DIRECT MEASUREMENT OF MERCURY REACTIONS IN COAL POWER PLANT PLUMES

Final Technical Report, March 2006

Prepared for:

AAD Document Control

U.S. Department of Energy National Energy Technology Laboratory PO Box 10940, MS 921-107 Pittsburgh, PA 15236-0940

DOE Award DE-FC26-03NT41724
Performance Monitor: William Aljoe

Cosponsor(s)

National Energy Technology Laboratory
U.S. Department of Energy
Pittsburgh, PA

Wisconsin Focus on Energy
Madison, WI

Electric Power Research Institute
Palo Alto, CA

Prepared by

Leonard Levin

Electric Power Research Institute
3412 Hillview Ave.
Palo Alto, California 94303

March 2006

DISCLAIMER OF WARRANTIES AND LIMITATION OF LIABILITIES

THIS DOCUMENT WAS PREPARED BY THE ORGANIZATION(S) NAMED BELOW AS AN ACCOUNT OF WORK SPONSORED OR COSPONSORED BY THE ELECTRIC POWER RESEARCH INSTITUTE, INC. (EPRI). NEITHER EPRI, ANY MEMBER OF EPRI, ANY COSPONSOR, THE ORGANIZATION(S) BELOW, NOR ANY PERSON ACTING ON BEHALF OF ANY OF THEM:

(A) MAKES ANY WARRANTY OR REPRESENTATION WHATSOEVER, EXPRESS OR IMPLIED, (I) WITH RESPECT TO THE USE OF ANY INFORMATION, APPARATUS, METHOD, PROCESS, OR SIMILAR ITEM DISCLOSED IN THIS DOCUMENT, INCLUDING MERCHANTABILITY AND FITNESS FOR A PARTICULAR PURPOSE, OR (II) THAT SUCH USE DOES NOT INFRINGE ON OR INTERFERE WITH PRIVATELY OWNED RIGHTS, INCLUDING ANY PARTY'S INTELLECTUAL PROPERTY, OR (III) THAT THIS DOCUMENT IS SUITABLE TO ANY PARTICULAR USER'S CIRCUMSTANCE; OR

(B) ASSUMES RESPONSIBILITY FOR ANY DAMAGES OR OTHER LIABILITY WHATSOEVER (INCLUDING ANY CONSEQUENTIAL DAMAGES, EVEN IF EPRI OR ANY EPRI REPRESENTATIVE HAS BEEN ADVISED OF THE POSSIBILITY OF SUCH DAMAGES) RESULTING FROM YOUR SELECTION OR USE OF THIS DOCUMENT OR ANY INFORMATION, APPARATUS, METHOD, PROCESS, OR SIMILAR ITEM DISCLOSED IN THIS DOCUMENT.

ORGANIZATION(S) THAT PREPARED THIS DOCUMENT

Energy & Environmental Research Center
Grand Forks, North Dakota

Electric Power Research Institute
Palo Alto, California

Electric Power Research Institute and EPRI are registered service marks of the Electric Power Research Institute, Inc. EPRI. ELECTRIFY THE WORLD is a service mark of the Electric Power Research Institute, Inc.

Copyright © 2006 Electric Power Research Institute, Inc. All rights reserved.

CITATIONS

This report was prepared by

Energy & Environmental Research Center
15 North 23rd Street
Grand Forks, ND 58203

Principal Investigator
D. Laudal

Electric Power Research Institute
3412 Hillview Ave.
Palo Alto, CA 94303

Project Manager
L. Levin

This report describes research sponsored by EPRI, the U.S. Department of Energy, and the State of Wisconsin.

The report is a corporate document that should be cited in the literature in the following manner:

EPRI, 2006; *Mercury Chemistry in Power Plant Plumes;* Electric Power Research Institute, Palo Alto, CA.

PROJECT DESCRIPTION

Recent field and pilot-scale results indicate that divalent mercury emitted from power plants may rapidly transform to elemental mercury within the power plant plumes. Simulations of mercury chemistry in plumes based on measured rates to date have improved regional model fits to Mercury Deposition Network wet deposition data for particular years, while not degrading model verification fits for remaining years of the ensemble. The years with improved fit are those with simulated deposition in grid cells in the State of Pennsylvania that have matching MDN station data significantly less than the model values.

This project seeks to establish a full-scale data basis for whether or not significant reduction or oxidation reactions occur to mercury emitted from coal-fired power plants, and what numerical redox rate should apply for extension to other sources and for modeling of power plant mercury plumes locally, regionally, and nationally.

Although in-stack mercury (Hg) speciation measurements are essential to the development of control technologies and to provide data for input into atmospheric fate and transport models, the determination of speciation in a cooling coal combustion plume is more relevant for use in estimating Hg fate and effects through the atmosphere. It is mercury transformations that may occur in the plume that determine the eventual rate and patterns of mercury deposited to the earth's surface. A necessary first step in developing a supportable approach to modeling any such transformations is to directly measure the forms and concentrations of mercury from the stack exit downwind to full dispersion in the atmosphere. As a result, a study was sponsored by EPRI and jointly funded by EPRI, the U.S Department of Energy (DOE), and the Wisconsin Department of Administration. The study was designed to further our understanding of plume chemistry.

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

Smaller-scale experiments in both test chambers and pilot-scale coal combustor exhaust streams have indicated the presence of rapid and relatively complete reduction reactions converting divalent into elemental mercury within power plant plumes prior to full dispersion in the atmosphere. These measurements, however, have been unable to identify whether the reactions occur during plume rise from physical to virtual stack height (during positive thermal buoyancy). The presence, rate, completeness, ubiquity, and dependence on source characteristics of these reactions, however, must be demonstrated in plume environments associated with fully operational power plants. That requirement, to capture either the reactions or the reaction products of chemistry 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 such plumes.

Applications, Values & Use

The linking of mercury atmospheric sources and downwind receptors, particularly receiving waters and watersheds with the potential for fish uptake and bioaccumulation of mercury, requires the use of atmospheric physicochemical models, since there is a lack of benign chemical tracers that fully mimic the behavior of mercury in the atmosphere and the biosphere. Current models either inadequately simulate chemical processes in-plume environments, or do not allow such inclusion at all; additionally, there is little direct evidence of what those processes applicable to mercury might entail. Establishing whether potentially rapid and complete mercury redox reactions occur in plume environments, enriched in sulfur and other co-emitted substances relative to the free atmosphere and not yet fully dispersed into the ambient environment, will allow model improvements to better simulate contributions of those power plants where such reactions are likely to occur. In turn, this will allow a better fit between model outcomes and actual processes in the atmosphere, 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 done at the Pleasant Prairie Power Plant is a fundamental contribution to understanding these differences mediated by the trace and major constituents in coal-fired power plant stack plumes. 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, a turboprop DHC-6-300 Twin Otter deHavilland Vistaliner aircraft and an automated Tekran

ambient Hg monitor were used. Aircraft sampling was done at three locations downwind of the plume, flying repeated “racetrack” closed loop arcs across the plume at centerline altitude. The first location was approximately 1500 ft downwind of the stack. The second and third locations were approximately 5 and 10 miles downwind of the stack, respectively.

Determining the altitude and direction of the plume was accomplished using a combination of visual inspection (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 sampling was completed during the flight, providing measurements of the Hg speciation in the stack. Hg sampling at the stack was completed using the Ontario Hydro Hg speciation sampling method and a continuous mercury monitor. In addition, upwind arcs were flown by the instrumented aircraft to set levels of incoming RGM and TGM contributions to the plume environment.

Keywords

Mercury
Utilities
Plume(s)
Reactive Gaseous Mercury
Elemental Mercury
Air Toxics

ABSTRACT

Studies of mercury sources, source emissions management, and source-receptor relationships rely on a knowledge of the chemical forms and amounts of mercury emitted from each source. Models of mercury atmospheric transport and chemistry similarly rely on source characterization to initiate reactions based on heterogeneous and homogeneous microenvironments in the free atmosphere, followed by models of aquatic and terrestrial cycling of the substance.

A key missing element of these simulations, and the data they are based on, is whether substantial mercury reactions occur within source emissions plumes to the atmosphere. The environments in these plumes can be expected to be turbulent and contain concentrations of co-emitted material that may be orders of magnitude higher than in the ambient atmosphere. These conditions, combined with elevated stack exit temperatures of approximately 200C or more, are favorable for reactions to occur with mercury under some conditions.

EPRI has conducted two field studies at operating power plants, in 2002 and 2003, to investigate the possible reduction or oxidation of mercury under plume conditions. The first study was at Plant Bowen, Cartersville, Georgia, operated by Georgia Power, part of Southern Company. The second study was at the Pleasant Prairie Power Plant, Pleasant Prairie, Wisconsin, operated by We Energies; there, surface and aircraft measurements were carried out by the University of North Dakota Energy and Environmental Research Center (EERC), with additional studies at the stack and in plume simulation chambers by Frontier Geosciences. The primary focus of this report is on the work at the Pleasant Prairie site.

The overall project objective was to gain an understanding of Hg chemistry as the stack emissions plume is transported downwind from the stack. This was carried out by ground and aircraft measurements conducted simultaneously. Ground measurements characterized mercury amounts and speciation from the plant boilers through air pollution control devices to the stack base, and additional measurements via stack ports at about 70% stack height. Aircraft measurements were carried out by flying a Twin Otter aircraft through the plume at several locations (a point nearest the stack, at approximately effective stack height; 5 miles from the stack; and 10 miles from the stack) and measure the speciated Hg composition in the plume using an automated ambient Hg monitor.

The results of the project appeared to show a reduction in reactive gas mercury (RGM) (with a corresponding increase in the fraction of elemental Hg) when the proportion of RGM in the plume is compared to the RGM in the stack. There was a 44% reduction of RGM from the stack to the first sample point and a 66% reduction of RGM from the stack to the 5-mile sample point, with no additional reduction between the 5- and 10-mile locations.

ACKNOWLEDGMENTS

This work would not have been possible without the efforts of many people. The authors would like to acknowledge the following people.

For their direction and leadership, appreciation is expressed to William Aljoe and Lynn Brickett of the U.S. Department of Energy National Energy Technology Laboratory, Pittsburgh. The work could also not have been completed without support from the Wisconsin Department of Administration, Wisconsin Focus on Energy, and Ingrid Kelley of that program.

At the University of North Dakota, thanks go to Grant Dunham, Blaise Mibek, and Richard Schulz from the Energy & Environmental Research Center and David Delene from the School of Aerospace Sciences,

For Frontier Geosciences, appreciation is extended to Eric Prestbo and his colleagues.

Deep appreciation is also expressed to the other researchers who contributed to the effort, including Ray Valente from the Tennessee Valley Authority.

Special thanks are expressed to Ed Morris and David Michaud of We Energies for facilitating the testing conducted at the Pleasant Prairie Power Plant and for all of the help their colleagues provided.

NOMENCLATURE

AF	atomic fluorescence
CEM	continuous emission monitor
CMM	continuous mercury monitor
CVAFS	cold-vapor atomic fluorescence spectroscopy
DOE	U.S. Department of Energy
EERC	Energy & Environmental Research Center
ESP	electrostatic precipitator
F_d	value relating gas volume to the heat content of the fuel, equal to dscf/10^6 Btu
GEM	gaseous elemental mercury
GPS	global positioning system
HCl	hydrochloric acid
Hg	mercury
Hg^0	elemental mercury
Hg^{+2}	divalent mercury
HYSPLIT	HYbrid Single-Particle Lagrangian Integrated Trajectory model
lpm	liters per minute
MW	megawatts
nm	nautical mile
NO_x	nitrogen oxides
NO_y	reactive nitrogen species
OH	Ontario Hydro mercury speciation method
ppb	parts per billion
PRB	Powder River Basin
RGM	reactive gaseous mercury
SCR	selective catalytic reduction
$SnCl_2$	stannous chloride
SO_2	sulfur dioxide
SPDC	static plume dilution chamber
TECO	Thermal Electron Corporation
TVA	Tennessee Valley Authority

EXECUTIVE SUMMARY

This report provides a detailed summary of the results obtained for the project entitled "Direct Measurement of Mercury Reactions in Coal Power Plant Plumes." The data were obtained during testing at the We Energies Pleasant Prairie Power Plant, Pleasant Prairie, Wisconsin during August-September of 2003. The project was sponsored by EPRI with key funding from the U.S. Department of Energy (DOE) National Energy Technology Laboratory and the Wisconsin Department of Administration.

Introduction

Characterization of environmental mercury (Hg) and its atmospheric processes, from emission to deposition, requires both measurement and model simulations for a full understanding. Although in-stack Hg speciation measurements are essential to the development of control technologies and to provide data for input into the atmospheric deposition models, the determination of speciation in a dispersing power plant stack emissions plume is more relevant for use in estimating Hg fate and effects after transit through the atmosphere. Mercury transformations that may occur in plumes determine the rate and the form of Hg transported in the free atmosphere. Source characterization alone, therefore, will provide an incomplete and perhaps misleading portrayal of the forms of mercury emitted into the atmosphere.

Given these considerations, the Electric Power Research Institute has undertaken a program of direct chemical measurements of plume mercury at operating power plants. The first field experiment in this program was at the Plant Bowen (operated by Georgia Power Company), with the Tennessee Valley Authority (TVA) conducting the aircraft studies and the EERC and Frontier Geosciences doing Hg measurements at the stack. The second study was conducted at the Pleasant Prairie Power Plant, operated by We Energies, with the EERC carrying out both the aircraft and stack Hg measurements, with additional surface measurements again done by Frontier Geosciences. This report provides insight into the work at Pleasant Prairie; that work was sponsored by EPRI, EPRI member companies, the U.S. Department of Energy (via the National Energy Technology Laboratory, Pittsburgh, PA), and the State of Wisconsin Department of Administration (via Wisconsin Focus on Energy).

Project Objectives

The overall project goal is to gain an understanding of Hg chemistry as a plume moves downwind from the stack. Specific objectives include:

- Develop sampling techniques to measure speciated Hg in the plume.
- Develop techniques to determine the location of the plume at various points downwind of the stack.
- Determine the speciated Hg emissions at the stack and compare these results to those obtained from the plume sampling.

- Compute a Hg mass balance using dilution factors and other relevant parameters.

Project Description

Power Plant Description

The Pleasant Prairie Power Plant is located near the city of Pleasant Prairie just west of Kenosha, Wisconsin. The Pleasant Prairie plant consists of two units (Units 1 and 2) identical in operation with the exception of one (Unit 2) having a selective catalytic reduction (SCR) system at the time of the measurements. Each unit has an electrostatic precipitator (ESP) for particulate control and share a common stack. Specifications of the Pleasant Prairie facility are as follows:

- Fuel type: Powder River Basin (PRB) subbituminous coal
- Boiler capacity: 617 MW (each unit)
- Boiler type: opposed-fired pulverized coal (both units)
- NO_x control: SCR on Unit 2, low-NO_x burners on both units
- SO_2 control: none, combustion of low-sulfur coal (both units)
- Particulate control: ESP (both units)

The coal is fairly typical of PRB in that both the Hg and chlorine levels in the coal are comparatively low; the Hg averaged 0.041 µg/g and the chlorine, 10 ppm.

Aircraft and Equipment Used for the Project

The aircraft used for the emission plume sampling was a turboprop DHC-6-300 Twin Otter deHavilland Vistaliner. The twin-engine plane had a relatively large capacity for equipment and sufficient onboard electrical supply and could be operated efficiently at low altitudes. These capabilities were accompanied by relatively low fuel consumption at all altitudes. Most importantly for the plume study project, it could be flown at relatively slow speeds (80–160 knots/150–300 km/hr) and in tight formation to allow consistent plume traverses at fixed heights and downwind distances.

The Hg analyzer used in the aircraft was a Tekran® Model 2537A mercury vapor analyzer coupled with a Tekran® Model 1130 mercury speciation unit and a Tekran® Model 1135 particulate module. The analyzer portion of the system is based on the principle of atomic fluorescence and has detection limits <1 pg/m^3. With this system, it was possible to simultaneously measure elemental mercury (Hg^0), reactive gas mercury (RGM), and particulate-bound Hg species during the flight.

To compare the Hg concentrations in the plume to those in the stack, a dilution factor was determined. Based on the earlier tests conducted at Plant Bowen [2], it was decided that the NO_x concentration in the stack vs. that in the plume be used to determine the dilution factor as shown in the following equation:

$$Dilution\ Ratio = \frac{(Stack\ NOx - Background\ NOx)}{(Plume\ NOx - Background\ NOx)}$$

In addition, the NO_x analyzer was used to determine the location of the plume. The analyzer that was used for this project was a dual range Model 42C Thermo Electron ambient air NO_x analyzer. This analyzer was able to measure 0–50 parts per billion (ppb) NO_x in the low range and up to 500 ppb NO_x in the high range.

Experimental Approach

Aircraft Sampling Locations

Following background sampling at a location upwind of the stack, aircraft sampling was done at three locations downwind of the plume. The first location was approximately 1500 ft from the stack, at approximately the effective stack height. The second and third locations were approximately 5 and 10 miles downwind of the stack, respectively. A number of different patterns were flown at the closest sampling point in an effort to maximize the sampling time within the emissions plume material. At the other two locations, a racetrack pattern was flown. To provide data on aircraft position as a function of time, a satellite-based global positioning system was used.

Aircraft sampling flights were conducted in daylight under atmospheric conditions that permitted adequate sampling of the stack plume. The weather conditions during the project field period were primarily fair weather days with visual flight conditions prevailing. Average wind speeds were somewhat above this, ranging from 5.3 to 8.3 m/s. These wind speeds were still low enough that the aircraft was able to locate the plume by NOx sensors, and sometimes visually.

Stack Sampling

To establish baseline conditions for comparison with the plume samples, in-stack sampling was carried out simultaneously with the flight, providing measurements of the Hg speciation in the stack. Hg sampling at the stack was completed using the Ontario Hydro (OH) Hg speciation sampling method and a continuous mercury monitor (CMM). Prior to the start of the testing, a CMM was placed at the stack outlet and remained there during the entire project. During each flight day, one OH sample was taken at the stack.

In addition to Hg measurements by the EERC, the plant operators continuously measured the NO_x concentration in the stack using a continuous emission monitor. Although the NO_x concentrations in the stack at the Pleasant Prairie Power Plant were somewhat lower than optimal for aircraft plume measurements (since half the flue gas was being treated using an SCR), it was still possible to detect a difference between the background and plume, even at 10 miles. The average stack NO_x concentration was 144 ppm(v).

Results and Discussion

Stack Results at Pleasant Prairie

The Hg concentrations in the stack were relatively constant during the entire duration of the project. RGM averaged 34.3% of the total Hg measured. These results were matched very well by the CMM as shown in Figure ES-1.

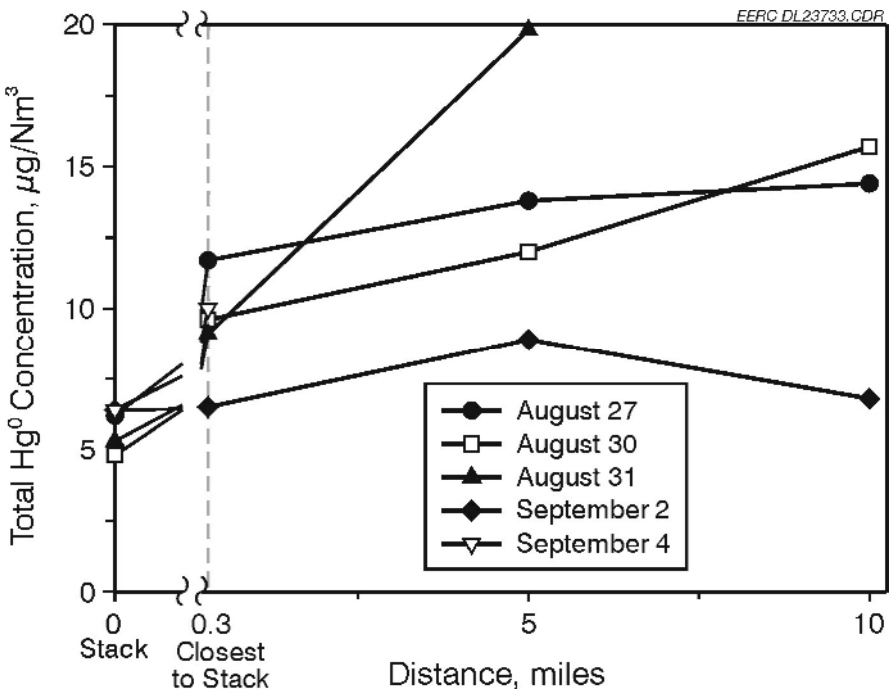

Figure ES-1
Plot of the % Hg^0 in the Plume Compared to the Stack Hg Concentration as a Function of Distance from the Stack

Plume Results at Pleasant Prairie

A summary of the results from the plume sampling at the Pleasant Prairie plant is presented in Table ES-1. The plume Hg concentrations have been converted to equivalent stack concentrations and are presented as such. The plume data were reduced by first correcting for the amount of sampling time in the plume. This gives a Hg concentration in the plume. The plume concentrations were then converted to an equivalent stack concentration by applying dilution factors which were based on the plume and stack NO_x concentrations.

Table ES-1
Average Mercury Speciation Results for Each Location*

	Hg_p, µg/Nm^3	Hg^0, µg/Nm^3	RGM, µg/Nm^3	Total Hg, µg/Nm^3	% Hg^0
Stack					
Average	0.00	3.2	6.2	9.4	66
Std. Dev.	0.00	0.5	0.7	0.7	5.1
0 Miles					
Average	0.06	10.4	2.0	12.4	84
Std. Dev.	0.04	3.1	0.5	3.2	5.0
5 Miles					
Average	0.10	15.7	1.7	17.5	89
Std. Dev.	0.06	8.7	0.8	9.3	4.0
10 Miles					

Average	0.09	12.4	1.6	14.1	88
Std. Dev.	0.08	4.8	0.7	5.4	2.6

* All concentrations are based on normal (N) conditions defined as 1 atmosphere pressure, 20°C, and 3% O_2.

A mass balance was calculated using the average total Hg data from each sampling point each day and the corresponding stack data. The results are presented in Table ES-2. The ratio of Hg^0 to RGM does show an evolution as the plume moves downwind from the stack, implying a change in speciation occurring solely within the plume itself between the stack exit and full dispersion into the atmosphere.

Table ES-2
Total Hg Mass Balance: Plume Hg Compared to Stack Hg

Sample Point Nearest the Stack			Sample Point 5 miles Out			Sample Point 10 miles Out		
Total Hg in Plume, µg/Nm^3	**Total Hg in Stack, µg/Nm^3**	**Balance, %**	**Total Hg in Plume, µg/Nm^3**	**Total Hg in Stack, µg/Nm^3**	**Balance, %**	**Total Hg in Plume, µg/Nm^3**	**Total Hg in Stack, µg/Nm^3**	**Balance, %**
13.5	9.3	145	15.1	9.3	162	16.5	9.3	177
12.2	8.5	144	14.4	8.5	169	17.8	8.5	209
10.8	7.6	142	22.2	7.6	292	7.9	9.2	86
7.8	9.2	85	9.6	9.2	104			
12.0	9.2	130						
18.6	9.2	202						

It should be noted there were a number of high readings that corresponded to very high dilution ratios. These results were not included in the averages. The high dilution ratios occurred during intermittent aircraft transit of smaller plume eddies separated from the main body of the plume. When this occurs, relatively high proportions of ambient air is sampled in a short time and is, therefore, not statistically characteristic of the plume material at that distance from the stack. Even with relatively stable winds, turbulent eddies would result in complex plume structures, causing some passes through the plume to only intersect edges of the plume rather than the cross-centerline transects that were sought. These peripheral intersects would capture relatively large proportions of ambient air with markedly lower NO_x values than the main body of the plume. During these sampling episodes, the NO_x concentration would be just high enough to trigger the zero air inlet valve in the sampling system. Once it was triggered, the valve was set with a delay to stay off for 5 seconds once the NO_x level again fell below the trigger point. This was done to prevent rapid cycling of the valve. Since the NO_x concentration was near ambient levels in these segments of the plume, the resulting dilution ratios were artificially high.

The overall results are shown in Figure ES-1 in a plot of the average percentage of Hg^0 in the plume as it moves from the stack exit to 10 miles downwind of the stack. There is a substantial increase in the concentration of Hg^0 from the stack to the first sample point, a smaller increase from the first to the second sample point, and then no change from there to the last sample location (10 miles). Overall, the Hg^0 increases from 67% of the total Hg to 89% by the time it reaches the 5-mile sample point.

Conclusions

The Pleasant Prairie Power Plant experiment on plume mercury chemistry resulted in the following general conclusions:

- Hg can be measured by aircraft in plumes with reasonable accuracy and precision. However, great care must be taken to prevent contamination in sampling lines and equipment used aboard the aircraft.

- Using a dilution factor based on the plume and stack NOx, a reasonable Hg mass balance can be obtained to compare the Hg in the stack to the Hg in the plume.

- There appeared to be a decline in the fraction of RGM at Pleasant Prairie when values in the plume are compared to those in the stack (with a corresponding increase in the proportion of Hg^0). There was a 38% reduction of RGM between the in-stack measurement and the first sample point closest to the stack, and a 47% reduction of RGM from the stack to the 5-mile sample point, with no additional reduction between the 5- and 10-mile locations.

