter $\leqslant 2.5\,\mu m$), and at identifying local, regional, and global sources.

Hg^0, RGM, and Hg_p are the three forms of mercury emitted by various natural and anthropogenic

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sources (Schroeder and Munthe, 1998). Due to its chemical inertness and low solubility in water, Hg^0 has an atmospheric residence time of 6 to 24 months (Lindqvist and Rodhe, 1985; Schroeder and Munthe, 1998). A long residence time provides ample time for mixing and circulation around the globe (Carpi, 1997). Hg^0 is eventually transformed to RGM through oxidation by species such as O_3, HCl, H_2O_2, Cl_2, $OH\cdot$, and Br_2. RGM has a much shorter residence time of a few hours to several days before departing the atmospheric cycle (Calvert and Lindberg, 2005; Lindberg and Stratton, 1998; Lin and Pehkonen, 1999).

The most important characteristic of RGM is its high water solubility, over one thousand times that of Hg^0 (Lindberg and Stratton, 1998). This allows for its dissolution in rainwater and subsequent wet deposition. Most of this deposited mercury is re-emitted to the atmosphere, but a small amount converts to methyl mercury and bio-accumulates in fish, causing serious damage to the ecosystem (US EPA, 1997). Although the anthropogenic emission of mercury is decreasing in industrialized countries resulting from emission controls, efficiency improvements, and environmental stewardship (US EPA, 1997), globally it appears that it is increasing (Friedli et al., 2004; Pacyna and Pacyna, 2002).

RGM and Hg_p are known to be emitted by various anthropogenic sources (Pirrone et al., 2001a; Schroeder and Munthe, 1998). However, they have also been discovered in high concentrations in the arctic troposphere and polar snow packs, far from any major sources (Lindberg et al., 2002; Schroeder et al., 1998). It is believed that atmospheric reactions of Hg^0 with halogens and oxidation–reduction mechanisms occurring in source plumes are central to the behavior of these mercury species. Understanding these mechanisms and their reaction rates is vital to developing sound and effective emissions–reduction policy.

Objectives of this study include: (1) determining the ambient concentrations of mercury, $PM_{2.5}$, and gaseous criteria pollutants along with important meteorological variables at a site located in the Ohio River Valley Region; (2) developing a three-dimensional regional-scale chemical transport model and validating it with data collected at the monitoring site; (3) evaluating local verses long-range transport processes that affect mercury and co-pollutant concentrations; and (4) identifying possible sources of these pollutants. This paper presents an overview of the monitoring program and some preliminary results.

2. Experimental

2.1. Sampling site and ambient monitoring program

The Ohio University surface air monitoring (SAM) station is located in a rural area approximately 3.5 km southwest of downtown Athens, Ohio (39°18′ North Latitude; 82°7′ West longitude), at a height of approximately 330 m (1000 ft) above mean sea level. Fig. 1 shows the site location and major point sources located throughout the region. Land use surrounding the site is primarily agricultural, with interspersed areas of fragmented forest. A 120-m aerial communications tower is located approximately 85 m from the site. The site location is the tallest visible point in the region, and is higher than any point south to the Ohio River and southwest to Cincinnati, Ohio.

Mercury species (Hg^0, RGM and Hg_p), gaseous co-pollutant and meteorological data reported here were collected from 27 July 2004, to 30 July 2005, and represent one year of continuous sampling. Ambient mass concentrations of $PM_{2.5}$ and its chemical constituents, which were collected with TEOM and filter-based samplers, are reported for thirteen months from 1 March 2004, to 31 March 2005.

2.2. Mercury analyzer

A Tekran (model 2537A) automated, high-temporal-resolution, cold vapor atomic florescence spectrophotometric (CVAFS) mercury analyzer along with speciation and particulate units (Tekran models 1130 and 1135) are used for measuring ambient concentrations of Hg^0, RGM and Hg_p. A complete description of the system and its methodology is found in Landis et al. (2002). At the Athens monitoring site, the system is positioned 2 m above ground level. It is programmed to sample at 10 L min^{-1} with a 2-h cycle for Hg^0, RGM and Hg_p (1-h concentrations collected every other hour resulting in 12 data points per day). Bi-weekly maintenance includes the replacement of the KCl-coated denuder, soda lime trap (to prevent gold cartridge passivation), and sample filters. The regenerable particulate filter (RPF) is changed once a month.