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Estimation of source locations of total gaseous mercury measured in New York State using trajectory-based models

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Abstract

Ambient gaseous phase mercury concentrations (TGM) were measured at three locations in NY State including Potsdam, Stockton, and Sterling from May 2000 to March 2005. Using these data, three hybrid receptor models incorporating backward trajectories were used to identify source areas for TGM. The models used were potential source contribution function (PSCF), residence time weighted concentration (RTWC), and simplified quantitative transport bias analysis (SQTBA). Each model was applied using multi-site measurements to resolve the locations of important mercury sources for New York State.

PSCF results showed that southeastern New York, Ohio, Indiana, Tennessee, Louisiana, and Virginia were important TGM source areas for these sites. RTWC identified Canadian sources including the metal production facilities in Ontario and Quebec, but US regional sources including the Ohio River Valley were also resolved. Sources in southeastern NY, Massachusetts, western Pennsylvania, Indiana, and northern Illinois were identified to be significant by SQTBA. The three modeling results were combined to locate the most important probable source locations, and those are Ohio, Indiana, Illinois, and Wisconsin. The Atlantic Ocean was suggested to be a possible source as well.

Keywords: TGM; New York; Trajectory; PSCF; RTWC; SQTBA; Ohio river valley; Atlantic Ocean

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1. Introduction

Mercury can exist in three oxidation states. Since the +1 oxidation state is rare in the environment, the important environmental species are elemental mercury (Hg^0) and divalent mercury (Hg^{2+}). Divalent mercury is easily removed from atmosphere via wet and dry deposition resulting in low ambient concentrations although it is emitted from sources at a significant rate (about 70% of the total Hg emitted from coal utilities; NESCAUM, 2005). Alternatively, elemental mercury has a low deposition velocity and is relatively inert, so that it constitutes the majority of mercury in the atmosphere (generally, over 95%) (Slemr et al., 1985; Tokos et al., 1998). Because of these different chemical characteristics, proximity to sources plays a key role in the concentration of divalent mercury

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while Hg^0 is vertically well mixed in the troposphere and its typical concentration is ~1–4 ng m^{-3} at rural sites (Slemr and Langer, 1992; Lin and Pehkonen, 1999). Divalent mercury can also exist in the particulate phase.

Atmospheric mercury has both natural and anthropogenic sources. The biggest anthropogenic sources in the United States are combustion point sources including coal-fired power plants and waste combustors, which contribute approximately 87% of the total anthropogenic emissions (USEPA, 1997a). However, EPA issued final regulations for waste incinerators in 1995 (municipal), 1997 (medical), and 1999 (hazardous waste incinerators) and these regulations are expected to reduce mercury emissions from these facilities by over 90% (USEPA, 1997a) when fully implemented. According to national emissions inventory (NEI) for 1999, coal-fired power plants contributed 44% of the total emissions from point sources. Natural sources include the outgassing of the earth's mantle/crustal material, evasion from surficial soils, water bodies (both fresh- and salt-water) and vegetation surfaces, wood fires, volcanoes, and geothermal sources (Schroeder and Munthe, 1998). The primary mercury species emitted from natural sources is elemental mercury.

Only a few direct measurements of mercury fluxes and speciation from natural sources are available in the literature (Gustin et al., 1999; Wallschlager et al., 1999; Engle et al., 2001; Engle and Gustin, 2002; Lindberg et al., 2002; Zhang et al., 2002). Recent studies strongly emphasize the importance of air–water exchange of mercury as well as biologically mediated volatilization in both marine and terrestrial environments (USEPA, 1997a). These sources represent a relatively constant flux to the atmosphere and may comprise 30–50% of the total natural emissions. Re-emission of mercury is sometimes included as a different category from natural sources, because a significant portion of this source originates from previous anthropogenic sources (USEPA, 1997a, b). The current emissions inventory for anthropogenic sources was established using an emission factor-based approach that typically has great uncertainty (about 30%). The estimates for natural sources must be viewed with greater uncertainty than estimates of anthropogenic sources (USEPA, 1997a).

To reduce the concentration of any pollutant, the main sources that affect an area of interest must be identified. Receptor modeling techniques can be used for such identification, especially when an accurate emissions inventory does not exist (such as in the case of mercury). Hybrid receptor modeling utilizing back-trajectories and measured concentrations has been shown to be a powerful tool for locating source areas (Ashbaugh et al., 1985; Keeler, 1987; Seibert et al., 1994; Stohl, 1996). There have been only a few studies attempting to locate mercury sources using hybrid receptor models (Lin et al., 2001; Poissant, 1999), and none of them compared the results of different receptor models. This research was undertaken to identify the locations of mercury sources that affect New York State and determine the contribution of in-state versus out-of-state sources, using several different hybrid receptor models. The results of each receptor model were compared with a recent emissions inventory of mercury and the advantages/disadvantages of each model were investigated. The objectives of this study were (1) identification of TGM source areas using back-trajectory-based hybrid receptor models, (2) comparison of the modeling results, and (3) determination of the relative importance of in-state and out-of-state sources of mercury to concentrations measured in New York State.

2. Data source and model description

2.1. Ambient air TGM data

During the two summers of 2000 and 2001, TGM concentrations were measured using gold-coated sand traps followed by glass fiber filter (47 mm) from 11:00 to 10:00 a.m. of the next day (ET) at the Potsdam and Stockton sites in New York State (Table 1). After daily sampling at these two sites during the summers of 2000 and 2001, samples were collected every third day from midnight to midnight at both sites year-round until August 2005. In addition, a temporary sampling site in Sterling, NY was added in April 2002 and Hg samples were collected every sixth day for 24 h (from 9:00 to 9:00 a.m. of the next day). All three sites are located in rural areas (Fig. 1).

Quality assurance/quality control was performed as required by the EPA standard methodology. The overall precision obtained by side-by-side TGM samples was 7.6 ± 5.4% ($R^2 = 0.97$, $n = 13$) for the sampling and analytical method used in this study. A minimum of one field blank was taken for every six samples collected, and the method detection