CONTENTS

1 **INTRODUCTION 1-1**

2 **PROJECT DESCRIPTION 2-1**

2.1 Power Plant Description 2-1

2.2 Mercury Analyzers 2-2

2.2.1 Aircraft Hg Measurement System 2-2

2.2.2 Stack Hg Analyzer 2-3

2.3 NO_x Analyzer 2-4

2.4 Plume Dilution Chambers 2-4

3 **EXPERIMENTAL APPROACH 3-1**

3.1 Plume Sampling 3-1

3.1.1 Aircraft Sampling Arcs 3-1

3.1.3 Plume-Sampling Procedures 3-3

3.2 Stack Sampling 3-4

4 **RESULTS AND DISCUSSION 4-1**

4.1 Stack Results at Pleasant Prairie 4-1

4.2 Plume Results at Pleasant Prairie 4-2

4.2.1 Data Censoring 4-4

4.2.2 Mass Balance Calculations 4-4

4.2.3 Plume Hg Speciation Results 4-6

4.3 Vertical Mercury Profile 4-9

4.4 Static Plume Dilution Chamber Findings 4-10

5 **CONCLUSIONS AND RECOMMENDATIONS 5-1**

6 **REFERENCES 1**

LIST OF FIGURES

Figure 2-1 Schematic of the Pleasant Prairie Power Plant 2-2
Figure 3-1 Flight Track on August 27, 2003 3-1
Figure 3-2 Flight Track on August 30, 2003 3-2
Figure 3-3 Flight Track on August 31, 2003 3-2
Figure 3-4 Flight Track on September 2, 2003 3-3
Figure 4-1 Stack CMM Mercury Speciation Results 4-2
Figure 4-2 Plot of the Concentration of Hg^0 in the Plume As It Moves from the Stack to 10 miles Downwind of the Stack 4-7
Figure 4-3 Plot of the % Hg^0 in the Plume Compared to the Stack Hg Concentration As a Function of Distance from the Stack 4-7
Figure 4-4 Plot of the Concentration of Total Mercury in the Plume As It Moves from the Stack to 10 miles Downwind of the Stack 4-8
Figure 4-5 Plot of the Concentration of RGM in the Plume As It Moves from the Stack to 10 miles Downwind of the Stack 4-8

LIST OF TABLES

Table 2-1 Location of Major Cities in Relationship to the Plant.....2-1
Table 2-2 Pleasant Prairie Coal Analysis (on an as-received basis).....2-2
Table 4-1 Stack Ontario Hydro Mercury Speciation Results.....4-1
Table 4-2 Plume Mercury Speciation Data.....4-3
Table 4-3 Average Mercury Speciation Results for Each Location (from Table 6-2)* 4-4
Table 4-4 Total Hg Mass Balance: Plume Hg Compared to Stack Hg.....4-6

1
INTRODUCTION

Mercury (Hg) occurs in three primary forms, or "species," in the atmosphere, from both natural and anthropogenic sources. These forms are: elemental mercury, Hg^0; divalent mercury, Hg^{II}; and particulate-bound mercury, Hg-p. (There are a number of variants in how each of these forms is referred to, depending on the context, and how the chemical species is indicated; all of these different forms are equally acceptable.) During coal combustion, associated mercury may be in part transformed from the elemental to the divalent form due to thermal and catalyzed reductions, particularly in the presence of fuel chlorine. Flue gas emissions from a power plant furnace to the stack via intervening control devices may further alter the ratio of divalent and elemental mercury to total gaseous mercury in the flue gas. For example, sulfur capture via "scrubbers" and particulate capture by electrostatic precipitators will also capture a fraction of the divalent and particulate-bound mercury in the flue gas, while very little elemental mercury will be captured by these current technologies.

Once the flue gases, altered by control devices, reach the stack base, forced-draft and buoyant ascent occur along with gas temperature drops in and beyond the stack. Typical stack exit temperatures are 180-210C for coal-fired power plants; beyond the stack tip, exit plumes will both continue to rise due to positive buoyancy while they mix turbulently with the ambient atmosphere and are displaced by vertical and horizontal wind shear. The elevation above the physical stack height at which the plume reaches thermal equilibrium (zero buoyancy) is referred to as the "effective stack height." From there, turbulent mixing and downwind transit are governed by wind conditions (as well as such secondary effects as stack tip aerodynamic wake under strong winds). Plume concentrations right after stack exit quickly drop by a factor of 1000 or more, then further with downwind dissipation.

Although in-stack Hg speciation measurements are essential to the development of control technologies and to provide data for input into the atmospheric transport and fate models, the determination of speciation and speciation changes in a dissipating coal combustion plume is more relevant for use in estimating further mercury transformations in and deposition from the atmosphere. Substantial research has been done in the past on Hg transformations within energy conversion systems—determining the concentrations of speciated Hg at the stack and doing ground-level atmospheric measurements; however, little has been done to determine the Hg chemistry, kinetics, and thermodynamics in the flue gas plume [2]. It is the Hg transformations that occur in the plume that determine the rate and the form of Hg deposited in waterways. This report describes the experimental design, data findings, results, and interpretation of measurements of one such experiment at the We Energies Pleasant Prairie Power Plant, Pleasant Prairie, Wisconsin.

2
PROJECT DESCRIPTION

The power plant plume observations were carried out at the Pleasant Prairie Power Plant of We Energies in a combined field campaign involving in-plant, in-stack, and aircraft measurements of emitted mercury. Measurements of mercury within the flue gas stream were carried out by the University of North Dakota (UND) Energy and Environmental Research Center (EERC) at a number of locations from the power plant boilers to the stack. UND also flew sampling patterns that intersected the plume in a deHavilland Twin Otter modified for in-flight sampling of mercury. Full details of in-plant and aircraft sampling are described in Appendix A. Simultaneously, measurements of mercury reaction products were carried out by Frontier Geosciences using both a static plume dilution chamber (SPDC) and a dynamic plume dilution chamber (DPDC) situated adjacent to the stack on an elevated platform, accessing flue gases via stack sampling ports.

2.1 Power Plant Description

The Pleasant Prairie Power Plant, owned and operated by We Energies, is located in Pleasant Prairie, Wisconsin, just west of Kenosha. The distance and direction from the power plant to nearby major cities within a 50-mile radius is shown in Table 2-1.

Table 2-1
Location of Major Cities in Relationship to the Plant

City	Distance,[1] miles	Direction
Kenosha	7	NE
Milwaukee	31	NNW
Chicago	45	SSE
Racine	17	NNE

[1] Distance from Kenosha Regional Airport.

The Pleasant Prairie Plant consists of two units, identical with the exception of one (Unit 2) having a selective catalytic reduction system (SCR). Both units have an electrostatic precipitator (ESP) for particulate control. The two units share a single stack. A schematic of the plant is shown in Figure 2-1. Specifications of the Pleasant Prairie facility are:

- Fuel Type: Powder River Basin (PRB) subbituminous coal
- Boiler Capacity: 617 MW (both units)
- Boiler type: opposed-fired pulverized coal (both units)
- NO_x control: SCR on Unit 2, low-NO_x burners on both units.
- SO_2 control: none, low-sulfur coal (both units)
- Particulate control: ESP (both units)

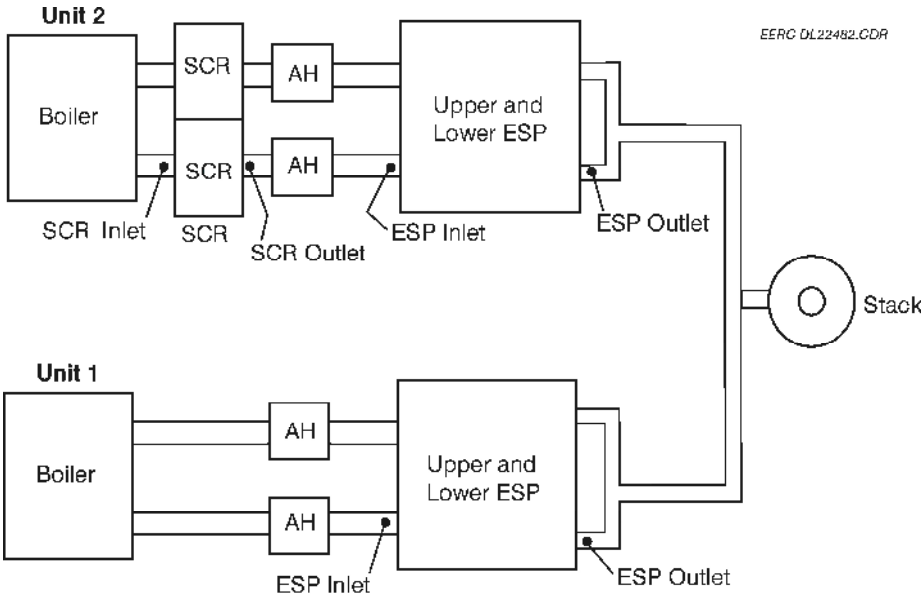

Figure 2-1
Schematic of the Pleasant Prairie Power Plant

The analysis of the coal fired at the Pleasant Prairie Power Plant is shown in Table 4-2. The coal is typical of a PRB in that the Hg concentration is relatively low, <0.05 ppm, and the chlorine content is very low, 10 ppm.

Table 2-2
Pleasant Prairie Coal Analysis (on an as-received basis)

Component	Value
Hg, ppm (dry)	0.041
Chlorine, ppm (dry)	10
Proximate Analysis	
Moisture, wt%	30.0
Volatile Matter, wt%	33.0
Fixed Carbon, wt%	31.5
Ash, wt%	5.5
Ultimate Analysis	
Hydrogen, wt%	6.6
Carbon, wt%	46.9
Nitrogen, wt%	0.9
Sulfur, wt%	0.4
Oxygen, wt%	39.7
Heating Value, Btu/lb	8,190
F_d, dscf/10^6 Btu*	9,519

* Emission factor.

2.2 Mercury Analyzers

2.2.1 Aircraft Hg Measurement System

The Hg analyzer used in the aircraft was a Tekran® Model 2537A mercury vapor analyzer coupled with a Tekran® Model 1130 mercury speciation unit and a Tekran® Model 1135

particulate module. Figure 2-1 shows a schematic of the Tekran® components. Several modifications were made to the Tekran® setup:

- Addition of an optional impactor
- Adding an external pump to pull an isokinetic sample from the probe
- Adding a probe and heated sample transfer line to the sample path
- Adding a soda-lime trap
- Adding a zero-air valve trigger

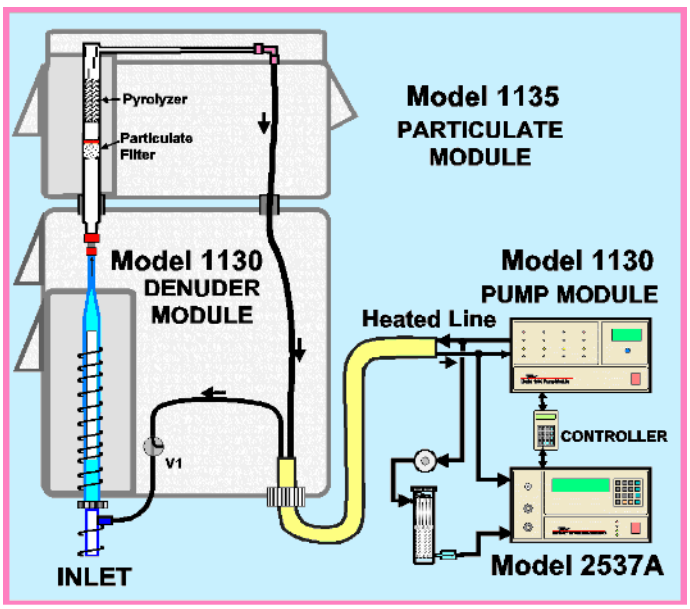

Figure 2-1
Schematic of the Tekran Mercury System

The analyzer portion of the system (Model 2537A) uses cold-vapor atomic fluorescence spectroscopy (CVAFS). The system uses a gold-impregnated trap for preconcentrating the Hg and separating it from potential interferences that degrade sensitivity. The denuder (Model 1130) and particulate modules (1135) are integrated with the analyzer and are automated, allowing simultaneous monitor of Hg^0, RGM, and particulate-bound Hg species during aircraft operations. One sampling cycle would consist of one hour's sample recovery and analysis, during periods when the aircraft was in both the free atmosphere and the plume environment; time within the plume environment was summed via records from the rapid-response NOx analyzer. Further details are provided in Appendix A.

2.2.2 Stack Hg Analyzer

A Tekran Hg analyzer (Model 2537A modified to operate at the higher concentrations of Hg found in flue gas) was used at the stack to provide Hg speciation data continuously during the experimental period (August 25–September 6, 2003). The system is calibrated using Hg^0 as the primary standard. The Hg^0 is contained in a closed vial, which is held in a thermostatic bath. The temperature of the Hg is monitored, and the amount of Hg is determined using vapor pressure calculations. The unit calibration proved stable over a 24-hour period.

Upstream of the Tekran, a wet-chemistry PS Analytical conversion/pretreatment system was used. The purpose of the pretreatment/conversion system was to remove acid gases (HCl) that can swamp the gold traps, to convert all the Hg to Hg^0 so that it can be measured by the atomic fluorescence detector, and to allow the instrument to speciate Hg. The wet-chemistry conversion unit used $SnCl_2$ to convert all of the Hg to Hg^0 prior to analysis; a KCl solution was used to strip out the Hg^{2+} (for speciation purposes), and a sodium hydroxide solution removed the acid gases.

2.3 NO_x Analyzer

Aboard the aircraft, the zero-air valve on the Tekran Model 1130 pump module was triggered using an ambient air NO_x analyzer. It was expected that a NO_x differential between ambient air and the plume environment would be detectable well downwind of the stack. The detection of this gradient along with a global positioning system (GPS) was then used to determine the location of the plume and thereby control the zero-air valve. A rapid-response NO_x analyzer was necessary to allow recording of NO_x concentration changes as the aircraft crossed the edges of elevated plume concentrations, and assumed that NOx dispersed identically with total gaseous mercury (TGM). The assumption of neutral buoyancy and equivalent Froude numbers for all plume constituents at and beyond equivalent stack height and distance was used to calculate in-plume portions of the Hg concentration.

The analyzer that was used for this project was a rapid response, dual-range TECO Model 42C ambient air NO_x analyzer. This analyzer was able to measure 0–50 ppb NO_x in the low range and up to 500 ppb NO_x in the high range, which based on the test at Bowen appeared to be adequate. By the removal of an external filter and replacement of ¼” lines with 1/8” Teflon lines, the analyzer response time from the inlet of the sample probe was decreased to 2 seconds. A separate TECO Model 111 calibration unit was used to calibrate the analyzer. The system required a tank of NO calibration gas and a source of zero air. The TECO Model 111 uses mass flow controllers to mix the calibration and zero gases to produce a desired calibration concentration.

2.4 Plume Dilution Chambers

During aircraft operations, and at times between measurements aloft, a static and (later) a dynamic plume dilution chamber were operated from scaffolding attached to the outside of the Pleasant Prairie stack structure. The static plume dilution chamber (SPDC) (Figure 2-2) is a 0.5-m^3 partially evacuated stainless steel flask into which, successively, flue gas and ambient air (total of 3 to 5 l) are introduced. The SPDC is equipped with switchable caps allowing either artificial rainfall, artificial sunlight, or both to be introduced. Successive samples are withdrawn from the SPDC and analyzed using a Tekran instrument to gauge the changes in speciation and concentration of mercury that occur over the sampling period.

The flue gas diluted with filtered ambient air is allowed to react for a fixed amount of time, typically 4 minutes, before sampling begins. The air pressure is maintained near ambient (1 atm) in the SPDC. Dilution ratios [ambient air:flue gas bulk concentrations] were held at approximately 140:1. The Tekran determines the initial mass-balance of gas-phase Hg^0. Simultaneously with flue gas introduction into the SPDC, speciation of the flue gas at the

stack probe was determined using the Ontario-Hydro method and the FMSS method (Frontier Geosciences). Semi-automated Hg speciation measurements in the SPDC were carried out using a Tekran 2537A total gaseous Hg instrument with a KCl-denuder and particulate filter inlet. This method has been shown in lab and field tests to be precise, accurate, and free of artifacts (Landis et al., 2002). Elemental Hg was determined continuously in the SPDC using the Tekran 2537A. During the time that the Tekran 2537A measured Hg^0, both gaseous Hg^{+2} and particulate Hg were collected by the KCl-denuder and filter inlet. By collecting a number of Hg^{+2} and particulate Hg samples in series, the changes in these species could be monitored over time. This required several KCl-denuders and particulate filters be prepared for each sample run. After the conclusion of the sampling, the KCl-denuders and particulate filters were directly analyzed in the Tekran 2537 by thermal desorption.

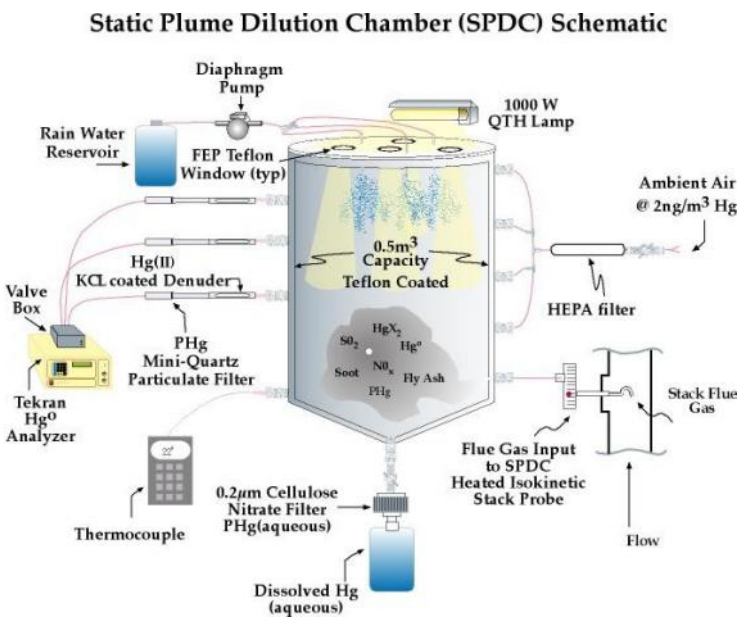

Figure 2-2
Static Plume Dilution Chamber

3
EXPERIMENTAL APPROACH

3.1 Plume Sampling

3.1.1 Aircraft Sampling Arcs

Following background sampling at a location upwind of the stack, aircraft sampling was done using cross-plume arcs at three locations downwind of the stack. The first location was approximately 1500 ft from the stack (the closest the plane was permitted to approach the stack), at approximately effective stack height (initial thermal equilibrium of the plume). The second and third locations were approximately 5 and 10 miles downwind of the stack, respectively. Figures 3-1 through 3-4 are diagrams of the sampling locations and patterns that were done for each flight event. A number of different patterns were flown at the closest sampling point in an effort to maximize the time in the plume. At the other two locations, a racetrack pattern was flown. Aircraft position and time were determined using a GPS system.

