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Project Summary

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Mercury Chemistry in Power Plant Plumes

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PROJECT SUMMARY

Recent field and pilot-scale results indicate that divalent mercury emitted from power plants may be rapidly transformed to elemental mercury within the power plant plumes. Such evidence has been found from laboratory plume simulation experiments, single-source comparisons of mercury emissions speciation with downwind plume impingement measurements, and one set of measurements by air and ground at a full-scale operational coal-fired power plant. Simulations of mercury chemistry in plumes have been carried out based on chemical reduction rates measured to date. Such simulations demonstrate improved fits between regional model results and wet deposition data, at least for particular years, while not degrading model performance for remaining years of the data record.

This project seeks to establish a data basis for whether or not significant reduction or oxidation reactions occur in mercury species emitted in the plume from a coal-fired power plant. The project also seeks to assign what chemical redox rate should apply to extend the results to other such sources for modeling power plant mercury plume chemistry.

The determination of mercury speciation in a dispersing emissions plume is most relevant for estimating mercury transformation and fate in the atmosphere. In particular, such transformations determine the eventual deposition rates and patterns of mercury downwind of its multiple sources. The million-fold greater solubility of divalent mercury in water drives its deposition behavior vs. that of elemental mercury, as well as the resulting downwind surface concentrations due to upwind sources.

The importance of these potential plume reactions for mercury deposition led to a joint field study jointly sponsored by EPRI, the U.S Department of Energy (DOE), and the State of Wisconsin Department of Administration. The study was carried out at the We Energies Pleasant Prairie Power Plant, Pleasant Prairie, Wisconsin, just west of Kenosha.

Results & Findings

Aircraft and ground measurements support the occurrence of a reduction in the fraction of reactive gaseous mercury (RGM) (with a corresponding increase in elemental mercury) as part of the Total Gaseous Mercury (TGM) emitted from the Pleasant Prairie stack. This occurrence is based on comparison of the RGM concentrations in the plume (at standard conditions) compared to the RGM in the stack. There was found to be a 44% drop in the fraction of RGM between the stack exit and the first sampling arc and a 66% reduction from the stack to the 5-mile sampling arc, with no additional drop between the 5- and 10-mile arcs.

Challenges & Objectives

Experiments have been carried out in both test chambers and pilot-scale coal combustors to determine whether mercury in power plant plumes may be oxidized or reduced in valence state. These experiments have indicated the presence of rapid and relatively complete reduction reactions converting divalent into elemental mercury within such plumes prior to full dispersion in the atmosphere. The measurements, however, have been unable to identify whether the reactions occur during plume rise (during positive thermal buoyancy) or downwind dispersion. To fully demonstrate the occurrence of these reactions, they must also be shown to be present in plume environments associated with fully operational power plants. That requirement, to capture reaction products that may be occurring very close to stack exits in highly turbulent environments, constrains the precision and reproducibility with which such full-scale experiments can be carried out. The work described here is one of several initial steps required to test whether, and in what direction, such rapid mercury redox reactions might be occurring in emissions plumes.

Applications, Values & Use

The linking of mercury atmospheric sources and downwind receptors, particularly receiving waters with the potential for fish uptake and bioaccumulation of mercury, requires the use of atmospheric physicochemical models. Current models either inadequately simulate chemical processes in plume environments, or do not include such processes at all. Additionally, there is little evidence of what such processes involving mercury might require in terms of physical environment or other constituents. Establishing whether mercury redox reactions occur in plume environments will allow improvements in simulation models of power plant contributions. In turn, this will allow a better fit between model outcomes and observed data, to allow more realistic allocation of deposited mercury to its sources.

EPRI Perspective

The chemical form of inorganic mercury, whether elemental or divalent, strongly determines its solubility in precipitable water in the atmosphere. This, in turn, may have orders-of-magnitude effects on ground-level concentrations and deposition rates at local and regional scales. The work described here that was done at the Pleasant Prairie Power Plant is a fundamental contribution to understanding these differences. The reactions implied may substantially alter the relative contributions of nearby vs. distant sources to Hg deposition patterns.

Approach

The overall project objective was to gain an understanding of Hg chemistry as a plume moves downwind from the stack and to determine what changes occur. To accomplish this, an aircraft-mounted sensor/analyzer was employed. The aircraft, a turboprop DHC-6-300 Twin Otter deHavilland Vistaliner, carried an automated Tekran ambient mercury monitor. Aircraft sampling was done at three locations downwind of the stack exit,

flying repeated “racetrack” closed loops across the plume at plume centerline altitude. The first location was approximately 1500 ft downwind of the stack. The second and third locations were approximately 5 and 10 statute miles downwind of the stack, respectively.

Determining the altitude and direction of the plume was accomplished using a combination of visual inspection (on the flight arc closest to the stack) and measurements of NO_x concentrations with a rapid-response sensor. Except for the closest location, the Tekran Hg analyzer was triggered by a NO_x set point.

To establish baseline conditions for comparison with the plume samples, in-stack ground sampling was carried out during each flight, providing measurements of the Hg speciation in the stack. Hg sampling at the stack was accomplished using the Ontario Hydro mercury speciation wet-chemistry method along with a continuous mercury monitor. In addition, arcs upwind of the stack were flown by the instrumented aircraft to establish levels of reactive gaseous mercury and total gaseous mercury in background ambient air for calculating plume contributions to those levels.

Keywords

Mercury

Utilities

Plume(s)

Reactive Gaseous Mercury

Elemental Mercury

Air Toxics