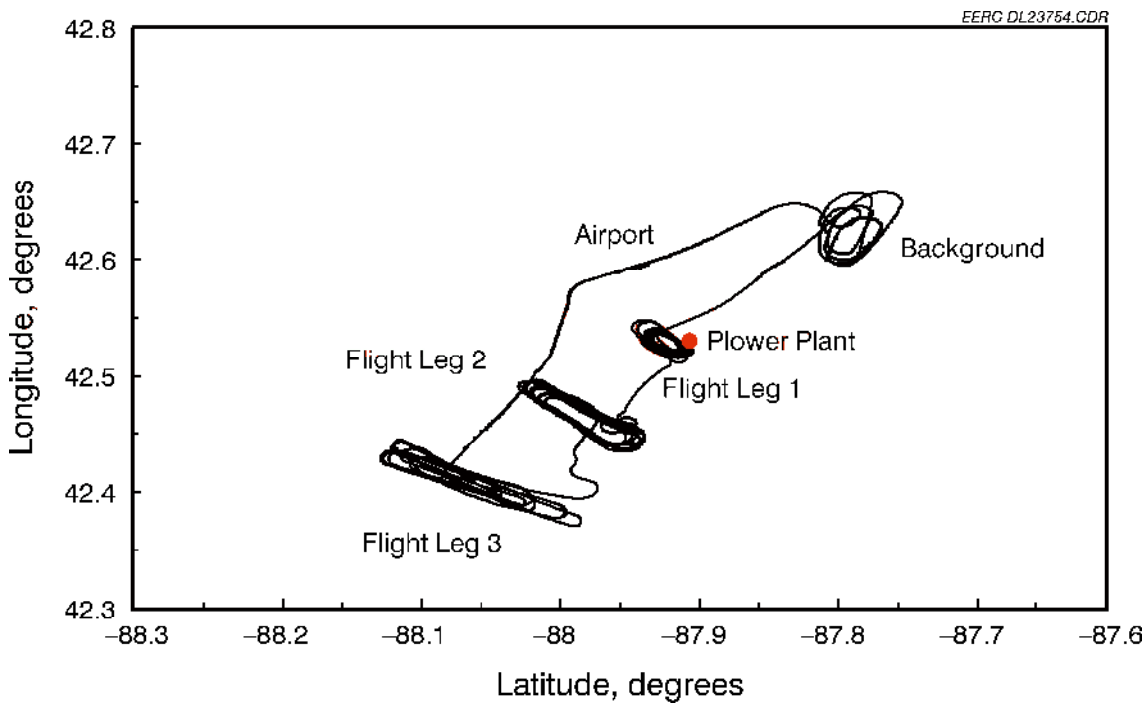

Figure 3-1
Flight Track on August 27, 2003

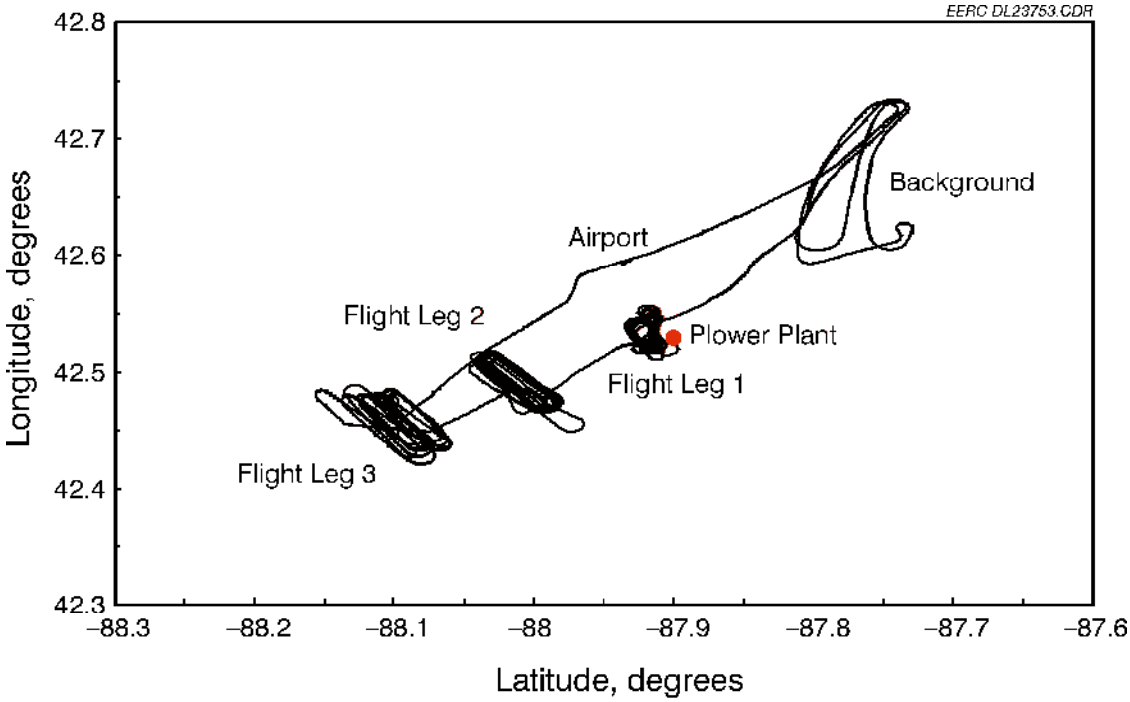

Figure 3-2
Flight Track on August 30, 2003

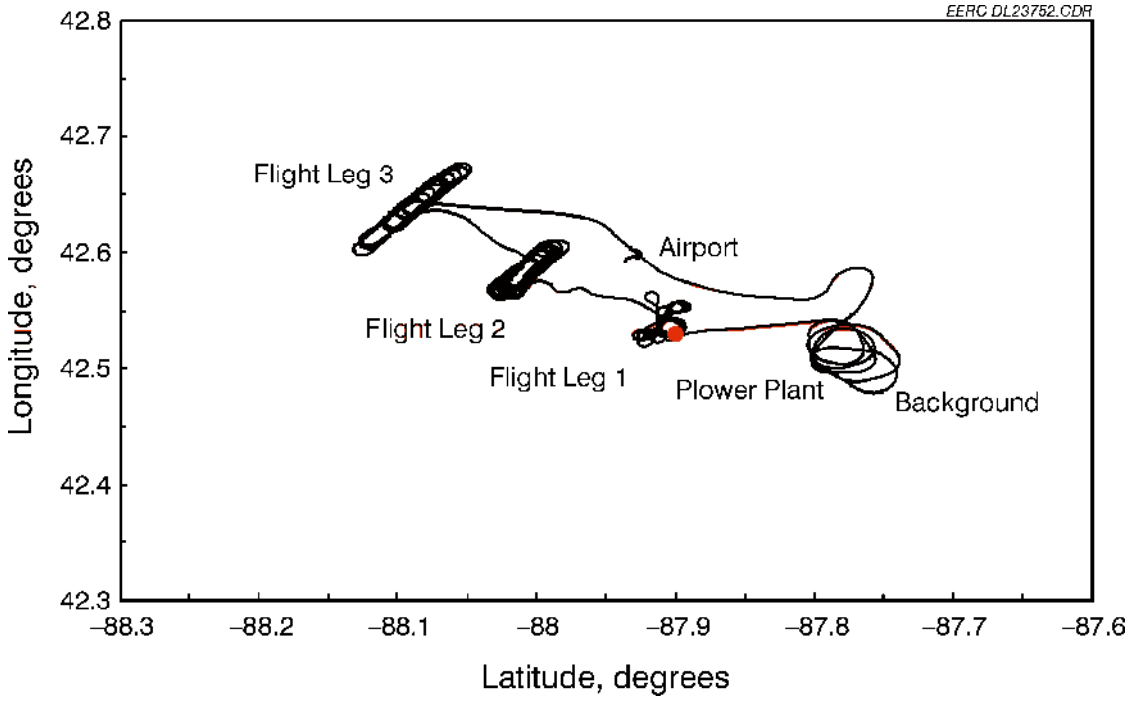

Figure 3-3
Flight Track on August 31, 2003

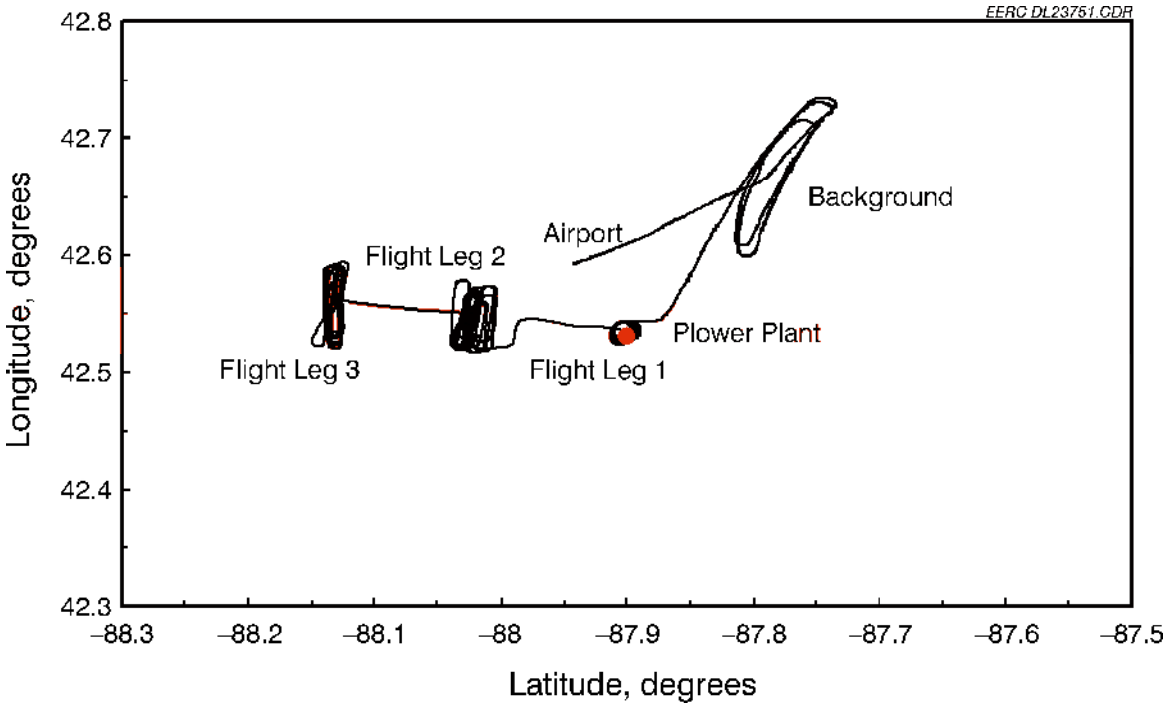

Figure 3-4
Flight Track on September 2, 2003

Determining the altitude and direction of the plume was done based on a combination of visual inspection (location closest to the stack) and the measurements of NO_x concentrations. Except for the closest location, the Tekran Hg analyzer was triggered by a NO_x set point.

In addition to plume sampling, a vertical Hg profile was established at a location about 15–20 km downwind of the plume. The first sample was taken in the plume (approximately 2500 ft), and the second point was taken below the plume at 500 ft. Because of the limited flight time, it was decided to climb to the highest sample point before dropping to the 8500-ft sample point.

Details of each sampling flight, including local weather conditions during the flights, are presented in Appendix A of this report.

3.1.3 Plume-Sampling Procedures

A total of five flight days was carried out during the experimental period of August 25-September 6, 2003. The following steps were carried out prior to flight and during in-flight sampling(full description is found in Appendix A):

- The Hg analyzer was zeroed and then calibrated using primary injections of Hg^0.
- The NOx analyzer was zeroed and spanned.
- The particulate module and denuder system were manually desorbed to remove any residual Hg.
- Zero-Hg ambient air was sampled through the entire system for one cycle.

- Background samples were taken in the plane at a point approximately 5 miles upwind of the stack.
- The plume was then located by visual means at the point nearest to the stack (~1500 ft), and Hg samples were taken over a 25-minute period.
- After the plume was located at the 5-mile arc, the NOx trigger point was set at an appropriate level for that distance downwind of the stack to trigger sampling when the plume was entered.
- After the analysis of the first sample was completed, Hg sampling was done for another 25 minutes at the 5-mile location.
- The process was repeated at a point in the plume 10 miles downwind of the stack.

3.2 Stack Sampling

For comparison with plume mercury samples, in-stack sampling was carried out simultaneously during the flights. Hg sampling at the stack was carried out using the Ontario Hydro (OH) Hg speciation sampling method and a continuous mercury monitor (CMM) placed at the stack exit. One OH sample was taken per flight day.

During the sampling period, it was expected that the two units at the Pleasant Prairie Plant would be operating at or near normal operating conditions. Plant operating conditions (i.e., load, O_2, NO_x, SO_2, CO_2) were logged by plant personnel during the sampling period. From plant data, operating conditions were relatively constant for each day. Since stack NO_x values were used to calculate dilution ratios for the plume samples, relatively constant operating conditions were required to allow application of ground-calculated dilution ratios to aircraft-collected data.:

$$Dilution\ Ratio = \frac{(Stack\ NOx - Background\ NOx)}{(Plume\ NOx - Background\ NOx)} \qquad \text{[Eq. 1]}$$

Since one of the two Pleasant Prairie units had a selective catalytic reduction (SCR) device operational, the NO_x concentrations in the stack were somewhat lower than desired for aircraft plume measurement. It should be noted that the ESPs at Pleasant Prairie Power Plant were very efficient (>99.8%), which is illustrated by the low opacity (<10%). As a result, the plume was difficult to find visually from the air even at the closest location to the stack.

The Hg measurements by the aircraft and at the stack were compared to SPDC located at the stack by Frontier Geosciences, Inc.

4
RESULTS AND DISCUSSION

4.1 Stack Results at Pleasant Prairie

The Hg concentrations in the stack are shown in Table 4-1 and Figure 4-1 for OH and CMM sampling, respectively. As the results show in Table 4-1, the Hg concentrations were relatively constant during the entire duration of the project. The Hg^{2+} averaged 34.3% (65.7% Hg^0) of the total Hg measured. These results were well-matched by the CMM as shown in Figure 4-1.

Table 4-1
Stack Ontario Hydro Mercury Speciation Results

Date	Particulate-Bound Hg, µg/Nm^3	Hg^{2+}, µg/Nm^3*	Hg^0, µg/Nm^3	Hg (total), µg/Nm^3	Hg^0 as a % of Total Hg	Hg^{2+} as a % of Total Hg
08/27/03	0.00	3.30	6.70	10.00	67.0	33.0
08/29/03	0.00	3.43	6.06	9.49	63.9	36.1
08/30/03	0.00	3.02	6.63	9.65	68.7	31.3
08/31/03	0.00	4.01	5.10	9.11	56.0	44.0
09/02/03	0.00	2.51	5.66	8.17	69.3	30.7
09/04/03	0.00	3.07	6.83	9.90	69.0	31.0
Average	0.00	3.22	6.16	9.39	65.7	34.3
Std. Dev.	0.00	0.50	0.68	0.67	5.1	5.1

* All concentrations (µg/Nm^3) are based on 1 atmosphere pressure and 20°C

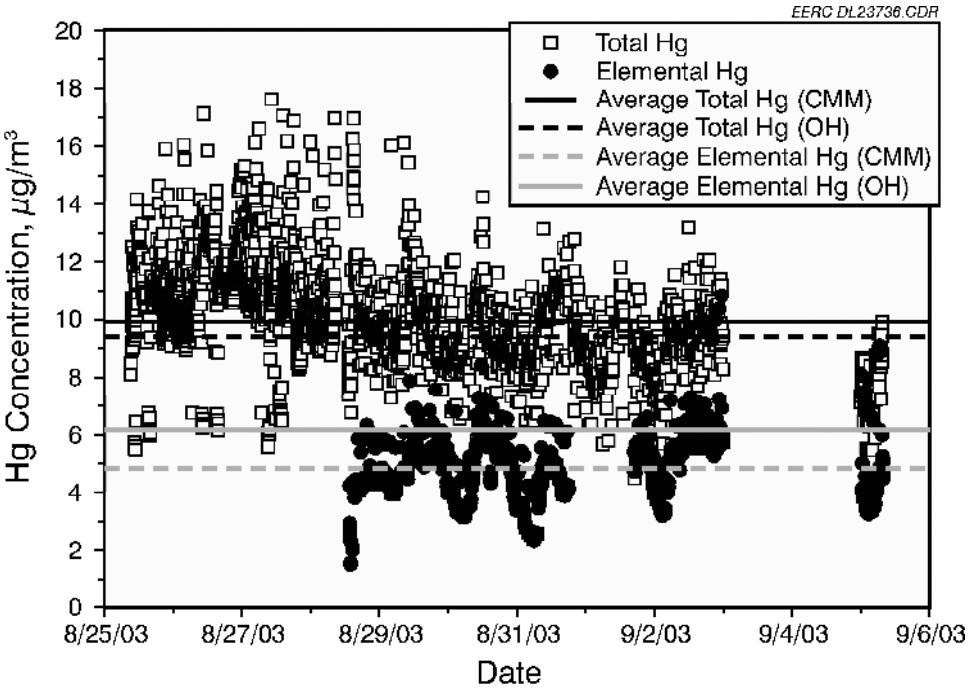

Figure 4-1
Stack CMM Mercury Speciation Results

4.2 Plume Results at Pleasant Prairie

A summary of the results from the plume sampling at the Pleasant Prairie Plant are presented in Table 4-2, with the average presented in Table 4-3. The plume Hg concentrations have been converted to equivalent stack concentrations and are presented as such. The complete data set is presented in Appendix A.I, and an explanation of the data reduction procedure is presented in Appendix A.II.

Table 4-2
Plume Mercury Speciation Data

Hg^0 Sample No.	Sample Point Nearest the Stack, µg/Nm^3							Sample Point Nominally 5 miles from Stack, µg/Nm^3					Sample Point Nominally 10 miles from Stack, µg/Nm^3			
	8-27	8-30	8-31	9-2	9-4	9-4	Avg.	8-27	8-30	8-31	9-2	Avg.	8-27	8-30	9-2	Avg.
1	6.0	6.4	1.6	5.5	16.2 *			2.8	9.2	5.6	7.6		1.2	4.1	1.6	
2	42.0	7.5	6.3	9.2	5.0	16.2		28.3	10.2	13.9	10.0		5.3	13.2	8.6	
3	10.6		4.7	5.7	4.0	16.5		33.5	12.0	15.7	24.4		7.8	12.8	7.6	
4	9.8	4.7	8.0	13.1	2.3	157.7		36.1	7.9	11.7	10.9		15.7	28.3	5.9	
5	11.9	9.0	15.6	15.4		18.0		11.8	16.3	25.9	10.3		7.9	13.0	16.9	
6	37.8	6.5	7.4	3.9	17.5			75.5	14.8	14.5	9.1		27.7	27.3	3.7	
7	12.9	14.5	18.2		15.0	43.9		56.1	12.5	49.8	16.4		17.2	21.0	14.0	
8	14.0	7.9	10.1	7.2	10.6	12.8		8.3	13.6	25.0	80.6		19.9	11.6	6.1	
9	15.5	5.8	10.2		9.8	19.2		17.8	15.7	21.6	5.3		14.8	22.7	17.4	
10	12.5	24.2	8.9	7.6	9.9	28.7		28.5	17.0	89.3	16.0		19.2	16.3	19.5	
Avg. Hg^0	11.7	9.6	9.1	6.5	10.0	18.6	***11.4***	13.8	12.0	19.8	8.9	***13.6***	14.4	15.7	6.8	***12.3***
Std. Dev	2.9	6.2	3.9	1.9	5.3	5.4	4.1	9.8	2.7	13.6	2.1	4.6	5.8	7.4	4.0	4.8
Hg (part.)	0.04	0.05	0.06	0.03	0.05	0.15	***0.06***	0.07	0.11	0.18	0.05	***0.10***	0.10	0.17	0.01	***0.09***
Std. Dev.	–	–	–	–	–	–	0.04					0.06				0.08
RGM	1.8	2.5	2.6	1.3	2.0	1.7	***2.0***	1.2	2.3	2.4	0.9	***1.7***	1.4	2.4	1.0	***1.6***
Std. Dev.	–	–	–	–	–	–	0.5	–	–	–	–	0.8	–	–	–	0.7
Total Hg	13.5	12.2	11.8	7.8	12.1	20.4	***13.5***	15.1	14.4	22.3	9.8	***15.4***	15.9	18.3	7.8	***14.0***
Std. Dev.	–	–	–	–	–	–	4.1	–	–	–	–	5.2	–	–	–	5.5
% Hg^0	86.4	78.8	77.4	83.0	83.0	91.0	***84.7***	91.6	83.3	88.5	90.4	***88.3***	90.6	85.9	87.1	***87.9***
% Hg(part)	0.3	0.5	0.5	0.4	0.4	0.7	***0.4***	0.5	0.8	0.8	0.5	***0.6***	0.6	0.9	0.1	***0.6***
% RGM	13.3	20.7	22.1	16.6	16.6	8.3	***14.9***	8.0	16.0	10.7	9.1	***11.0***	8.8	13.1	12.8	***11.4***

* The highlighted data were not used in calculating the averages or standard deviations.

Table 4-3
Average Mercury Speciation Results for Each Location (from Table 6-2)*

	Hg_p, µg/Nm^3	Hg^0, µg/Nm^3	RGM, µg/Nm^3	Total Hg, µg/Nm^3	% Hg^0
In the Stack					
Average	0.00	3.2	6.2	9.4	65.7
Std. Dev.	0.00	0.5	0.7	0.7	5.1
Location Nearest the Stack (~1500 ft)					
Average	0.06	11.4	2.0	13.5	84.7
Std. Dev.	0.04	4.1	0.5	4.1	5.0
Location Nominally 5 miles from Stack					
Average	0.10	13.6	1.7	15.4	88.3
Std. Dev.	0.06	4.6	0.8	5.2	4.0
Location Nominally 10 miles from Stack					
Average	0.09	12.3	1.6	14.0	87.9
Std. Dev.	0.08	4.8	0.7	5.5	2.6

* All concentrations are based on normal (N) conditions defined as 1 atmosphere pressure, 20°C, and 3% O_2.

4.2.1 Data Censoring

After the data were reduced, examination revealed a number of high Hg^0 concentrations that corresponded to very high dilution ratios (a high dilution ratio is defined as one greater than 3 times the average when that point is removed). The high dilution ratios occurred during intermittent aircraft transit of smaller plume eddies separated from the main body of the plume. These areas had relatively high proportions of ambient air sampled in short times and are not statistically characteristic of the plume material at that distance from the stack. During these sampling episodes, the NO_x concentration would be just high enough to trigger the zero-air inlet valve to shut off and begin the sampling process. Once the valve was triggered, the valve was set with a delay to stay off for 5 seconds once the NO_x level again fell below the trigger point. This was done to prevent rapid cycling of the valve, which would make the data nearly impossible to resolve. The highlighted data shown in Table 4-2 are those data points that were calculated based on high dilution ratios and were not used in the averages or determining the mass balances.

4.2.2 Mass Balance Calculations

The stack Hg concentration data were normalized to 3% O_2, 0°C, and 1 atmosphere. The plume data are also reported at 0°C and 1 atmosphere for comparison on an equal basis. The plume data were reduced by first correcting for the amount of sampling time in the plume. This allows a Hg concentration in the plume to be calculated. The plume concentrations were then converted to an equivalent stack concentration by applying dilution factors which were based on the plume and stack NO_x concentrations (shown previously in Equation 1). A complete explanation and examples of the data reduction procedures are presented in Appendix A.II. A

mass balance was calculated using the average total Hg data from each sampling point each day and the corresponding stack data. The results are presented in Table 4-4. Although many of the mass balance closures are somewhat high, they are quite reasonable considering the variability of the data and the difficult nature of the sampling. The most likely causes for the high Hg concentration are underreported NO_x concentration or Hg offgassing from the soda-lime traps used in the aircraft Hg analyzer when exposed to plume gas. These will be discussed in detail in Section 6.2.3.

Table 4-4
Total Hg Mass Balance: Plume Hg Compared to Stack Hg

Sample Point Nearest the Stack			Sample Point 5 miles Out			Sample Point 10 miles Out		
Total Hg in Plume, µg/Nm^3	Total Hg in Stack, µg/Nm^3	Balance, %	Total Hg in Plume, µg/Nm^3	Total Hg in Stack, µg/Nm^3	Balance, %	Total Hg in Plume, µg/Nm^3	Total Hg in Stack, µg/Nm^3	Balance, %
13.5	9.3	145	15.1	9.3	162	15.9	9.3	171
12.2	8.5	144	14.4	8.5	169	18.3	8.5	215
11.8	7.6	155	22.3	7.6	293	7.8	9.2	85
7.8	9.2	85	9.8	9.2	105			
12.1	9.2	131						
20.4	9.2	221						

4.2.3 Plume Hg Speciation Results

Figure 4-2 is a plot of the average percentage of Hg^0 in the plume as it moves from the stack to 10 miles downwind of the stack. There is a substantial increase in the relative concentration of Hg^0 from the stack to the first sample point, a smaller increase from the first to the second sample point, and then no change to the last sample location (10 miles). Overall, the Hg^0 increases from 67% of the total Hg to 88% by the time it reaches the 5-mile sample point. This is clearly seen in Figure 4-3. The question arises, is this increase real or does it represent a high bias in the Hg^0 concentration measurements in the plume? Figure 4-4 plots the average total plume Hg concentrations (as equivalent stack concentrations) at each location for each day of sampling. The graph shows that the total Hg concentration increased (4 of the 5 days) from the stack to the location nearest the stack and then remains relatively constant as the plume moves downwind. Figure 4-5 plots the RGM concentrations for each sampling point each day and shows that the RGM fraction decreases as the plume moves from the stack downwind. Overall, several factors could cause the Hg^0 concentration (and total Hg) to be reported higher in the plume than in the stack including:

- Low background Hg readings
- Inefficient trapping of the RGM in the Tekran denuder system
- Underreported plume NO_x concentrations
- Integration errors of the NO_x data
- Problems with the soda-lime traps

Each of these possibilities is discussed in more detail in Appendix A.

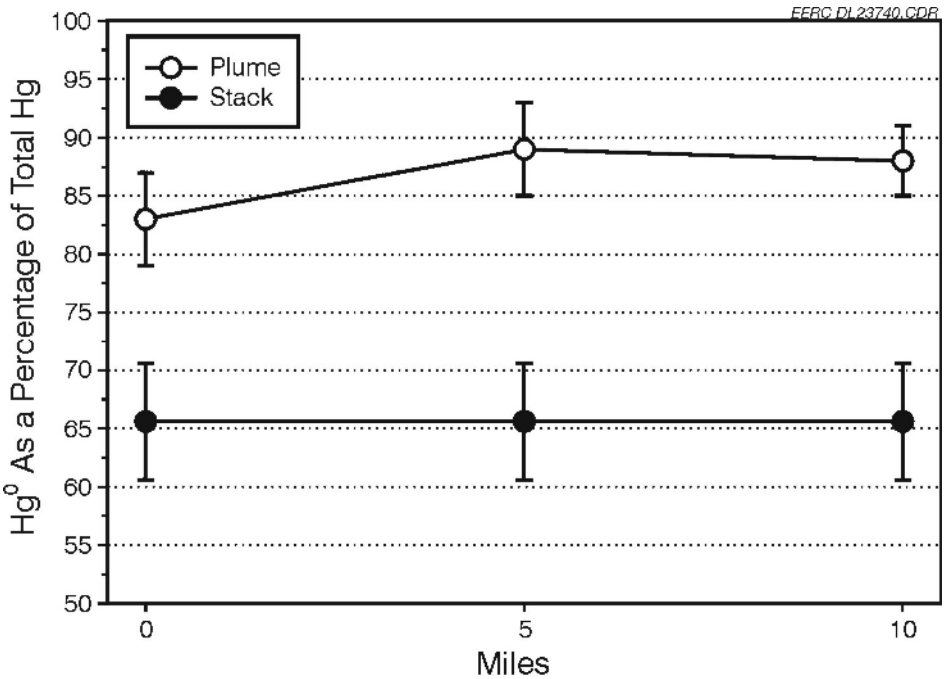

Figure 4-2
Plot of the Concentration of Hg^0 in the Plume As It Moves from the Stack to 10 miles Downwind of the Stack

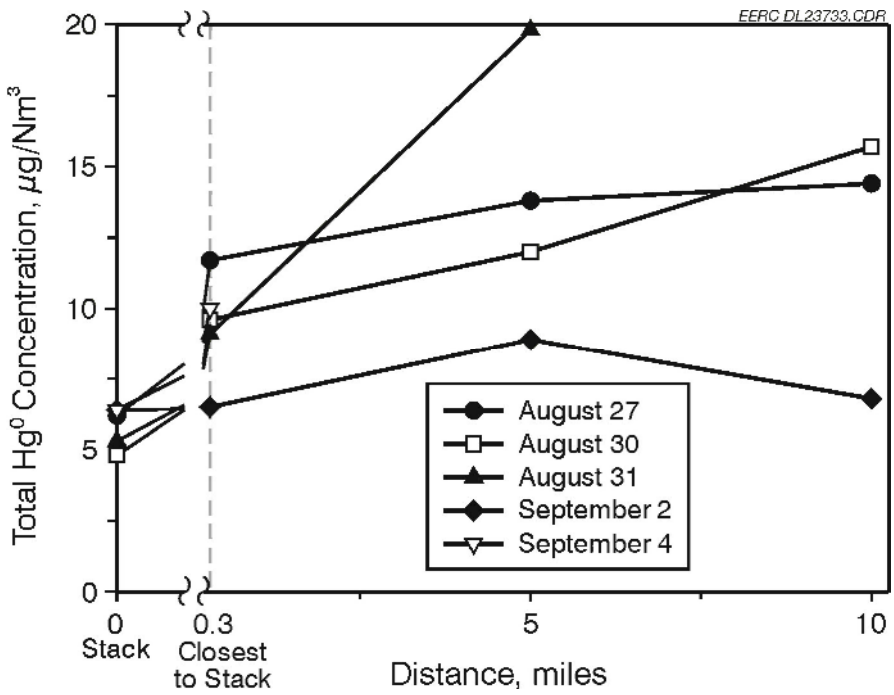

Figure 4-3
Plot of the % Hg^0 in the Plume Compared to the Stack Hg Concentration As a Function of Distance from the Stack

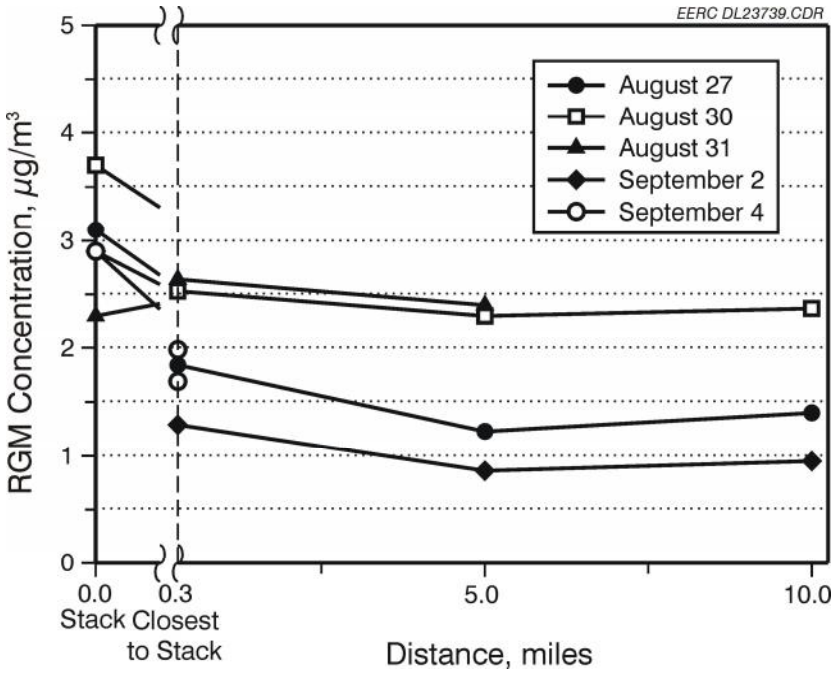

Figure 4-4
Plot of the Concentration of Total Mercury in the Plume As It Moves from the Stack to 10 miles Downwind of the Stack

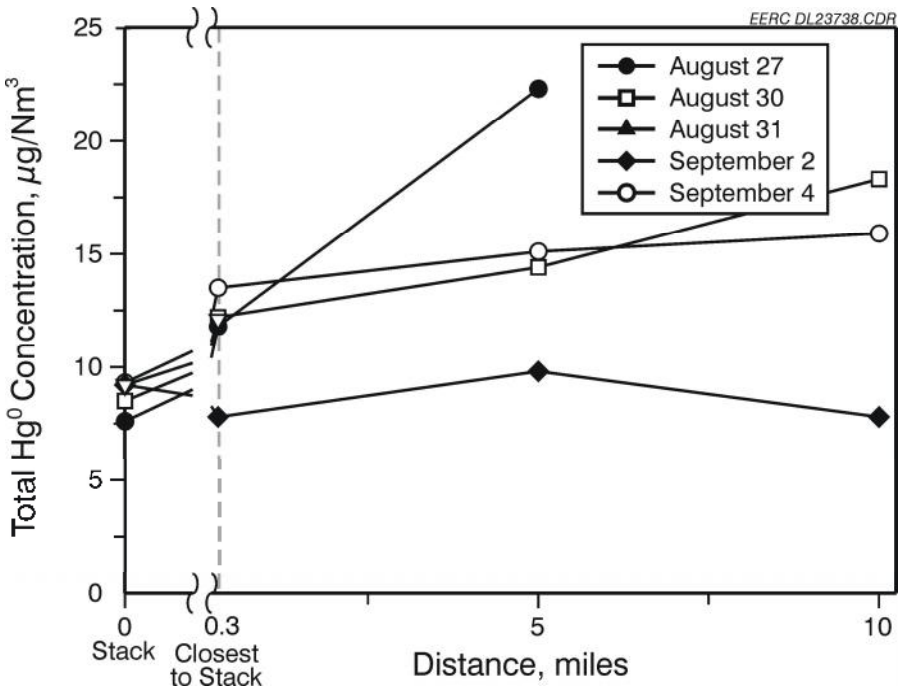

Figure 4-5
Plot of the Concentration of RGM in the Plume As It Moves from the Stack to 10 miles Downwind of the Stack

4.3 Vertical Mercury Profile

In addition to plume sampling, a vertical sounding flight was carried out to measure Hg concentration as a function of altitude. The first sample was collected 10 miles downwind of the power plant stack at an approximate altitude of 2500 feet, within the plume. The second sample point was at an approximate altitude of 500 feet and may have been in the plume. The NO_x concentrations at the 500-foot elevation were higher than at the 2500-foot elevation. These higher levels may have been caused by the plume, but may also be attributed to surface vehicle emissions from an underlying highway running north–south to the east of the sampling point. The third sampling point was at an approximate altitude of 16,500 feet, and the final sample point was at 8500 feet.

The results from this flight are presented in Table 4-5. The Hg concentrations at the two lower elevations are presented as measured. Any Hg contributed by the plume has not been subtracted, and no time correction has been made. The results show there is a significant increase in particulate-bound Hg above the boundary layer and that the RGM remains elevated above the background concentrations measured in the boundary layer.

Table 4-5
Vertical Profile Data

	@ 500 ft	@ 2500 ft	@ 8500 ft	@ 16,500 ft	Background
Hg^0 Sample No.			**Hg^0 Concentration, ng/Nm^3**		
1	1.142	1.292	1.151	0.687	0.961
2	1.400	1.616	0.968	0.547	1.369
3	1.650	1.824	0.814	0.437	1.533
4	1.795	1.686	0.881	0.493	1.503
5	1.516	1.748	0.828	0.428	1.613
6	1.532	1.791	0.704	0.370	1.514
7	1.567	1.590	0.873	0.312	1.701
8	1.636	1.625	0.812	0.329	0.659
9	1.903	1.322	0.753	0.288	0.313
10	1.409	1.678	0.751	0.322	0.890
Average	1.555	1.617	0.853	0.421	1.539
			Non-Hg^0 Concentrations, pg/Nm^3		
Hg(part.)	6.812	3.478	29.99	120.2	3.772
RGM	70.968	63.12	55.80	86.05	7.178

4.4 Static Plume Dilution Chamber Findings

As a supplement to the direct mercury speciation measurements carried out within the plant, at the stack, and aloft by aircraft, the Static Plume Dilution Chamber (SPDC) was run during or nearly in time with the aircraft soundings. The purpose of the SPDC runs during the experiment was to determine whether an alternative, less expensive measurement method could be employed for wider field measurement that would simulate plume chemistry at many power plants. Method testing of the SPDC simulation chamber along with full-scale measurements at a number of operating power plants would, if the method is verified by its replicating full-scale measurements, allow faster and more efficacious determination of plume mercury transformations at a great number of power plants. Such widespread use of an indirect, but replicative, method would allow more rapid closure on potential chemical mechanisms for any redox reactions, as well as allowing development of an iterative or projective computational method for redox rates and products in plumes to be applied to national modeling exercises.

Table 4-6 displays results from the SPDC runs at Pleasant Prairie. As is evident, the SPDC measurements, using both the automated Tekran device and the Fluegas Mercury Sorbent Speciation (FMSS) method, using wet chemistry and sorbent traps, failed to replicate the aircraft measurements of Hg^{+2} reduction in part to Hg^0. Indeed, the SPDC method in this case exhibited a relative loss of Hg^0 over time within the dilution chamber. Only Run 2 on 29 August 2003 appeared to show a reduction of the fraction occurring as Hg+2 and a relative increase of Hg0 over the 2.5 minute observation time elapsed from dilution of the intake flue gas by ambient air. Thus, the SPDC was unable to replicate the measured full-scale reduction of divalent to elemental mercury in the Pleasant Prairie plant emissions plume.

Table 4-6
Static Plume Dilution Chamber Results for Pleasant Prairie Power Plant Runs

Pleasant Prairie Power Plant (P4) SPDC Data Summary							
	Run ID	**0828-S1**	**0829-S2**	**0830-S3**	**0831-S4**	**Mean**	**Mean %**
Conditions, Files, Temp.	**Units**						
Input to SPDC	ng	-	14.16	20.36	45.23	26.6	95%
SPDC Background**	ng	1.52	2.01	1.00	1.06	1.4	4.9%
Background Hg^0	ng/m^3	2.64	3.50	1.75	1.84	2.4	
Expected Min. Hg^0	ng/m^3	2.67	22.18	30.79	53.39	35.5	
Observed Hg^0	ng/m^3	4.21	21.17	28.62	45.40	31.7	
Observed % Hg^0	%	158%	95%	93%	85%	89%	
Measured SPDC Gas Phase	ng	1.74	10.67	15.30	23.35	16.44	68%
Measured SPDC Rinse	ng	-	9.89	4.12	9.68	7.9	32%
Measured Total Hg in SPDC	ng	-	20.56	19.42	33.03	24.3	
Expected Total Hg in SPDC	ng	-	16.18	21.37	46.29	27.9	
Measured/Expected %		-	127%	91%	71%	96%	28.3%
with FMSS only							
Calcultions at T = 2.5 minutes							
Hg0 Expected	ng/m^3	2.67	22.18	30.79	53.39	42.09	
Hg0 Measured	ng/m^3	4.21	21.17	28.62	45.40	37.01	
Hg0 Net	ng/m3	1.54	-1.01	-2.17	-7.99	-5.08	-12%
	ng	0.77	-0.51	-1.09	-4.00	-2.54	
Hg(II) input	ng	-	4.8	5.8	19.5	12.65	
Hg(II) to Hg0 conversion	%	-	-10%	-19%	-21%	-0.20	5.3%

*Fluegas Mercury Sorbent Speciation (FMSS) Method

5
CONCLUSIONS AND RECOMMENDATIONS

Based on the overall testing program at the Pleasant Prairie Power Plant, the following conclusions can be supported:

- Using a dilution factor based on the plume and stack NO_x, a reasonable Hg mass balance can be obtained when the Hg in the stack is compared to the Hg in the plume.

- There appeared to be a chemical reduction in divalent mercury in the Pleasant Prairie Power Plant plume when the RGM in the plume is compared to the RGM in the stack. This reduction is matched by a corresponding increase in the proportion of Hg^0. Overall, there was a 44% reduction of RGM from the stack to the first sample point near the effective stack height, and a 66% reduction of RGM from the stack to the 5-mile sample point, with no additional reduction observed between the 5- and 10-mile locations.

Although the results from the ground and aircraft measurements of this test tend to support a reduction in RGM and a corresponding increase in Hg^0 in the plume, those results are still not definitive. The SPDC tests failed to show a similar reduction, instead showing an apparent net oxidation in the simulated plume. In addition, although the earlier measurements in this series (at Georgia Power Plant Bowen in 2002) also showed plume mercury reductions, and were matched there by SPDC measurements, additional measurements in a wider range of source and ambient conditions are needed. Also, a reasonable chemical mechanism for such reduction reactions is still lacking. A primary need is for a mechanism to be developed that can explain the results observed in non-heterogeneous (though generally not homogeneous) plume conditions.

In planning future field tests of this type, experimental sites with the following general characteristics should be sought:

- Predicted fraction of emitted mercury occurring at stack exit as Hg+2 is greater than 70%.
- Has a single stack to prevent complications from merged plumes exhausting furnaces or fuel feeds with large differences.
- Does not employee SCR technology (to favor higher concentrations of NOx as a co-tracer for the plume).
- Is relatively isolated from other upwind and near-downwind sources of atmospheric mercury.

6
REFERENCES

1. Toxicological Effects of Methylmercury. *National Academies Press*, Washington, D.C., 2000.

2. Lindqvist, O.; Rodhe, H. Atmospheric Mercury—A Review. *Tellus* **1995**, 37B, 136–159.

3. Danilchik, P; Imhoff, R.; Liang, L.; Valente, R.; Dismukes, E.; Brown, C.; Spurling, D.; Huang, Z.; Prestbo, E. A Comparison of the Fate of Mercury in Flues and Plumes of Coal-Fired Boilers. Presented at the Mercury as a Global Pollutant Conference, July 10–14, 1994, Whistler, British Columbia.

4. Imhoff, R.E. *Preliminary Report on Measurements of Gas- and Particle-Phase Mercury in the Plumes of Coal-Fired Boilers*; Atmospheric Sciences Department, Environmental Research Center, Tennessee Valley Authority, March 15, 1995

5. Prestbo, E.M.; Calhoun, J.A.; Brunette, R.C.; Paladini, M. Hg Speciation in a Simulated Coal Combustion Plume. In *Proceedings of Air Quality: Mercury, Trace Elements, and Particulate Matter Conference*; McLean, VA, Dec 1–4, 1998.

6. Laudal, D.L; Prestbo, E. *Investigation of the Fate of Mercury in a Coal Combustion Plume Using a Static Plume Dilution Chamber*; Final Report for U.S. Department of Energy Contract No. DE-FC-26-95FT40321; Energy & Environmental Research Center: Grand Forks, ND, Oct 2001.

7. Edgerton, E.; Hartsell, B.; Jansen, J. Field Observations of Mercury Partitioning in Power Plant Plumes. In *Proceedings of the International Conference on Air Quality III: Mercury, Trace Elements, and Particulate Matter*; Arlington, VA, Sept 2002

8. Banic, C.M.; Beauchamp, S.T.; Tordon, R.J.; Schroeder, W.H.; Steffen, A.; Anlauf, K.A.; Wong, H.K.T. Vertical Distribution of Gaseous Elemental Mercury in Canada. *J. Geophys. Res.* **2003**, *108* (D9), 4264.

Evaluation of Mercury Speciation in a Power Plant Plume

Product ID 1011113

Final Report, May 2005

Cosponsor(s)
Energy & Environmental Research Center
15 North 23rd Street
Grand Forks, ND, 58203

Project Manager
D. Laudal

EPRI Project Manager
L. Levin

EPRI • 3412 Hillview Avenue, Palo Alto, California 94304 • PO Box 10412, Palo Alto, California 94303 • USA
800.313.3774 • 650.855.2121 • askepri@epri.com • www.epri.com

APPENDIX A

DISCLAIMER OF WARRANTIES AND LIMITATION OF LIABILITIES

THIS DOCUMENT WAS PREPARED BY THE ORGANIZATION(S) NAMED BELOW AS AN ACCOUNT OF WORK SPONSORED OR COSPONSORED BY THE ELECTRIC POWER RESEARCH INSTITUTE, INC. (EPRI). NEITHER EPRI, ANY MEMBER OF EPRI, ANY COSPONSOR, THE ORGANIZATION(S) BELOW, NOR ANY PERSON ACTING ON BEHALF OF ANY OF THEM:

(A) MAKES ANY WARRANTY OR REPRESENTATION WHATSOEVER, EXPRESS OR IMPLIED, (I) WITH RESPECT TO THE USE OF ANY INFORMATION, APPARATUS, METHOD, PROCESS, OR SIMILAR ITEM DISCLOSED IN THIS DOCUMENT, INCLUDING MERCHANTABILITY AND FITNESS FOR A PARTICULAR PURPOSE, OR (II) THAT SUCH USE DOES NOT INFRINGE ON OR INTERFERE WITH PRIVATELY OWNED RIGHTS, INCLUDING ANY PARTY'S INTELLECTUAL PROPERTY, OR (III) THAT THIS DOCUMENT IS SUITABLE TO ANY PARTICULAR USER'S CIRCUMSTANCE; OR

(B) ASSUMES RESPONSIBILITY FOR ANY DAMAGES OR OTHER LIABILITY WHATSOEVER (INCLUDING ANY CONSEQUENTIAL DAMAGES, EVEN IF EPRI OR ANY EPRI REPRESENTATIVE HAS BEEN ADVISED OF THE POSSIBILITY OF SUCH DAMAGES) RESULTING FROM YOUR SELECTION OR USE OF THIS DOCUMENT OR ANY INFORMATION, APPARATUS, METHOD, PROCESS, OR SIMILAR ITEM DISCLOSED IN THIS DOCUMENT.

ORGANIZATION(S) THAT PREPARED THIS DOCUMENT

Energy & Environmental Research Center

ORDERING INFORMATION

Requests for copies of this report should be directed to EPRI Orders and Conferences, 1355 Willow Way, Suite 278, Concord, CA 94520. Toll-free number: 800.313.3774, press 2, or internally x5379; voice: 925.609.9169; fax: 925.609.1310.

Electric Power Research Institute and EPRI are registered service marks of the Electric Power Research Institute, Inc. EPRI. ELECTRIFY THE WORLD is a service mark of the Electric Power Research Institute, Inc.

Copyright © 2003 Electric Power Research Institute, Inc. All rights reserved.

CITATIONS

This report was prepared by

Energy & Environmental Research Center
15 North 23rd Street
Grand Forks, ND 58203

Principal Investigator
D. Laudal

This report describes research sponsored by EPRI.

The report is a corporate document that should be cited in the literature in the following manner:

Evaluation of Mercury Speciation in a Power Plant Plume, EPRI, Palo Alto, CA, and Energy & Environmental Research Center, Grand Forks, ND: 2004. Product ID 1011113.

PRODUCT DESCRIPTION

Although in-stack mercury (Hg) speciation measurements are essential to the development of control technologies and to provide data for input into the atmospheric deposition models, the determination of speciation in a cooling coal combustion plume is more relevant for use in estimating Hg fate and effects through the atmosphere. Substantial research has been done in the past on Hg transformations within energy conversion systems—determining the concentrations of speciated Hg at the stack and doing ground-level atmospheric measurements; however, little has been done to determine the Hg chemistry, kinetics, and thermodynamics in the flue gas plume. It is the Hg transformations that occur in the plume that determine the rate and the form of Hg deposited in waterways. Therefore, a logical step in Hg research is to apply what we know and extend this understanding beyond the power plant stack to the plume region. As a result, a study was sponsored by EPRI and was jointly funded by EPRI, the U.S Department of Energy (DOE), and the Wisconsin Department of Administration. The study was designed to further our understanding of plume chemistry.

Results & Findings

There appeared to be a reduction in reactive gas mercury (RGM) (with a corresponding decrease in elemental mercury) at Pleasant Prairie when the RGM in the plume was compared to the RGM in the stack. There was a 44% reduction of RGM from the stack to the first sample point and a 66% reduction of RGM from the stack to the 5-mile sample point, with no additional reduction between the 5- and 10-mile locations.

Challenges & Objectives

Smaller-scale experiments in both test chambers and pilot-scale coal combustor exhaust streams have indicated the presence of rapid and relatively complete reduction reactions converting divalent into elemental mercury within plumes representing partially dispersed conditions. The presence, rate, completeness, and ubiquity of these reactions, however, must be demonstrated in plume environments from fully operational power plant sources. That requirement, to capture either the reactions or the reaction products of chemistry that may be occurring very close to stack exits in highly turbulent environments, constrains the precision and reproducibility of such full-scale experiments. 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 such plumes.

Applications, Values & Use

The linking of mercury atmospheric sources and downwind receptors, particularly receiving waters with the potential for fish enrichment of mercury, requires the use of atmospheric

physicochemical models, since we lack benign chemical tracers that fully mimic the behavior of mercury in the atmosphere. Current models either inadequately simulate chemical processes in-plume environments, or do not allow such inclusion at all. Establishing whether potentially rapid and complete mercury redox reactions occur in such environments, enriched in sulfur and other co-emitted substances and not yet fully dispersed into the ambient atmosphere, will allow model improvements to better simulate contributions of those power plants where such reactions are likely to occur. In turn, this will allow a better fit between model outcomes and actual processes in the atmosphere, to allow more realistic allocation of deposited mercury to its sources.

EPRI Perspective

The chemical form of inorganic Hg, 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 near sources vs. long-range dispersion. The work done at the Pleasant Prairie Power Plant is a fundamental contribution to understanding these differences mediated by the trace and major constituents in coal-fired power plant stack plumes. 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, a turboprop DHC-6-300 Twin Otter deHavilland Vistaliner aircraft and an automated Tekran ambient Hg monitor were used. Aircraft sampling was done at three locations downwind of the plume. The first location was approximately 1500 ft from the stack (the closest the plane could legally fly to the stack). The second and third locations were approximately 5 and 10 miles downwind of the stack, respectively.

Determining the altitude and direction of the plume was done based on a combination of visual inspection (location closest to the stack) and the measurements of NO_x concentrations. 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 sampling was completed during the flight, providing measurements of the Hg speciation in the stack. Hg sampling at the stack was completed using the Ontario Hydro Hg speciation sampling method and a continuous mercury monitor.

Keywords

Mercury
Utilities
Plume(s)
Reactive Gaseous Mercury
Elemental Mercury
Air Toxics

ABSTRACT

Although in-stack mercury (Hg) speciation measurements are essential for the development of Hg control technologies and to provide source data for atmospheric deposition models, the determination of Hg speciation in a cooling coal combustion plume is more relevant for use in estimating Hg fate and effects through the atmosphere. It is the Hg transformations that occur in the plume that determine the rate and the form of Hg deposited in waterways. Yet such processes are poorly understood and are not currently incorporated in atmospheric models of Hg. Therefore, a logical step in Hg research is to apply what we know and extend this understanding slightly beyond the power plant stack to the plume region. Therefore, EPRI and the U.S. Department of Energy have funded surface and aircraft studies of stack emissions and chemistry at two power plants. The first study was at Plant Bowen, Cartersville, Georgia, operated by Georgia Power, part of Southern Company. Aircraft studies were conducted by Tennessee Valley Authority, with stack measurements by the Energy & Environmental Research Center (EERC) and by Frontier Geosciences. The second study was at the Pleasant Prairie Power Plant, Pleasant Prairie, Wisconsin, operated by WE Energies; there, surface and aircraft measurements were carried out by the EERC, with additional studies of the stack by Frontier Geosciences. The primary focus of this report is on the work conducted by the EERC at Pleasant Prairie.

The overall project objective was to gain an understanding of Hg chemistry as a plume is transported downwind from the stack. This was carried out by flying a Twin Otter aircraft through the plume at several locations (a point nearest the stack, 5 miles from the stack, and 10 miles from the stack) and measure the speciated Hg composition in the plume using an automated ambient Hg monitor.

The results of the project appeared to show a reduction in reactive gas mercury (RGM) (with a corresponding decrease in elemental Hg) when the RGM in the plume is compared to the RGM in the stack. There was a 44% reduction of RGM from the stack to the first sample point and a 66% reduction of RGM from the stack to the 5-mile sample point, with no additional reduction between the 5- and 10-mile locations.

ACKNOWLEDGMENTS

This work would not have been possible without the efforts of many people. The authors would like to acknowledge the following people.

For their direction and leadership, recognition is given to Leonard Levin and Paul Chu of EPRI and William Aljoe and Lynn Brickett of the U.S. Department of Energy National Energy Technology Laboratory. The work could also not have been completed without funding support from the Wisconsin Department of Administration.

At the University of North Dakota from the Energy & Environmental Research Center, thanks go to Grant Dunham, Blaise Mibek, and Richard Schulz and from the School of Aerospace Sciences, David Delene.

We would also like to thank the other EPRI contractors who contributed to the effort, including Eric Prestbo from Frontier Geosciences and Ray Valente from the Tennessee Valley Authority.

Last, special thanks are expressed to WE Energies for allowing the testing to be conducted at the Pleasant Prairie Power Plant and for all of the help their personnel gave us.

NOMENCLATURE

AF	atomic fluorescence
CEM	continuous emission monitor
CMM	continuous mercury monitor
CVAFS	cold-vapor atomic fluorescence spectroscopy
DOE	U.S. Department of Energy
EERC	Energy & Environmental Research Center
ESP	electrostatic precipitator
F_d	value relating gas volume to the heat content of the fuel, equal to dscf/10^6 Btu
GEM	gaseous elemental mercury
GPS	global positioning system
HCl	hydrochloric acid
Hg	mercury
Hg^0	elemental mercury
Hg^{2+}	oxidized mercury
HYSPLIT	HYbrid Single-Particle Lagrangian Integrated Trajectory model
lpm	liter per minute
MW	megawatts
nm	nautical mile
NO_x	nitrogen oxides
NO_y	reactive nitrogen species
OH	Ontario Hydro mercury speciation method
ppb	parts per billion
PRB	Powder River Basin
RGM	reactive gas mercury
SCR	selective catalytic reduction
$SnCl_2$	stannous chloride
SO_2	sulfur dioxides
SPDC	simultaneous plume dilution chamber
TECO	Thermal Electron Corporation
TVA	Tennessee Valley Authority

EXECUTIVE SUMMARY

The objective of this report is to provide a detailed summary of the results that the Energy & Environmental Research Center (EERC) obtained for the project entitled "Evaluation of Mercury Speciation in a Power Plant Plume." The data were obtained during testing at the Pleasant Prairie Power Plant during August of 2003. The project was sponsored by EPRI with funding from the U.S. Department of Energy (DOE) National Energy Technology Laboratory and the Wisconsin Department of Administration.

Introduction

Characterization of environmental mercury (Hg) and its atmospheric process, from emission to deposition, requires both measurement and model simulations for a full understanding. Although in-stack Hg speciation measurements are essential to the development of control technologies and to provide data for input into the atmospheric deposition models, the determination of speciation in a cooling coal combustion plume is more relevant for use in estimating Hg fate and effects through the atmosphere. Substantial research has been done in the past on Hg transformations within energy conversion systems—determining the concentrations of speciated Hg at the stack and doing ground-level atmospheric measurements; however, little has been done to determine the Hg chemistry, kinetics, and thermodynamics in the flue gas plume [1]. It is the Hg transformations that occur in the plume that determine the rate and the form of Hg deposited in waterways. Therefore, a logical step in Hg research is to apply what we know and extend this understanding beyond the power plant stack to the plume region.

Therefore, EPRI and DOE funded plume studies at two power plants. The first was at the Bowen Power Plant (operated by Georgia Power, part of Southern Company), with the Tennessee Valley Authority (TVA) conducting the aircraft studies and the EERC and Frontier Geosciences doing Hg measurements at the stack. The second study was conducted at the Pleasant Prairie Power Plant, owned by WE Energies, with the EERC carrying out both the aircraft and stack Hg measurements, with additional surface measurements again done by Frontier Geosciences. The primary focus of this paper is the work conducted by the EERC at Pleasant Prairie. However, the importance of the previous work conducted by TVA [2,3], the static plume dilution chamber work done by Frontier Geosciences [1,4], and the measurements made by Atmosphere Research & Analysis [5] at the Yorkville SEARCH site indicating that there is change in Hg speciation in the plume cannot be overstated.

Project Objectives

The overall project goal is to gain an understanding of Hg chemistry as a plume moves downwind from the stack. Specific objective are as follows:

- Develop sampling techniques to measure speciated Hg in the plume.
- Develop techniques to determine the location of the plume at various points downwind of the stack.
- Determine the speciated Hg emissions at the stack and compare these results to those obtained from the plume sampling.
- Compute a Hg mass balance using dilution factors and other relevant parameters.

Project Description

Power Plant Description

The Pleasant Prairie Power Plant, owned and operated by WE Energies, is located near the city of Pleasant Prairie just west of Kenosha, Wisconsin. The Pleasant Prairie plant consists of two units (Units 1 and 2) identical in operation with the exception of one (Unit 2) having a selective catalytic reduction (SCR) system at the time of the measurements. Each unit has an electrostatic precipitator (ESP) for particulate control and share a common stack. Specifications of the Pleasant Prairie facility are as follows:

- Fuel type: Powder River Basin (PRB) subbituminous coal
- Boiler capacity: 617 MW (each unit)
- Boiler type: opposed-fired pulverized coal (both units)
- NO_x control: SCR on Unit 2, low-NO_x burners on both units
- SO_2 control: none, combustion of low-sulfur coal (both units)
- Particulate control: ESP (both units)

The coal is fairly typical of PRB in that both the Hg and chlorine levels in the coal are comparatively low; the Hg averaged 0.041 µg/g and the chlorine, 10 ppm.

Aircraft and Equipment Used for the Project

The aircraft used for the emission plume sampling was a turboprop DHC-6-300 Twin Otter deHavilland Vistaliner, which is a highly maneuverable, versatile aircraft. The aircraft and crew were provided by Twin Otter International out of Las Vegas, Nevada. The pilots were very experienced in doing research involving ambient air sampling. The aircraft is shown in Figure ES-1. This type of aircraft had a number of design and performance characteristics that made it an ideal platform for the project. The twin-engine plane had a relatively large capacity for equipment and sufficient onboard electrical supply and could be operated efficiently at low altitudes. These capabilities were accompanied by relatively low fuel consumption at all altitudes. Most importantly for the plume study project, it could be flown at relatively slow speeds (80–160 knots/150–300 km/hr) and in tight formation to allow consistent plume traverses at fixed heights and downwind distances.

Figure ES-1
Photograph of the DHC-6-300 Twin Otter deHavilland Vistaliner

The Hg analyzer used in the aircraft (shown in Figure ES-2) was a fully automated Tekran® Model 2537A mercury vapor analyzer coupled with a Tekran® Model 1130 mercury speciation unit and a Tekran® Model 1135 particulate module. The analyzer portion of the system is based on the principle of atomic fluorescence and has detection limits <1 pg/m^3. With this system, it was possible to simultaneously measure elemental mercury (Hg^0), reactive gas mercury (RGM), and particulate-bound Hg species during the flight. Therefore, it was possible to rapidly evaluate data each day to make sampling decisions for succeeding flights.

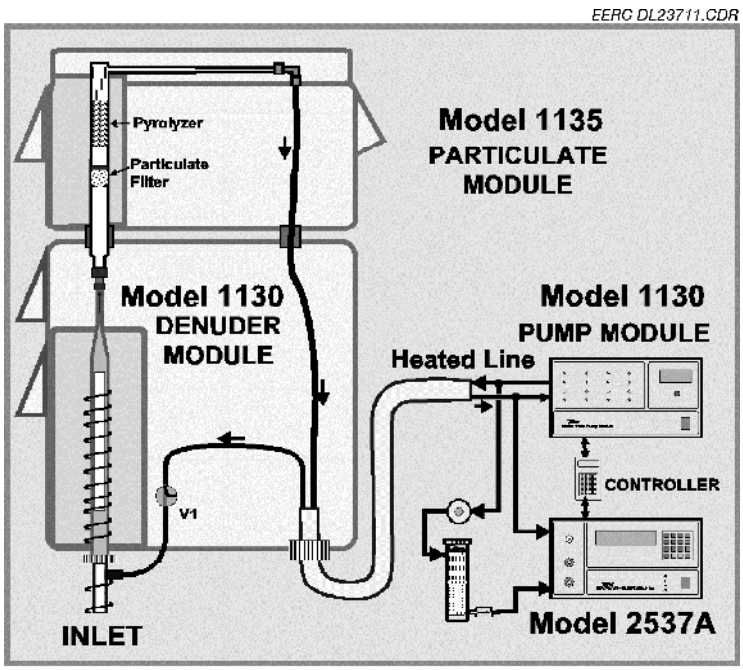

Figure ES-2
Schematic of the Tekran Mercury System

To compare the Hg concentrations in the plume to those in the stack, a dilution factor was determined. Based on the earlier tests conducted at Plant Bowen [2], it was decided that the NO_x concentration in the stack vs. that in the plume be used to determine the dilution factor as shown in the following equation:

$$\text{Dilution Ratio} = \frac{(\text{Stack NO}_x - \text{Background NO}_x)}{(\text{Plume NO}_x - \text{Background NO}_x)}$$

In addition, the NO_x analyzer was used to determine the location of the plume. The analyzer that was used for this project was a dual range Model 42C Thermo Electron ambient air NO_x analyzer. This analyzer was able to measure 0–50 parts per billion (ppb) NO_x in the low range and up to 500 ppb NO_x in the high range.

Experimental Approach

Aircraft Sampling Locations

Following background sampling at a location upwind of the stack, aircraft sampling was done at three locations downwind of the plume. The first location was approximately 1500 ft from the stack (the closest the plane could get to the stack). The second and third locations were approximately 5 and 10 miles downwind of the stack, respectively. Figure ES-3 is an example of the flight diagram showing sampling locations and patterns. As can be seen, a number of different patterns were flown at the closest sampling point in an effort to optimize the time in the plume. At the other two locations, a racetrack pattern was flown. To provide data as to the aircraft position as a function of time, a satellite-based global positioning system was used.

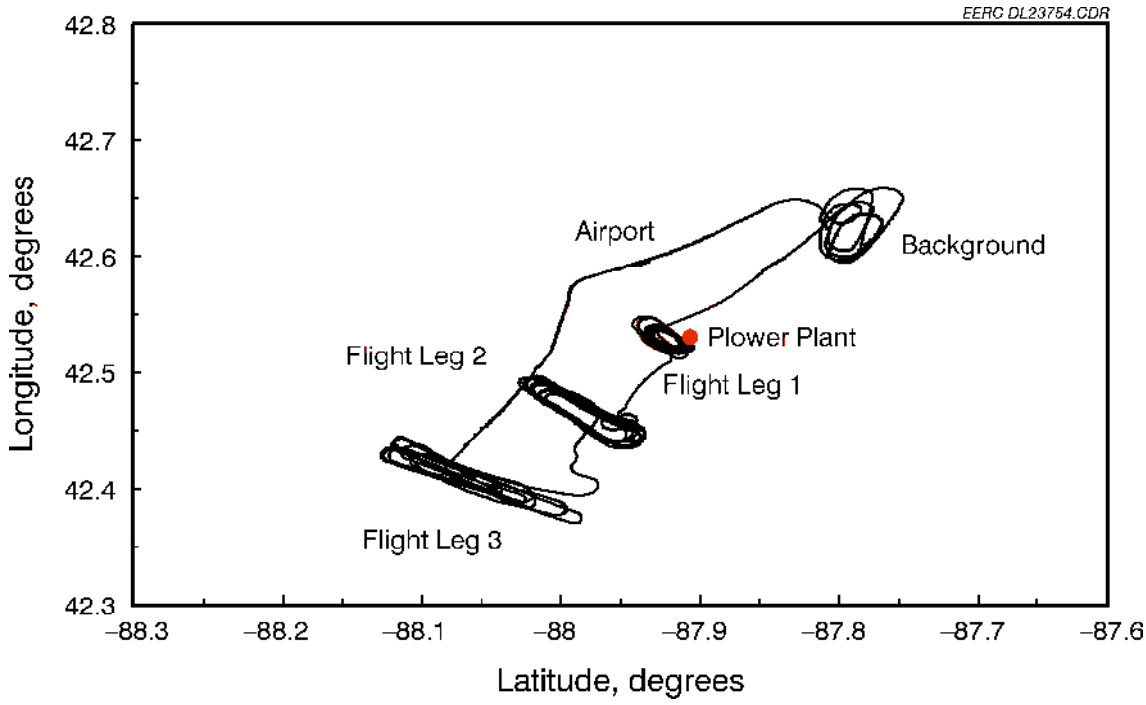

Figure ES-3
Flight Track on August 27, 2003

Determining the altitude and direction of the plume was done based on a combination of visual inspection (location closest to the stack) and the measurements of NO_x concentrations. Except for the closest location, the Tekran Hg analyzer was triggered by a NO_x set point.

Aircraft sampling flights were conducted in daylight under atmospheric conditions that permitted adequate sampling of the stack plume. The weather conditions during the project were fairly consistent with the historical climate record with many fair weather days. In the original test plans, the ideal wind velocities were considered to be approximately 2.5–5 m/s; however, the average wind speeds were somewhat above this, ranging from 5.3 to 8.3 m/s. These wind velocities were still low enough that the aircraft was able to find the plume and good sampling was able to be completed.

Stack Sampling

To establish baseline conditions for comparison with the plume samples, in-stack sampling was carried out simultaneously with the flight, providing measurements of the Hg speciation in the stack. Hg sampling at the stack was completed using the Ontario Hydro (OH) Hg speciation sampling method and a continuous mercury monitor (CMM). Prior to the start of the testing, a CMM was placed at the stack outlet and remained there during the entire project. During each flight day, one OH sample was taken at the stack.

In addition to Hg measurements by the EERC, the plant operators continuously measured the NO_x concentration in the stack using a continuous emission monitor. Although the NO_x concentrations in the stack at the Pleasant Prairie Power Plant were somewhat lower than desired

for aircraft plume measurements (since half the flue gas was being treated using an SCR), it was still possible to detect a difference between the background and plume, even at 10 miles. The average stack NO_x concentration was 144 ppm(v).

Results and Discussion

Stack Results at Pleasant Prairie

The Hg concentrations in the stack are shown in Table ES-1 and the OH and CMM sampling in Figure ES-4. As the results show in Table ES-1, the Hg concentrations were relatively constant during the entire duration of the project. The RGM averaged 34.3% of the total Hg measured. These results were matched very well by the CMM as shown in Figure ES-5.

Table ES-1
Stack Ontario Hydro Mercury Speciation Results

Date	Particulate-Bound Hg, µg/Nm^3*	RGM, µg/Nm^3	Hg^0, µg/Nm^3	Hg (total), µg/Nm^3	RGM as a % of Total Hg
08/27/03	0.00	3.30	6.70	10.00	33.0
08/29/03	0.00	3.43	6.06	9.49	36.1
08/30/03	0.00	3.02	6.63	9.65	31.3
08/31/03	0.00	4.01	5.10	9.11	44.0
09/02/03	0.00	2.51	5.66	8.17	30.7
09/04/03	0.00	3.07	6.83	9.90	31.0

* All concentrations (µg/Nm^3) are based on 1 atmosphere pressure and 20°C.

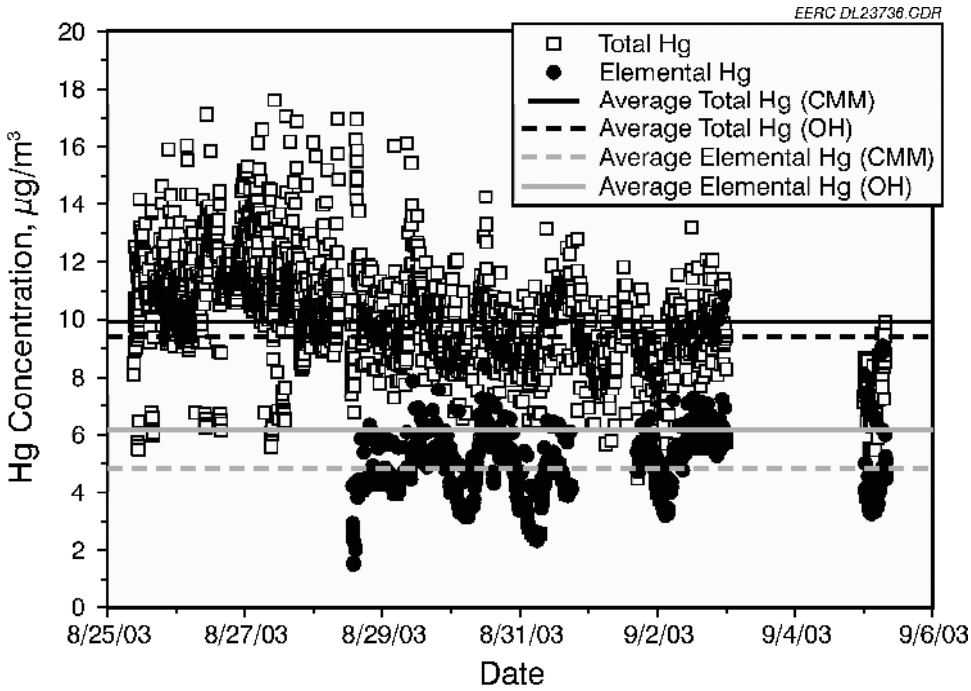

Figure ES-4
Stack CMM Speciation Results

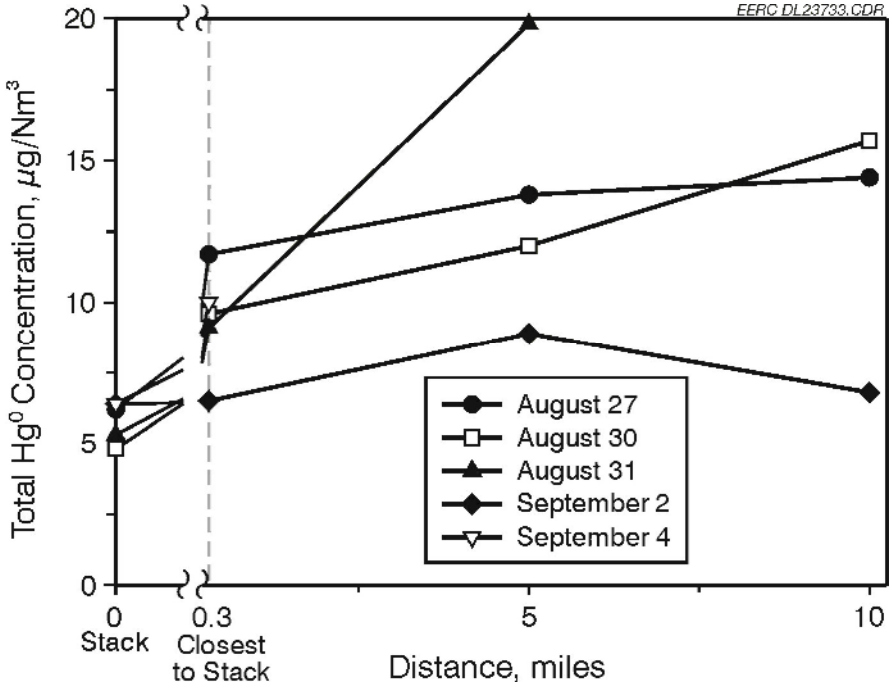

Figure ES-5
Plot of the % Hg^0 in the Plume Compared to the Stack Hg Concentration as a Function of Distance from the Stack

Plume Results at Pleasant Prairie

A summary of the results from the plume sampling at the Pleasant Prairie plant is presented in Table ES-2. The plume Hg concentrations have been converted to equivalent stack concentrations and are presented as such. The plume data were reduced by first correcting for the amount of sampling time in the plume. This gives a Hg concentration in the plume. The plume concentrations were then converted to an equivalent stack concentration by applying dilution factors which were based on the plume and stack NO_x concentrations.

Table ES-2
Average Mercury Speciation Results for Each Location*

	Hg_p, µg/Nm^3	Hg^0, µg/Nm^3	RGM, µg/Nm^3	Total Hg, µg/Nm^3	% Hg^0
Stack					
Average	0.00	3.2	6.2	9.4	66
Std. Dev.	0.00	0.5	0.7	0.7	5.1
0 Miles					
Average	0.06	10.4	2.0	12.4	84
Std. Dev.	0.04	3.1	0.5	3.2	5.0
5 Miles					
Average	0.10	15.7	1.7	17.5	89
Std. Dev.	0.06	8.7	0.8	9.3	4.0
10 Miles					
Average	0.09	12.4	1.6	14.1	88
Std. Dev.	0.08	4.8	0.7	5.4	2.6

* All concentrations are based on normal (N) conditions defined as 1 atmosphere pressure, 20°C, and 3% O_2.

A mass balance was calculated using the average total Hg data from each sampling point each day and the corresponding stack data. The results are presented in Table ES-3. Although many of the mass balance closures are somewhat high, they are quite reasonable considering the variability of the data and the difficult nature of the sampling. The two most likely causes for the high Hg concentrations are underreported NO_x concentration, which does not affect the ratio of Hg^0 to RGM, or Hg offgassing from the soda-lime traps used in the aircraft sampling line when exposed to plume gas. Nonetheless, the ratio of Hg^0 to RGM does show an evolution as the plume moves downwind from the stack, implying a change in speciation occurring solely within the plume itself between the stack exit and full dispersion into the atmosphere.

Table ES-3
Total Hg Mass Balance: Plume Hg Compared to Stack Hg

Sample Point Nearest the Stack			Sample Point 5 miles Out			Sample Point 10 miles Out		
Total Hg in Plume, $\mu g/Nm^3$	Total Hg in Stack, $\mu g/Nm^3$	Balance, %	Total Hg in Plume, $\mu g/Nm^3$	Total Hg in Stack, $\mu g/Nm^3$	Balance, %	Total Hg in Plume, $\mu g/Nm^3$	Total Hg in Stack, $\mu g/Nm^3$	Balance, %
13.5	9.3	145	15.1	9.3	162	16.5	9.3	177
12.2	8.5	144	14.4	8.5	169	17.8	8.5	209
10.8	7.6	142	22.2	7.6	292	7.9	9.2	86
7.8	9.2	85	9.6	9.2	104			
12.0	9.2	130						
18.6	9.2	202						

It should be noted there were a number of high readings that corresponded to very high dilution ratios. These results were not included in the average. The high dilution ratios occurred during intermittent aircraft transit of smaller plume eddies separated from the main body of the plume. When this occurs, relatively high proportions of ambient air is sampled in a short time and is, therefore, not statistically characteristic of the plume material at that distance from the stack. Even with relatively stable winds, turbulent eddies would result in complex plume structures, causing some passes through the plume to only intersect edges of the plume rather than the cross-centerline transects that were sought. These peripheral intersects would capture relatively large proportions of ambient air with markedly lower NO_x values than the main body of the plume. During these sampling episodes, the NO_x concentration would be just high enough to trigger the zero air inlet valve in the sampling system. Once it was triggered, the valve was set with a delay to stay off for 5 seconds once the NO_x level again fell below the trigger point. This was done to prevent rapid cycling of the valve. Since the NO_x concentration was near ambient levels in these segments of the plume, the resulting dilution ratios were artificially high.

The overall results are shown in Figure ES-4 in a plot of the average percentage of Hg^0 in the plume as it moves from the stack exit to 10 miles downwind of the stack. There is a substantial increase in the concentration of Hg^0 from the stack to the first sample point, a smaller increase from the first to the second sample point, and then no change from there to the last sample location (10 miles). Overall, the Hg^0 increases from 67% of the total Hg to 89% by the time it reaches the 5-mile sample point.

The question arises, is this increase real, or does it represent a high bias in the Hg^0 concentration measurement in the plume? Several factors could cause the Hg^0 concentration (and total Hg) to be reported higher in the plume than in the stack. These include the following:

- Low background Hg readings

- Inefficient trapping of the RGM in the Tekran denuder
- Underreported plume NO_x concentrations
- Problems with the soda-lime traps

Low Background Mercury Readings

The subtraction of low background concentrations from the measured plume concentrations would result in higher in-plume Hg concentrations when they are converted to equivalent stack Hg concentrations. However, this does not appear to be the case because the measured background concentrations were fairly consistent and in the expected range. Also, low background RGM concentrations would have caused those values to be higher as well, and this is not the case.

Inefficient Trapping of the RGM in the Annular Denuder

If the RGM were not trapped in the denuder but passed through to the analyzer, it would be reported as Hg^0. However, if the RGM were to pass through the annular denuder, it would most likely be trapped on the particulate filter and be reported instead as particulate-bound Hg. The data for the particulate-bound Hg concentrations do not suggest this was the case.

Underreported Plume NO_x Concentrations

This would result in larger dilution ratios and higher equivalent stack concentrations, but it would affect both the Hg^0 and the RGM concentrations. However, if the plume NO_x concentrations were underreported, it would affect both the Hg^0 and RGM concentrations in the same sense, and this is clearly not the case.

Problems with the Soda-Lime Traps

Modified soda-lime traps were used to scrub acid gases from the sample gas stream before it reached the Hg analyzer. At the Bowen Plant, it was observed that Hg desorbed from these traps when they were exposed to ambient air rather than the scrubbed zero air. There did not appear to be any offgassing of Hg when ambient air was sampled at the Pleasant Prairie Plant, but a different type of soda lime trap (supplied by Frontier GeoSciences) was used.

Conclusions

The following conclusions can be stated based on the Pleasant Prairie Power Plant stack and plume Hg sampling:

- Hg can be measured by aircraft in plumes with reasonable accuracy and precision. However, great care must be taken to prevent contamination in sampling lines and equipment used aboard the aircraft.
- Using a dilution factor based on the plume and stack NO_x, a reasonable Hg mass balance can be obtained to compare the Hg in the stack to the Hg in the plume.

- There appeared to be a decline in the fraction of RGM at Pleasant Prairie when values in the plume are compared to those in the stack (with a corresponding increase in the proportion of Hg^0). There was a 38% reduction of RGM between the in-stack measurement and the first sample point closest to the stack, and a 47% reduction of RGM from the stack to the 5-mile sample point, with no additional reduction between the 5- and 10-mile locations. This is consistent with earlier measurements by Frontier Geosciences of Hg reduction reactions in its static plume dilution chamber, which indicated rapid reduction reactions after flue gas emissions were mixed with ambient air in conditions representing the region just outside of the stack exit.

References

1. Prestbo, E.M.; Calhoun, J.A.; Brunette, R.C.; Paladini, M. Hg Speciation in a Simulated Coal Combustion Plume. In *Proceedings of Air Quality: Mercury, Trace Elements, and Particulate Matter Conference*; McLean, VA, Dec 1–4, 1998.

2. Danilchik, P; Imhoff, R.; Liang, L.; Valente, R.; Dismukes, E.; Brown, C.; Spurling, D.; Huang, Z.; Prestbo, E. A Comparison of the Fate of Mercury in Flues and Plumes of Coal-Fired Boilers. Presented at the Mercury as a Global Pollutant Conference, July 10–14, 1994, Whistler, British Columbia.

3. Imhoff, R.E. *Preliminary Report on Measurements of Gas- and Particle-Phase Mercury in the Plumes of Coal-Fired Boilers*; Atmospheric Sciences Department, Environmental Research Center, Tennessee Valley Authority, March 15, 1995.

4. Laudal, D.L; Prestbo, E. *Investigation of the Fate of Mercury in a Coal Combustion Plume Using a Static Plume Dilution Chamber*; Final Report for U.S. Department of Energy Contract No. DE-FC-26-95FT40321; Energy & Environmental Research Center: Grand Forks, ND, Oct 2001.

5. Edgerton, E.; Hartsell, B.; Jansen, J. Field Observations of Mercury Partitioning in Power Plant Plumes. In *Proceedings of the International Conference on Air Quality III: Mercury, Trace Elements, and Particulate Matter*; Arlington, VA, Sept 2002.

CONTENTS

1 INTRODUCTION 1-1

2 BACKGROUND 2-1

2.1 Field Observations of Mercury Partitioning in Power Plant Plumes 2-1

2.2 Airborne Measurement of Plume Mercury at Plant Bowen, Cartersville, Georgia 2-2

3 PROJECT OBJECTIVES 3-1

4 PROJECT DESCRIPTION 4-1

4.1 Power Plant Description 4-1

4.2 Aircraft 4-3

4.3 Mercury Analyzers 4-5

4.3.1 Aircraft Hg Measurement System 4-5

Instrument Sampling Sequence 4-6

4.3.2 Stack Hg Analyzer 4-8

4.4 NO_x Analyzer 4-9

4.5 Other Equipment 4-9

5 EXPERIMENTAL APPROACH 5-1

5.1 Plume Sampling 5-1

5.1.1 Aircraft Sampling Locations 5-1

5.1.2 Plume-Sampling Weather Conditions 5-3

5.1.3 Plume-Sampling Procedures Used 5-10

Preflight 5-10

In-Flight 5-10

5.2 Stack Sampling 5-11

6 RESULTS AND DISCUSSION 6-1

6.1 Stack Results at Pleasant Prairie 6-1

6.2 Plume Results at Pleasant Prairie 6-2
6.2.1 Data Outliers 6-4
6.2.2 Mass Balance Calculations 6-5
6.2.3 Plume Hg Speciation Results 6-6
Low Background Mercury Readings 6-9
Inefficient Trapping of the RGM in the Annular Denuder 6-9
Underreported Plume NO_x Concentrations 6-9
Integration Errors of the NO_x Data 6-10
Problems with the Soda-Lime Traps 6-10
6.3 Vertical Mercury Profile 6-10

7 CONCLUSIONS AND RECOMMENDATIONS 7-1

8 REFERENCES 8-1

A MERCURY WORKSHEETS A-1

B DATA REDUCTION PROCEDURES A-1

LIST OF FIGURES

Figure 2-1 Schematic of the Hg-Sampling System Used by TVA at the Bowen Power Plant 2-3
Figure 2-2 Changes in RGM Normalized by NO_x As a Function of Distance from the Stack 2-5
Figure 4-1 Schematic of the Pleasant Prairie Power Plant 4-2
Figure 4-2 Aerial Photograph of the Pleasant Prairie Power Plant 4-2
Figure 4-3 Photograph of the DHC-6-300 Twin Otter deHavilland Vistaliner 4-4
Figure 4-4 Photograph Showing External Sampling Probe on Aircraft 4-5
Figure 4-5 Schematic of the Tekran Mercury System 4-6
Figure 4-6 Illustration of the Sampling and Desorption Phases of the Tekran Model 1130 4-7
Figure 5-1 Flight Track on August 27, 2003 5-1
Figure 5-2 Flight Track on August 30, 2003 5-2
Figure 5-3 Flight Track on August 31, 2003 5-2
Figure 5-4 Flight Track on September 2, 2003 5-3
Figure 5-5 Weather Conditions During the August 27, 2003, Plume-Sampling Flight 5-5
Figure 5-6 Weather Conditions During the August 30, 2003, Plume-Sampling Flight 5-6
Figure 5-7 Weather Conditions During the August 31, 2003, Plume-Sampling Flight 5-7
Figure 5-8 Weather Conditions During the September 2, 2003, Plume-Sampling Flight 5-8
Figure 5-9 Weather Conditions During the September 4, 2003, Plume-Sampling Flight 5-9
Figure 5-10 View of the Plume from the Air and from the Ground 5-12
Figure 6-1 Stack CMM Mercury Speciation Results 6-2
Figure 6-2 Plot of the Concentration of Hg^0 in the Plume As It Moves from the Stack to 10 miles Downwind of the Stack 6-7
Figure 6-3 Plot of the % Hg^0 in the Plume Compared to the Stack Hg Concentration As a Function of Distance from the Stack 6-7
Figure 6-4 Plot of the Concentration of Total Mercury in the Plume As It Moves from the Stack to 10 miles Downwind of the Stack 6-8
Figure 6-5 Plot of the Concentration of RGM in the Plume As It Moves from the Stack to 10 miles Downwind of the Stack 6-8

LIST OF TABLES

Table 4-1 Location of Major Cities in Relationship to the Plant....4-1
Table 4-2 Pleasant Prairie Coal Analysis....4-3
Table 5-1 Wind Velocities for Each Day of Plume Sampling with the Aircraft (10 a.m. and 6 p.m. at the aircraft sampling level over Kenosha, Wisconsin)....5-4
Table 5-2 Process Data as Measured at the Stack....5-11
Table 6-1 Stack Ontario Hydro Mercury Speciation Results....6-1
Table 6-2 Plume Mercury Speciation Data....6-3
Table 6-3 Average Mercury Speciation Results for Each Location....6-4
Table 6-4 Total Hg Mass Balance: Plume Hg Compared to Stack Hg....6-6
Table 6-5 Background Mercury Concentrations....6-9
Table 6-6 Vertical Profile Data....6-11

Table A-1 Complete Data Mercury Worksheet: August 27, 2003....A-2
Table A-2 Complete Data Mercury Worksheet: August 30, 2003....A-3
Table A-3 Complete Data Mercury Worksheet: August 31, 2003....A-4
Table A-4 Complete Data Mercury Worksheet: September 2, 2003....A-5
Table A-5 Complete Data Mercury Worksheet: September 4, 2003....A-6
Table B-1 Data Format for Converting Plume Hg Data to Equivalent Stack Hg Data....A-2
Table B-2 Format for Sample Time....A-3
Table B-3 Sample Data Format....A-4
Table B-4 Sample Integration....A-7

1
INTRODUCTION

Mercury (Hg) is emitted by both natural and human processes and cycles through atmospheric, aquatic, and terrestrial environments. Forms of Hg that appear most important in these environments are elemental mercury (Hg^0), inorganic or oxidized Hg (primarily Hg^{2+}), and methylmercury. The chemical form of Hg affects its transport through air, land, and water, as well as chemical and biological behavior. Hg^0 is known to circulate in the atmosphere for about 1 to 2 years before it is deposited [1]. Hg^{2+}, also referred to as reactive gas mercury (RGM) by atmospheric scientists, in the atmosphere can be deposited directly to water bodies or can be transported from land by runoff and enter ponds, streams, rivers, lakes, etc. The water bodies contain microorganisms that have the metabolic capability to carry out chemical reactions that bind Hg^{2+} to methyl groups, producing methylmercury.

Although in-stack Hg speciation measurements are essential to the development of control technologies and to provide data for input into the atmospheric deposition models, the determination of speciation in a cooling coal combustion plume is more relevant for use in estimating Hg fate and effects through the atmosphere. Substantial research has been done in the past on Hg transformations within energy conversion systems—determining the concentrations of speciated Hg at the stack and doing ground-level atmospheric measurements; however, little has been done to determine the Hg chemistry, kinetics, and thermodynamics in the flue gas plume [2]. It is the Hg transformations that occur in the plume that determine the rate and the form of Hg deposited in waterways. Therefore, a logical step in Hg research is to apply what we know and extend this understanding beyond the power plant stack to the plume region. Therefore, EPRI and the U.S. Department of Energy have funded stack and aircraft Hg measurements at two power plants. The primary focus of this report is work conducted by the Energy & Environmental Research Center (EERC) at Pleasant Prairie.

2
BACKGROUND

In the mid 90s the Tennessee Valley Authority (TVA) attempted to evaluate Hg in plumes with mixed success [3,4]. Also Frontier Geosciences developed a static dilution chamber to simulate Hg chemistry downwind of a stack. Because of the rapid changes in Hg chemistry that occur and the wall effects of a relatively small vessel, it was difficult to interpret the results [5,6]. These studies clearly suggest that there are changes in the chemical form (Hg^0 vs. Hg^{2+}) and in the physical state (gaseous vs. particulate) of Hg occurring as the plume moves downwind of the stack.

2.1 Field Observations of Mercury Partitioning in Power Plant Plumes

Measurements of Hg^0, RGM, and total particulate Hg; SO_2; reactive nitrogen species (NO_y); CO; surface meteorology; and fine particle mass and composition were made at the Yorkville, Georgia, SEARCH site from 2001 through 2003 by Edgerton et al. [7]. Yorkville is a rural site located approximately 55 km west-northwest of Atlanta, Georgia, and 40 km south-southwest of Rome, Georgia.

Trace gas data (i.e., SO_2, NO_y, and CO) were used to screen for periods of influence from point and non-point sources and to identify specific point sources. Coal data and continuous emission monitor (CEM) data for coal-fired power plants in the vicinity of Yorkville were obtained from Southern Company for specific days when a plume event was observed at the site. Coal data included estimated emissions of total Hg, Hg^0, RGM, and total particulate Hg, while CEM data included measured emissions of SO_2 and NO_x. These data were used to calculate a variety of emission ratios, which were then compared with observed ratios at Yorkville. For example, SO_2:NO_x was used for source identification, while total Hg:SO_2 was used to verify conservation of mass between the point source and Yorkville.

Observed and expected Hg emissions information for 15 point-source plume events were tabulated, and within the combined uncertainties of measurements and calculations, mass closure was observed for all events, ruling out significant losses (e.g., dry deposition) of Hg in transit from the plumes to Yorkville. The data showed that observed emission ratios are much higher for Hg^0 than for RGM and that this difference is statistically significant. Comparison of observed and expected emission ratios for Hg^0 shows that the former is invariably greater than the latter. In aggregate, Hg^0 is expected to represent 48% of emissions. Observational data, in contrast, show that Hg^0 represents almost 90% of the increment above background during plume events.

The above results may point to an important gap in the understanding of Hg emissions from coal-fired power plants. On the one hand, total Hg is accounted for, and there is good agreement

between field observations and estimated emissions. On the other hand, there is substantial disagreement in the partitioning between Hg^0 and RGM. Possible explanations include 1) loss of RGM during transport from the point source to Yorkville, 2) errors in field measurements, and/or 3) chemical conversion of RGM during transport.

Loss of RGM cannot explain the observations, because there is reasonable mass closure for plume events. In addition, most events occurred during dry periods, which would limit losses to dry deposition. Results of modeling studies show that dry deposition cannot account for apparent losses of RGM, even if the deposition velocity is increased significantly above the generally accepted range of reasonable values. Gross error in field measurements is effectively ruled out by the comparison of manual and automated data for RGM. Beyond this, the excellent agreement for SO_2:NO_y ratios (observed vs. CEM) suggests that these species are conserved and well quantified. Chemical conversion of RGM following emission from the point source could account for the shift in partitioning; however, the mechanism for such a conversion, under plume conditions, is not readily apparent. The results obtained at Yorkville are also supported by results obtained by Frontier Geosciences in tests using a static plume dilution chamber [5,6]. Although there were substantial wall effects, there appeared to be a very fast reduction of RGM to Hg^0.

These findings, to the extent they are applicable for the fleet of coal-fired power plants across the United States, have important implications to the current debate about allowing trading in a program to control Hg emissions from power plants. More specifically, these results would suggest that the concerns (i.e., about so-called “hot spots”) are possibly not justified.

2.2 Airborne Measurement of Plume Mercury at Plant Bowen, Cartersville, Georgia

As a result of the Yorkville observation, a surface and aircraft study was done at the Bowen Power Plant (operated by Georgia Power, part of Southern Company). The idea was to apply an in-the-field airborne measurement system capable of measuring the speciation of Hg in a power plant plume to possibly determine what, if any, Hg speciation changes occur.

The aircraft measurements were made by TVA with stack measurements made by the EERC. In addition, Frontier Geosciences made Hg measurements using its simultaneous plume dilution chamber (SPDC). This unit was designed to simulate plume chemistry, and comparisons were made to those obtained using the aircraft. At the Bowen Plant, three of four units operated during the study period. The experiment was designed to sample from all three units in the stack simultaneously with airborne measurements made downwind.

Hg in a power plant stack is typically present in quantities about 3–15 $\mu g/m^3$. Upon emission from the stack, the Hg concentration is quickly diluted several hundred times, bringing the levels down into the realm of ng/m^3. Although varying with meteorological conditions, at a distance of 6 nautical miles (nm) downwind, the dilution of the stack gas can be up to 10,000 to one. In order to measure the Hg quantitatively, an approach was taken to perform ten passes through the plume at each of the distances downwind. At these extremely low levels, quality control was essential to eliminate the possibility of contamination.

A deHavilland Twin Otter was used for the airborne measurements (as will be discussed in more detail later in this report; this was the same plane used by the EERC for the plume study at Pleasant Prairie). A schematic of the sampling system used by TVA is shown in Figure 2-1. Differences and similarities of the sampling equipment and procedures used by the EERC compared to those used by TVA will be discussed later in this report.

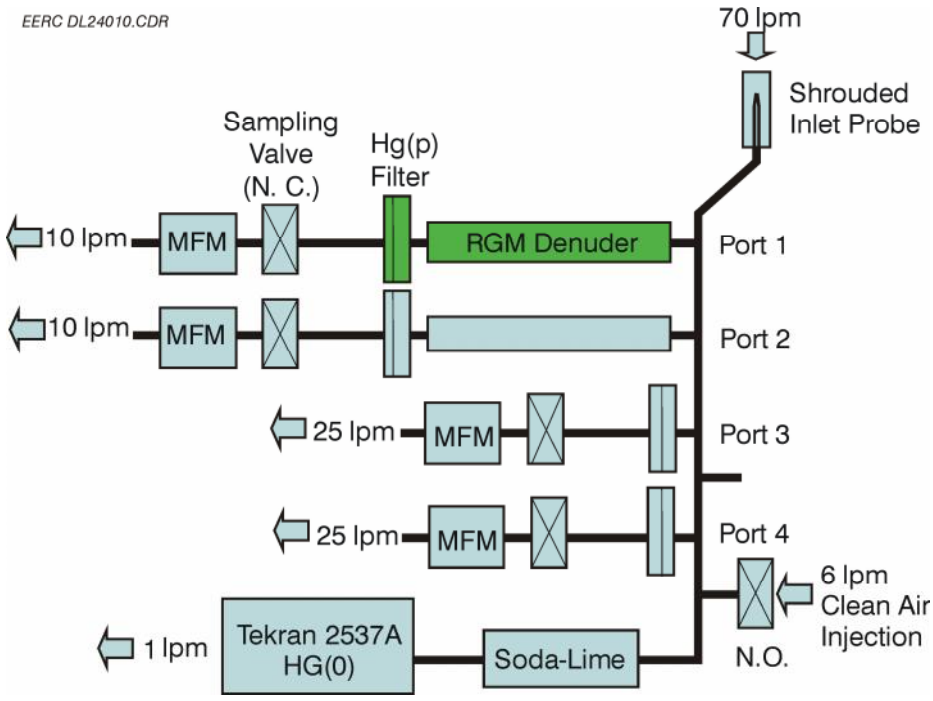

Figure 2-1
Schematic of the Hg-Sampling System Used by TVA at the Bowen Power Plant

To reduce the possibility of contamination, TVA used a charcoal scrubber and filter to provide a source of Hg-free ambient air. When not sampling, the solenoid valves downstream from the denuders and filters were automatically closed, and the charcoal-filtered Hg-free ambient air purged the system. When the aircraft entered the plume, the charcoal-filtered air valve closed, the sample valves opened, and the pumps pulled 60 liters per minute (lpm) of ambient air from the plume into the measurement system

In order to have an indication of plume dilution at the various sampling distances and to trigger sampling when the aircraft entered the plume, a modified Thermal Electron Corporation (TECO) Model 42C NO_x analyzer was employed. The modifications to the instrument reduced the dead volume so that overall response lag (the time from a step change in concentration at the inlet until the data logger records a change from the NO_x analyzer) was reduced to about 1 second. At the distances of 6 and 12 nm downwind, the automatic system was effective at collecting good plume samples. For runs directly above the stacks, it proved more effective to use a manual trigger to start the sampling. Weather conditions were deemed acceptable when it was not raining, and boundary layer winds were between 5 and 15 knots with fairly steady wind direction. The protocol for a full experimental flight was as follows:

Background

- After departing the airport, the plane proceeded to a point slightly upwind of the power plant to collect a background sample (RGM, particulate, and Hg^0).
- Then the filters and denuders were swapped, and samples were taken of the plumes as close to the stacks as possible.
- Next as the plane moved downwind, the denuders and filters were changed out again. Passes were made at a 6-nm radius from the plant downwind.
- Finally, another set of passes at 12 nm were performed on another set of sample denuders and filters.
- During each flight, an additional pair of filters and denuders were installed on the sampling manifold and then removed and used as field blanks. These blanks received the same handling and numbering as the sample units and were submitted blind to the labs for analysis along with the sample denuders and filters.

The results of the Bowen study indicate that the bulk of the Hg emissions from Bowen Plant (about 80%) were in the form of RGM. Plume RGM and NO_x are defined as the value found in the plume minus the value measured upwind of the power plant. By normalizing the in-stack and aircraft plume RGM values by the stack and plume NO_x values, respectively, it is possible to investigate the relative change in the proportion of plume Hg RGM as a function of downwind distance. Figure 2-2 shows the results of this analysis. Since the aircraft measures the mixed plume from the two stacks, the in-stack average values are calculated by weighting the individual unit Hg results by the volumetric flow from each unit into the stacks. In general, the RGM is seen to be declining only slightly with distance from the source, and there is surprisingly good consistency from flight to flight in the results at 6 and 12 nm downwind. RGM does not appear to undergo a rapid change upon emission from the stack; instead it appears to be only gradually decreasing such that at 12 km from the source, there is, on average, 84% of the RGM remaining when normalized to NO_x levels.

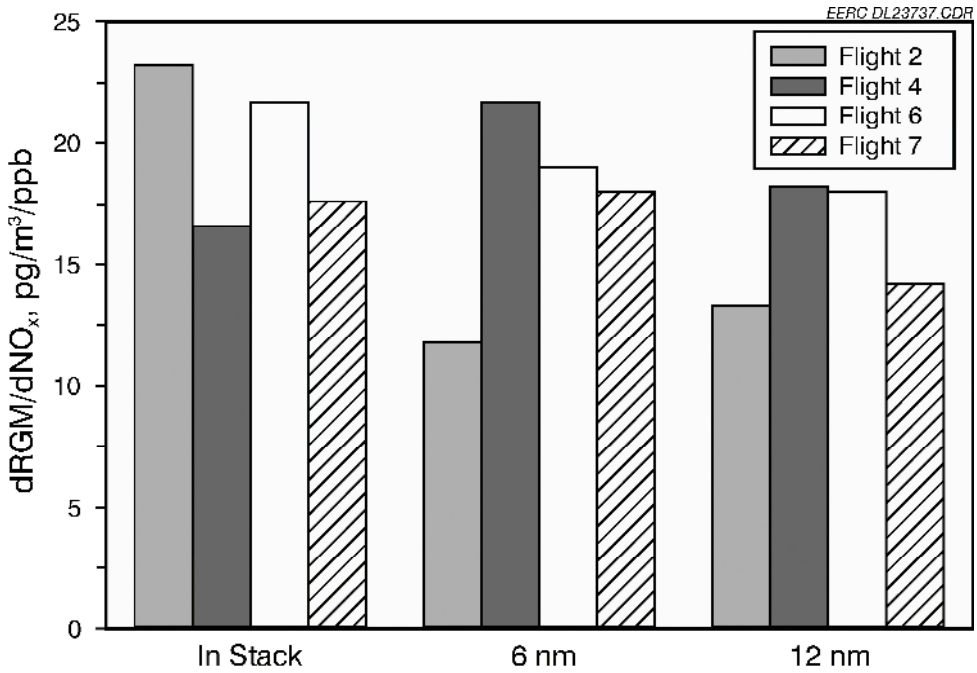

Figure 2-2
Changes in RGM Normalized by NO_x As a Function of Distance from the Stack

A problem occurred during the test attempting to measure Hg^0 in the plume. Hg^0 in the background air (typically 1500 pg/m^3) quickly dominates the plume Hg^0 signal as the aircraft moves downwind. This is particularly significant at Bowen where only a small percentage of the emitted Hg was Hg^0. At 6 and 12 nm, the dilution of the stack emissions by the ambient air renders the Hg^0 signal indistinguishable from the background levels. All the aircraft Hg^0 data have been invalidated because of this fact. As a side note, a source of variability in the Hg^0 baseline was also identified. It appeared that the soda-lime traps, which were found to be desorbing essentially no Hg when charcoal-filtered ambient air is passed through, released Hg when nonfiltered ambient air was passed through it. The cause of this phenomenon is unknown. As a result of the inconclusive results, a second plume study at WE Energies Pleasant Prairie plant was done. This report presents the results of this study.

3
PROJECT OBJECTIVES

The overall project goal is to gain an understanding of Hg chemistry as a plume is transported downwind from the stack. Specific objective are to:

- Develop sampling techniques to measure speciated Hg in the plume.
- Develop techniques to determine the location of the plume at various points downwind of the stack.
- Determine the speciation of Hg emissions at the stack and compare these results to those Hg species obtained from the plume sampling.
- Calculate a Hg mass balance using dilution factors and other relevant parameters.

To meet these objectives, the initial focus of the work was to assemble and test a sampling package that could be placed on an aircraft in such a manner that Hg could be sampled at various locations in the plume. Once the sampling techniques were shown to work, actual testing at a power plant was completed.

4
PROJECT DESCRIPTION

4.1 Power Plant Description

The Pleasant Prairie Power Plant, owned and operated by WE Energies, is located just outside of Kenosha, Wisconsin. On a straight-line basis, the distance and direction from the power plant to the major cities in a 50-mile radius is shown in Table 4-1.

Table 4-1
Location of Major Cities in Relationship to the Plant

City	Distance,[1] miles	Direction
Kenosha	7	NE
Milwaukee	31	NNW
Chicago	45	SSE
Racine	17	NNE

[1] Distance from airport.

The Pleasant Prairie Plant consists of two identical units (Units 1 and 2), with the exception of one having a selective catalytic reduction system (SCR) (Unit 2). Both have an electrostatic precipitator (ESP) for particulate control. It should be noted that although Pleasant Prairie has two units, they have a common stack. A schematic of the plant is shown in Figure 4-1, and an aerial photograph showing the single stack is shown in Figure 4-2. Specifications of the Pleasant Prairie facility are bulleted below:

- Fuel Type: Powder River Basin (PRB) subbituminous coal
- Boiler Capacity: 617 MW (both units)
- Boiler type: opposed-fired pulverized coal (both units)
- NO_x control: SCR on Unit 2, low-NO_x burners on both units.
- SO_2 control: none, low-sulfur coal (both units)
- Particulate control: ESP (both units)

Project Description

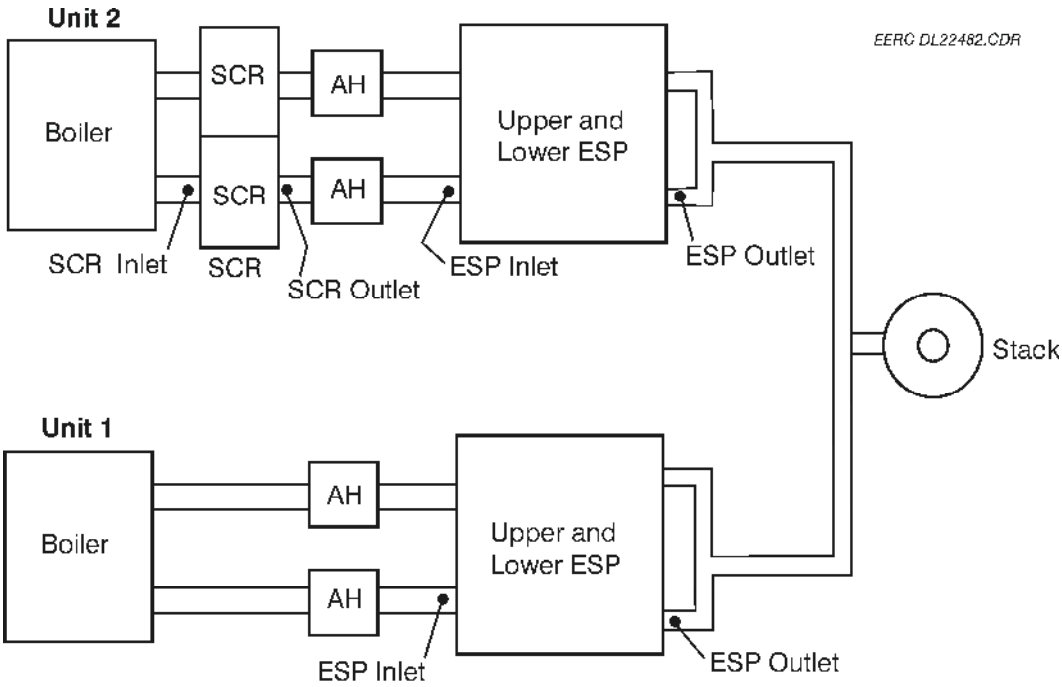

Figure 4-1
Schematic of the Pleasant Prairie Power Plant

Figure 4-2
Aerial Photograph of the Pleasant Prairie Power Plant

The analysis of the coal fired at the Pleasant Prairie Power Plant is shown in Table 4-2. The coal is typical of a PRB in that the Hg concentration is relatively low, <0.05 ppm, and the chlorine content is very low, 10 ppm.

Table 4-2
Pleasant Prairie Coal Analysis (on an as-received basis)

Component	Concentration
Hg, ppm (dry)	0.041
Chlorine, ppm (dry)	10
Proximate Analysis	
Moisture, wt%	30.0
Volatile Matter, wt%	33.0
Fixed Carbon, wt%	31.5
Ash, wt%	5.5
Ultimate Analysis	
Hydrogen, wt%	6.6
Carbon, wt%	46.9
Nitrogen, wt%	0.9
Sulfur, wt%	0.4
Oxygen, wt%	39.7
Heating Value, Btu/lb	8,190
F_d, dscf/10^6 Btu*	9,519

* Emission factor.

4.2 Aircraft

The aircraft used for the plume sampling was a turboprop DHC-6-300 Twin Otter deHavilland Vistaliner, which is a highly maneuverable, versatile aircraft. Aircraft and crew were supplied by Twin Otter International, Las Vegas, Nevada. The pilots were very experienced in doing research program involving ambient air sampling. A photograph of the aircraft is shown in Figure 4-3. This type of aircraft had a number of design and performance characteristics that made it an ideal platform for the project. The twin engine plane had a relatively large capacity for equipment, sufficient onboard electrical supply, and the ability to operate efficiently at low altitudes. These capabilities were accompanied by relatively low fuel consumption at all altitudes. Most importantly for the plume study project, it could be flown at relatively slow speeds (80–

Figure 4-3
Photograph of the DHC-6-300 Twin Otter deHavilland Vistaliner

160 knots, 150–300 km/hr) and in tight formation to allow consistent plume traverses at fixed heights and downwind distances.

The modifications that were made to the plane by EERC personnel were relatively minor. The primary modifications were the removing of seats to provide space for the racks for mounting sampling equipment, installing an inverter to provide additional electrical capacity, and installing an external probe for sampling the ambient air. The external probe is shown in Figure 4-4. As can be seen, the probe was fairly simple and consisted of a heated quartz nozzle sized to provide a reasonable approximation of isokinetic sampling. In addition, the nozzle was provided with a system to backflush zero-Hg air through the probe when the plane was not in the plume. It should also be noted to ensure transport of the sample to the sampling system, all connecting valves, sample lines, fitting, etc., were heated.

Figure 4-4
Photograph Showing External Sampling Probe on Aircraft

4.3 Mercury Analyzers

4.3.1 Aircraft Hg Measurement System

The Hg analyzer used in the aircraft was a fully automated Tekran® Model 2537A mercury vapor analyzer coupled with a Tekran® Model 1130 mercury speciation unit and a Tekran® Model 1135 particulate module. Figure 4-5 shows a schematic of the Tekran® components. Several modifications were made to the Tekran® setup:

- Using an optional impactor
- Adding an external pump to pull an isokinetic sample from the probe
- Adding a probe and heated sample transfer line to the sample path
- Adding a soda-lime trap
- Adding a zero-air valve trigger

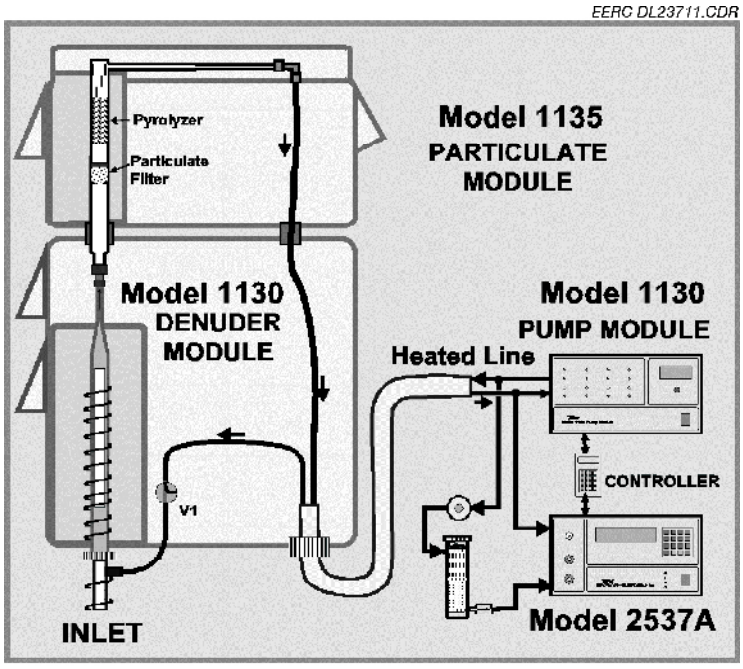

Figure 4-5
Schematic of the Tekran Mercury System

The analyzer portion of the system (Model 2537A) is based on the principle of cold-vapor atomic fluorescence spectroscopy (CVAFS), which provides an inherently more sensitive signal than cold-vapor atomic absorption spectroscopy. The system uses a gold-impregnated trap for preconcentrating the Hg and separating it from potential interferences that degrade sensitivity. The primary difference between the system used by the EERC and the one used by TVA for the Bowen project is that the Model 1130 and 1135 are integrated with the 2537A and are completely automated. Therefore, the denuders and filter did not have to be removed and desorbed manually. This gave the Model 2537A Hg vapor analyzer the ability to simultaneously monitor Hg^0, RGM, and particulate-bound Hg species during the flight. A total of 1 hour was needed to complete one sampling cycle (from the point at which sample collection began to when the analysis for the RGM and particulate-bound Hg was finished). The Hg^0 was obtained during the RGM and particulate bound Hg collection period. Therefore, it was possible to rapidly evaluate data each day and make sampling decisions for succeeding flights.

Instrument Sampling Sequence

During sampling, the pump module pulls 9 lpm, and the Model 2537A pulls 1 lpm sample through the denuder and particulate modules. The RGM in the sample gas is captured in a specially coated annular denuder in the Model 1130 denuder module. Particulate-bound Hg and Hg^0 pass through the denuder module. Next in the gas path, the particulate-bound Hg is trapped onto a unique quartz regenerable filter located within the Model 1135. Hg^0 also passes through the particulate module and is continuously analyzed by the Model 2537A during the sample

collection portion of the cycle. After the sample collection portion of the cycle is complete, the components are sequentially desorbed during the analysis phase.

During the analysis (desorption) phase, the system is flooded with zero air. First, the particulate filter is heated to desorb the particulate-bound Hg, providing a measurement of particulate-bound Hg. During the heating cycle, the denuder is also heated to desorb the RGM and reduce it to Hg^0, providing a measurement of RGM captured during the previous sampling period. After cooling, the denuder and particulate filter are ready for another cycle. All timing parameters on the Model 1130 and Model 1135 are programmable, allowing automatic RGM and particulate-bound Hg readings to be taken at user-specified intervals (from 30 minutes to 6 hours). A schematic of the Model 1130 sampling and desorption phase is shown in Figure 4-6.

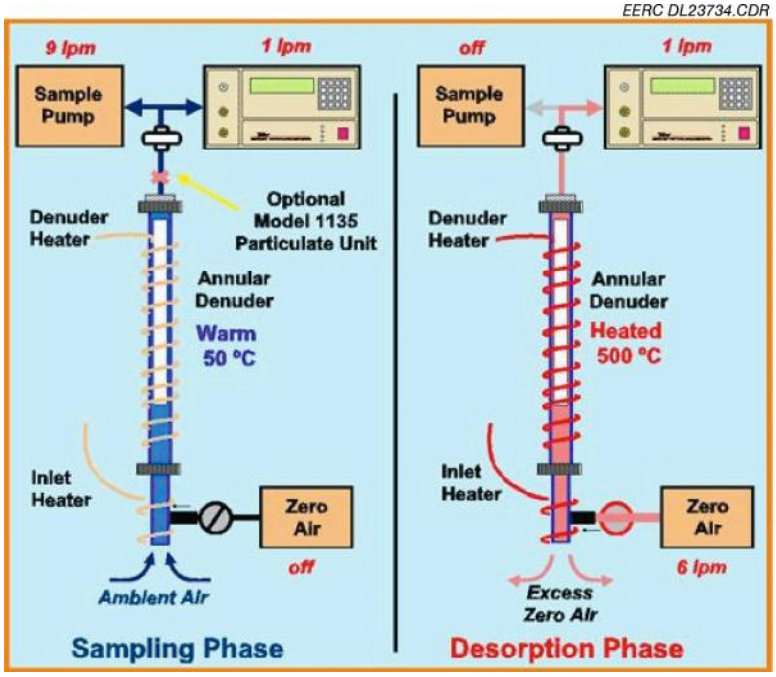

Figure 4-6
Illustration of the Sampling and Desorption Phases of the Tekran Model 1130

The desorption/analysis cycle used for this project was 25 minutes of sample collection followed by 35 minutes of desorption and analysis. During this period of time, a total of ten 2.5-minute Hg^0 measurements were made for each RGM and particulate-bound Hg measurement. When the plane was not in the plume, the sampling probe was flooded with zero air. At the Bowen Plant, the plume could be visually located at the closest sampling point. Because of the short time in the plume at this distance, TVA found that it worked best to manually trigger the zero air valve just before the plane entered the plume and after it exited the plume. At Pleasant Prairie, there was no visual indication of the plume location at the closest sampling point. Because the Hg concentrations at this point were high enough and would not be lost in the background readings, it was decided to sample continuously and not to flood the probe with zero air when the plane was not in the plume. This only affected the method for reducing the data from this sample point.

At the other two sampling locations, the NO_x analyzer was used to trigger the zero-air valve. Because the clocks were all synchronized, the NO_x data could be used to integrate the Hg concentration data.

One problem that occurred during the Bowen test was a Hg^0 contamination from the soda-lime traps which were used to ensure acid gases did not passivate the instrument's gold traps. This was also a concern for the Pleasant Prairie project because, as was the case at Plant Bowen, the background Hg^0 concentration was high with respect to the Hg^0 concentration in the plume, particularly at the 5- and 10-mile locations. To address this problem, discussions were held with Frontier Geosciences to determine what could be done in the manufacture of the soda-lime traps to eliminate or greatly reduce the problem. Frontier Geosciences was confident that it could do so, and as the results show, it was successful.

4.3.2 Stack Hg Analyzer

A Tekran Hg analyzer (Model 2537A modified to operate at the concentrations of Hg found in flue gas) with a pretreatment/conversion system was used at the stack to provide Hg speciation data around the clock (August 25–September 6, 2003). As stated above, the analyzer is based on the principle of CVAFS and uses a gold trap to preconcentrate the Hg.

A 4-step process is used to obtain a flue gas Hg measurement. In the first step, 2 L of flue gas is pumped through a gold trap, which is maintained at a constant temperature. Before the Hg is desorbed from the gold trap, a flushing step is initiated to remove any flue gas that may be present, because it has a damping effect on the Hg fluorescence. When this is completed, the analysis step begins. The heating coil is activated, and the gold trap is heated to approximately 500°C. This desorbs the Hg from the trap, and the Hg is carried into the atomic fluorescence (AF) detector. The gold trap is cooled rapidly in preparation for the next sample. The total time for the entire process is about 5 minutes. Utilizing dual traps, a Hg measurement is obtained every 2.5 minutes.

The system is calibrated using Hg^0 as the primary standard. The Hg^0 is contained in a closed vial, which is held in a thermostatic bath. The temperature of the Hg is monitored, and the amount of Hg is measured using vapor pressure calculations. Typically, the calibration of the unit has proven stable over a 24-hour period.

For this study, a wet-chemistry PS Analytical conversion/pretreatment system was used. The purpose of the pretreatment/conversion system is to remove acid gases (HCl) that can poison the gold traps, convert all the Hg to Hg^0 so that it can be measured by the AF detector, and allow the instrument to speciate Hg. The wet-chemistry conversion unit used $SnCl_2$ to convert all of the Hg to Hg^0 prior to analysis; a KCl solution was used to strip out the Hg^{2+} (for speciation purposes), and a sodium hydroxide solution removed the acid gases.

4.4 NO_x Analyzer

The zero-air valve on the Tekran Model 1130 pump module was triggered using an ambient air NO_x analyzer. It was expected that a NO_x gradient between the ambient air and plume would exist well downwind of the stack. The detection of this gradient along with a global positioning system (GPS) was then used to determine the location of the plume and thereby control the zero-air valve. A rapid response NO_x analyzer was necessary to allow recording of NO_x concentration changes as the aircraft crossed the edges of the plume material. The assumption of neutral buoyancy and equivalent Froude numbers for all plume constituents at and beyond equivalent stack height and distance was used to calculate in-plume portions of the Hg concentration.

The analyzer that was used for this project was a rapid response, dual-range TECO Model 42C ambient air NO_x analyzer. This analyzer was able to measure 0–50 ppb NO_x in the low range and up to 500 ppb NO_x in the high range, which based on the test at Bowen appeared to be adequate. By the removal of an external filter and replacement of ¼” lines with 1/8” Teflon lines, the analyzer response time from the inlet of the sample probe was decreased to 2 seconds. A separate TECO Model 111 calibration unit was used to calibrate the analyzer. The system required a tank of NO calibration gas and a source of zero air. The TECO Model 111 uses mass flow controllers to mix the calibration and zero gases to produce a desired calibration concentration.

4.5 Other Equipment

The following sampling equipment was used for the study:

- A heated probe and sample line were mounted out of the side near the front of the aircraft (the system was designed to pull an isokinetic sample).
- A GPS with an externally mounted antenna.
- A data acquisition system for logging Hg, GPS, and NO_x data.
- A zero-air valve on the Model 1130 pump module, modified to be controlled by the data acquisition system.
- A pump to pull a near-isokinetic sample through the probe and deliver sample gas to the NO_x analyzer and the Hg measurement system.
- A barometer and thermocouple to measure the conditions in the cabin of the airplane.
- A power inverter to supply additional electrical power in the airplane.

5
EXPERIMENTAL APPROACH

5.1 Plume Sampling

5.1.1 Aircraft Sampling Locations

Following background sampling at a location upwind of the stack, aircraft sampling was done at three locations downwind of the stack. The first location was approximately 1500 ft from the stack (the closest the plane could be permitted to approach the stack). The second and third locations were approximately 5 and 10 miles downwind of the stack, respectively. Figures 5-1 through 5-4 are diagrams of the sampling locations and patterns that were done for each flight event. A number of different patterns were flown at the closest sampling point in an effort to optimize the time in the plume. At the other two locations, a racetrack pattern was flown. Aircraft position and time were determined using a GPS system.

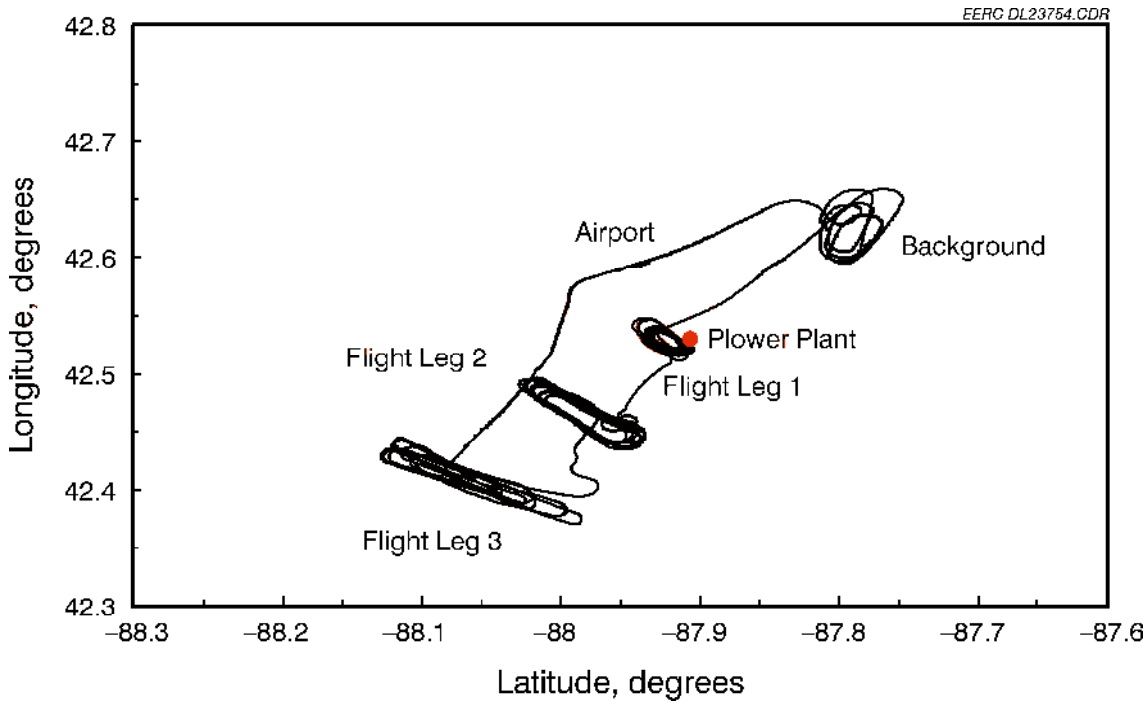

Figure 5-1
Flight Track on August 27, 2003

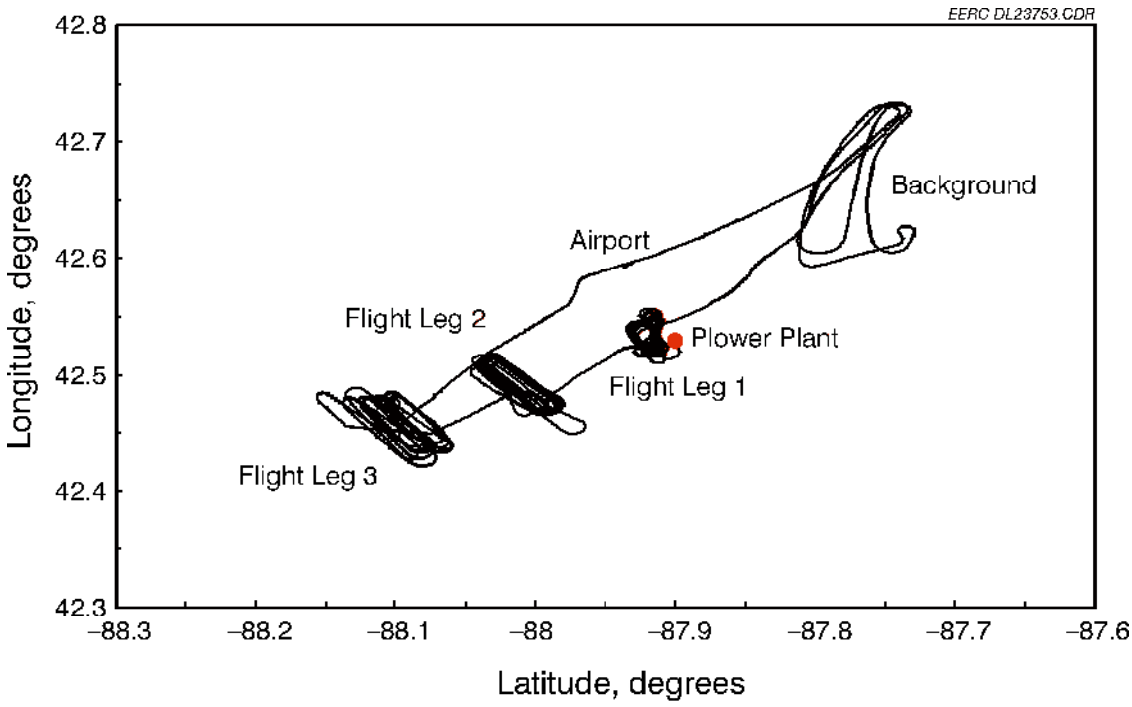

Figure 5-2
Flight Track on August 30, 2003

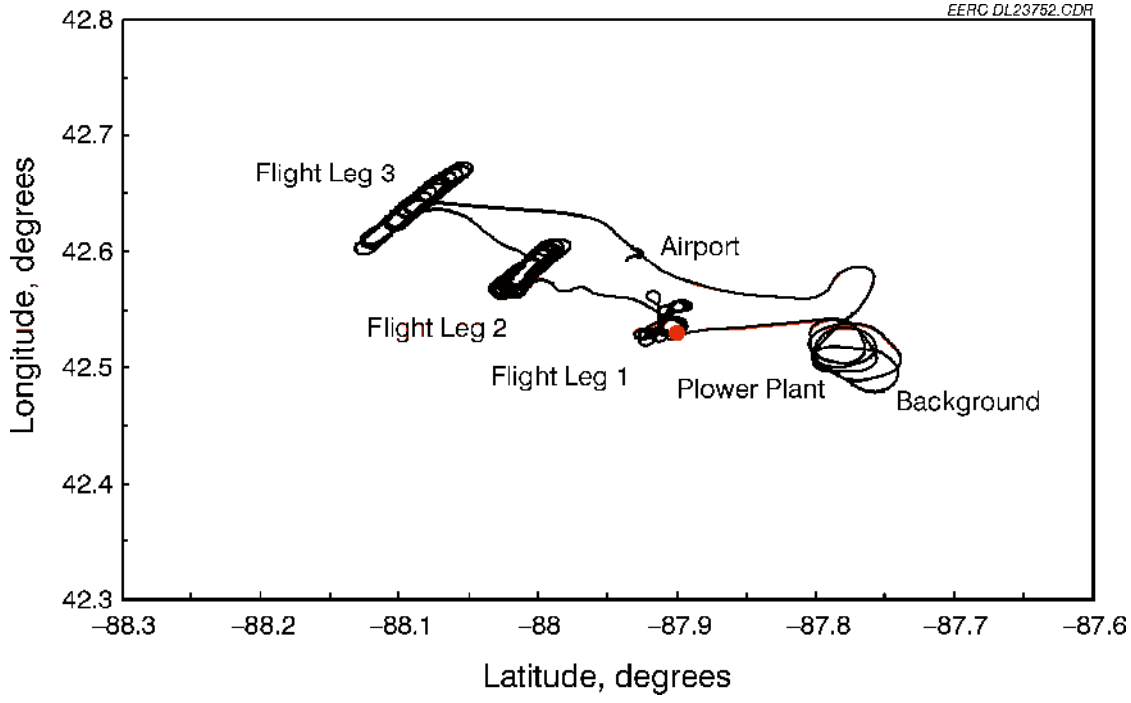

Figure 5-3
Flight Track on August 31, 2003

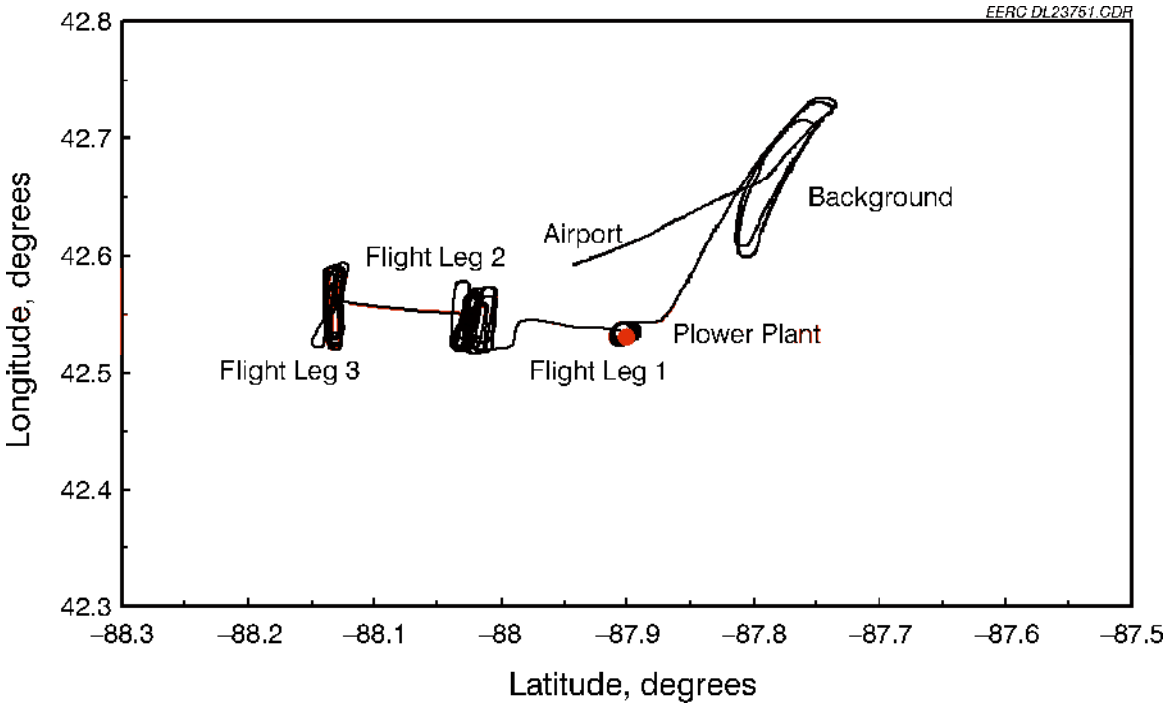

Figure 5-4
Flight Track on September 2, 2003

Determining the altitude and direction of the plume was done based on a combination of visual inspection (location closest to the stack) and the measurements of NO_x concentrations. Except for the closest location, the Tekran Hg analyzer was triggered by a NO_x set point.

In addition to plume sampling, a vertical Hg profile was established at a location about 15–20 km downwind of the plume. The first sample was taken in the plume (approximately 2500 ft), and the second point was taken below the plume at 500 ft. Because of the limited flight time, it was decided to climb to the highest sample point before dropping to the 8500-ft sample point.

5.1.2 Plume-Sampling Weather Conditions

As stated earlier, the Pleasant Prairie Power Plant is located just outside of Kenosha, Wisconsin, and the aircraft sampling took place between August 27, 2003, and September 4, 2003. Aircraft sampling flights were conducted in daylight under atmospheric conditions that permitted adequate sampling of the stack plume. The weather conditions during the project were fairly consistent, and as the historical climate record indicated, the days were generally fair. In the original test plan, the ideal wind velocities were considered to be approximately 2.5–5 m/sec; however as shown in Table 5-1, the average wind speed was somewhat above this, ranging from 5.3 to 8.3 m/s. These wind velocities were still low enough that the aircraft was able to find the plume, and good sampling was able to be completed.

Table 5-1
Wind Velocities for Each Day of Plume Sampling with the Aircraft (10 a.m. and 6 p.m. at the aircraft sampling level over Kenosha, Wisconsin)

Flight Date	Minimum Wind Speed, m/s	Maximum Wind Speed, m/s	Average Wind Speed, m/s
August 27, 2003	6.5	9.0	8.1
August 30, 2003	5.0	6.0	5.3
August 31, 2003	4.5	8.5	5.8
September 2, 2003	5.5	9.0	6.8
September 4, 2003	6.0	10.5	8.2

Figures 5-5–5-9 show the weather conditions during each of the five aircraft plume sampling flights. The cloud conditions during each sampling flight are given by the sky image of the western horizon taken in Kenosha, Wisconsin. Cloud conditions varied from clear skies on August 27 and 31, to high-level cirrus clouds on August 29, to fair weather cumulus clouds on September 2 and 4.

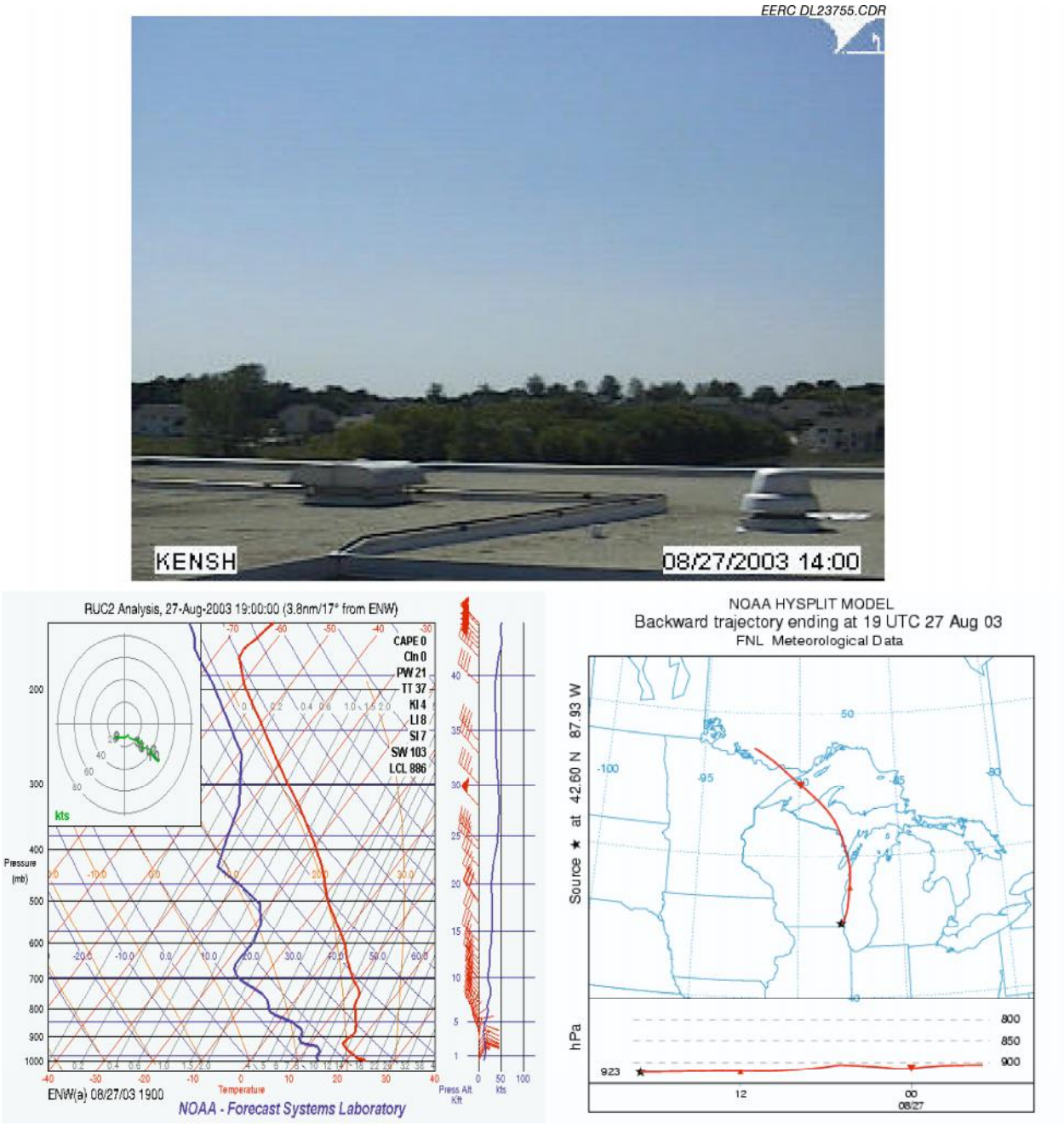

Figure 5-5
Weather Conditions During the August 27, 2003, Plume-Sampling Flight

Experimental Approach

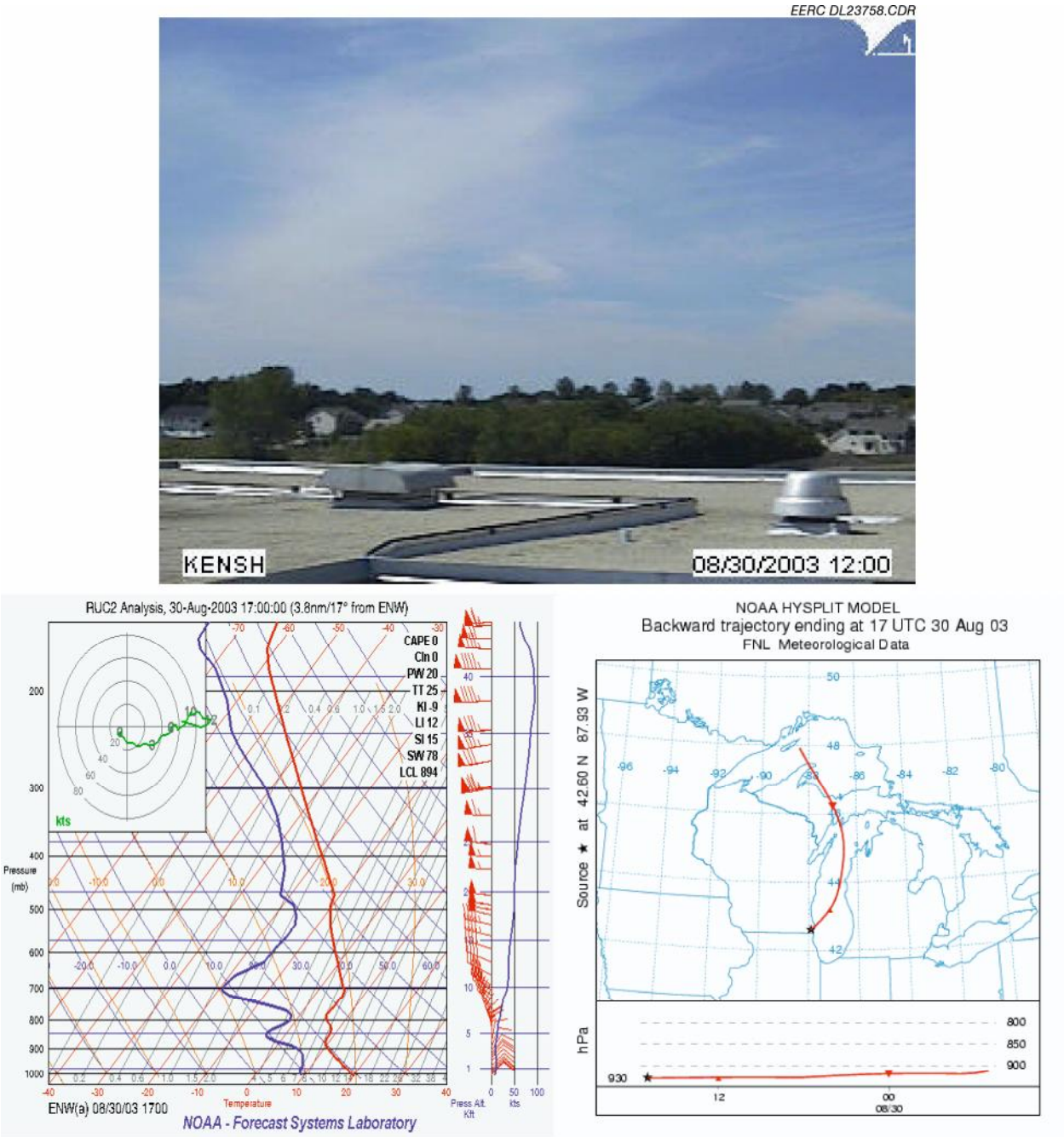

Figure 5-6
Weather Conditions During the August 30, 2003, Plume-Sampling Flight

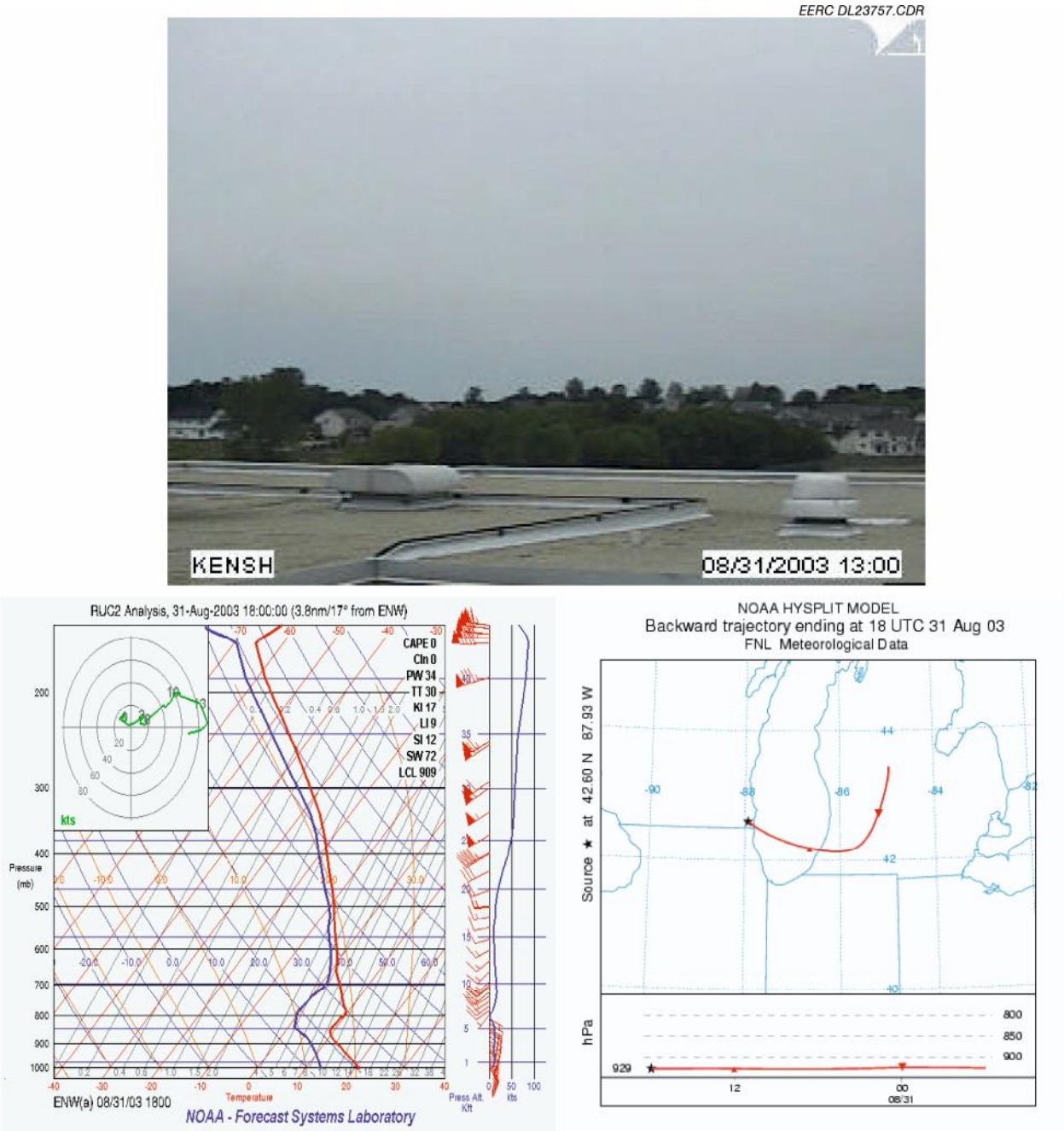

Figure 5-7
Weather Conditions During the August 31, 2003, Plume-Sampling Flight

Experimental Approach

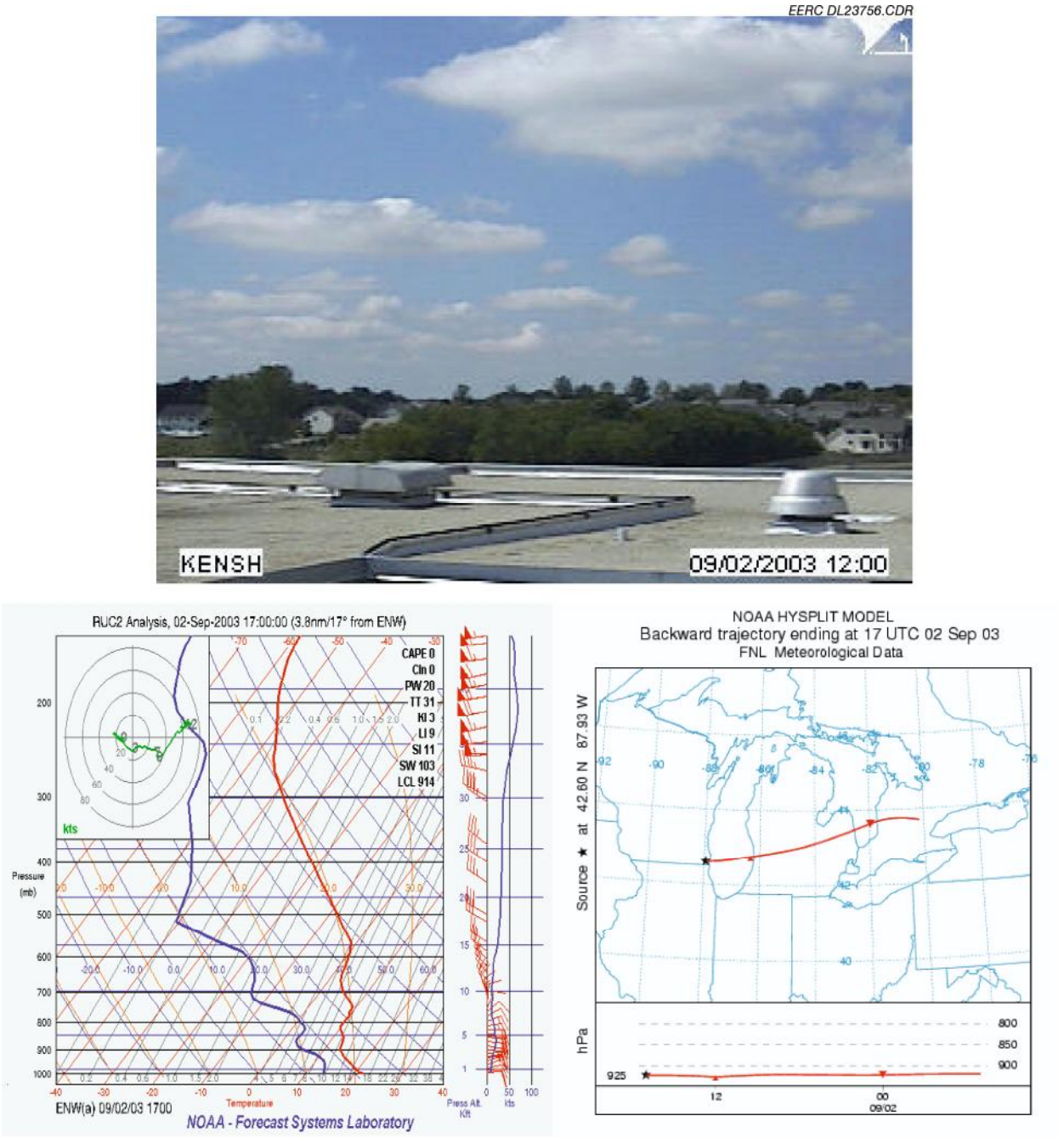

Figure 5-8
Weather Conditions During the September 2, 2003, Plume-Sampling Flight

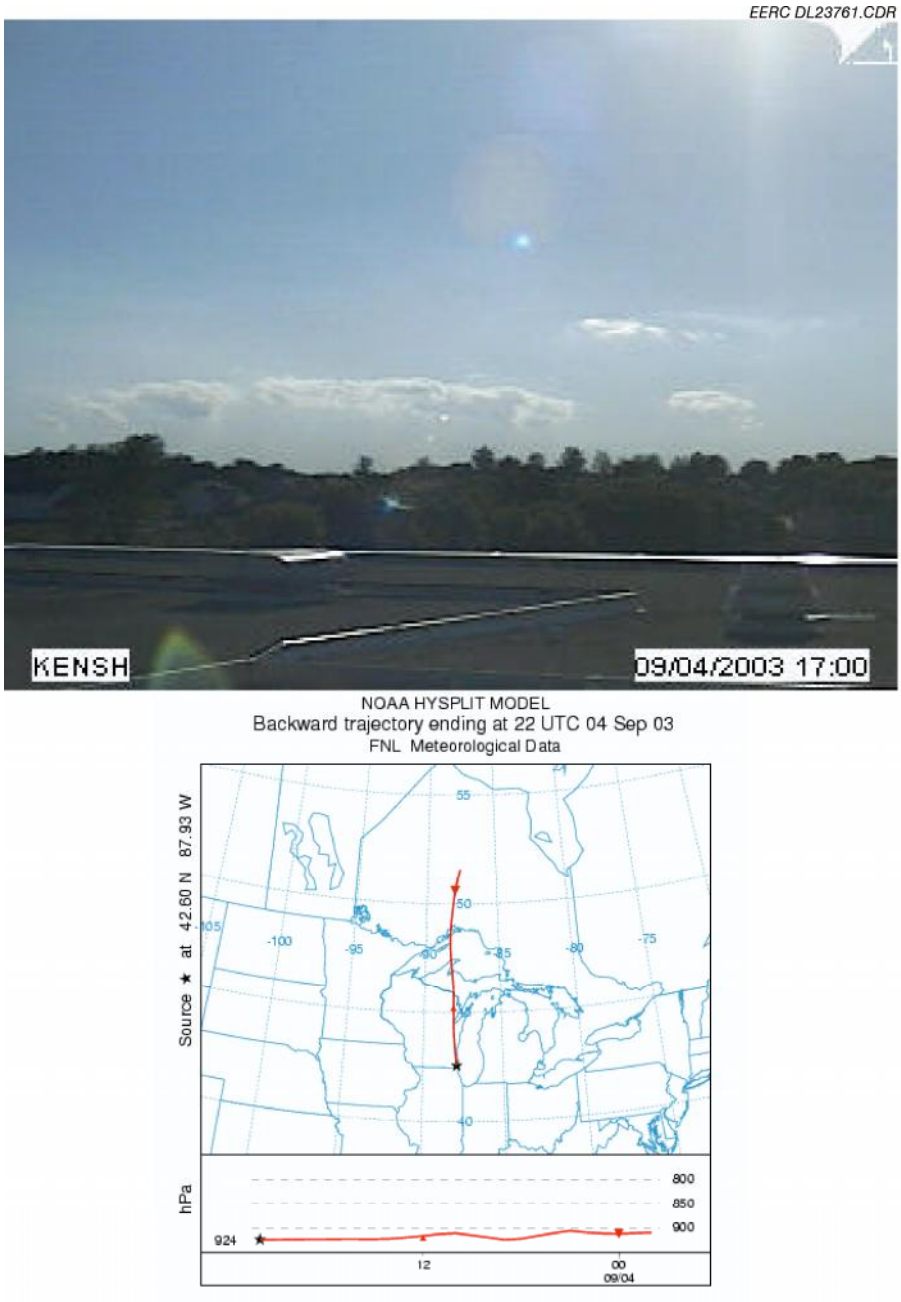

Figure 5-9
Weather Conditions During the September 4, 2003, Plume-Sampling Flight

Skew-T plots based on analysis data runs of the Rapid Update Cycle weather model (see http://maps.fsl.noaa.gov for information on the model) are given in the lower left panel. The lower right panel gives 24-hour back trajectories at the aircraft sampling height based on the HYbrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model (see http://www.arl.noaa.gov/ready/hysplit4.html for more information) and FNL data. In general, weather conditions during the field project were somewhat atypical in having air parcels moving in from the north (August 27, September 4), northeast (August 30), and east (August 31,

September 2) instead of the more typical directions of south or southwest. The cause for the wind pattern was the persistence of a low-pressure system over southeastern Canada and a high-pressure system over the central United Status throughout most of the field project. The result is that the two large cities (Chicago and Milwaukee) most likely had little influence on the background Hg levels (see Table 4-1).

5.1.3 Plume-Sampling Procedures Used

As was shown in Table 5-1, the testing at Pleasant Prairie included 5 flying days. The following is the sampling sequence that was followed during each flight day.

Preflight

- Computer clocks were synchronized with the GPS system.
- The Hg analyzer was zeroed and then calibrated using primary injections of Hg^0.
- The NO_x analyzer was zeroed and spanned.
- The particulate module and denuder system were manually desorbed to remove any residual Hg.
- Zero-Hg ambient air was sampled through the entire system for one cycle.

In-Flight

- The plane was flown to a point approximately 5 miles upwind of the stack, and background samples were taken (particulate-bound Hg, RGM, and Hg^0).
- The plume was then located by visual means at the point nearest to the stack (~1500 ft), and Hg samples were taken over a 25-minute period (this time period was long enough to ensure a good Hg sample).
- As the first Hg sample was desorbing and being analyzed by the onboard Tekran Hg instrument, the plume was then located using the NO_x analyzer at a location approximately 5 miles downwind of the stack.
- After the plume was located at the 5-mile spot, the NO_x trigger point was set at an appropriate level to trigger sampling when the plume was entered.
- After the analysis of the first sample was completed, Hg sampling was done for another 25 minutes at the 5-mile location.
- The same process was then repeated at a point in the plume 10 miles downwind of the stack.
- Following completion at the second Hg-sampling sequence, the aircraft landed, and the last Hg sample (10 miles downwind) was desorbed and analyzed.
- Before shutdown, the Hg system was desorbed on zero air for one cycle.

5.2 Stack Sampling

To establish baseline conditions for comparison with the plume samples, in-stack sampling was carried out simultaneously with the flights, providing measurements of the Hg speciation in the stack. Hg sampling at the stack was completed using the Ontario Hydro (OH) Hg speciation sampling method and a continuous mercury monitor (CMM). Prior to the start of the testing, a CMM was placed at the stack outlet and remained there during the entire project. During the setup, two OH samples were taken to verify the CMM was operating properly; in addition, the instrument was zeroed and calibrated each day. During each flight day, one OH sample was taken.

During the sampling period, it was expected that the two units at the Pleasant Prairie Plant would be operating at or near normal conditions. Plant operating conditions (i.e., load, O_2, NO_x, SO_2, CO_2) were logged by plant personnel during the sampling period. As can be seen by the small deviations, in Table 5-2 (data were taken from 7:00 to 17:00 each day), operating conditions were relatively constant for each day. This was particularly important as the stack NO_x values were used to calculate dilution ratios for the plume samples as shown below:

$$\text{Dilution Ratio} = \frac{(\text{Stack NO}_x - \text{Background NO}_x)}{(\text{Plume NO}_x - \text{Background NO}_x)} \qquad \text{[Eq. 1]}$$

Table 5-2
Process Data as Measured at the Stack

Date	Generating Capacity, MW*	Stack Temp., °F	NO_x, ppm(v)	SO_2, ppm(v)	CO_2, %	Opacity, %
08/27/03	1248 ± 39	309 ± 4	144 ± 6	373 ± 8	11.9 ± 0.1	8.0 ± 0.4
08/29/03	1249 ± 7	312 ± 6	137 ± 4	321 ± 14	11.9 ± 0.1	7.6 ± 0.4
08/30/03	1229 ± 39	304 ± 7	161 ± 32	305 ± 18	11.8 ± 0.3	7.4 ± 0.4
08/31/03	1087 ± 59	296 ± 3	143 ± 17	281 ± 12	11.4 ± 0.4	7.0 ± 0.2
09/02/03	1247 ± 36	305 ± 5	136 ± 37	321 ± 13	12.1 ± 0.3	7.3 ± 0.3
09/04/03	1258 ± 15	300 ± 3	140 ± 5	311 ± 7	12.1 ± 0.2	7.2 ± 0.3

* Combined generating capacity for Units 1 and 2.

Although the NO_x concentrations in the stack are somewhat lower than desired for aircraft plume measurement (because one-half of the flue gas was being treated using an SCR), it was still possible to detect a difference between the background and plume even at 10 miles. As shown in Table 5-2, the average stack NO_x concentration was 144 ppm(v).

It should be noted that the ESPs at Pleasant Prairie Power Plant were very efficient (>99.8%), which is illustrated by the low opacity (<10%). As a result, the plume was difficult to find

visually from the air even at the closest location to the stack, as can be seen in photographs presented in Figure 5-10.

Figure 5-10
View of the Plume from the Air and from the Ground

The Hg measurements by the aircraft and at the stack were compared to SPDC located at the stack by Frontier Geosciences, Inc. Frontier Geosciences will prepare a separate report detailing the results from the SPDC.

6
RESULTS AND DISCUSSION

6.1 Stack Results at Pleasant Prairie

The Hg concentrations in the stack are shown in Table 6-1 and Figure 6-1 for OH and CMM sampling, respectively. As the results show in Table 6-1, the Hg concentrations were relatively constant during the entire duration of the project. The Hg^{2+} averaged 34.3% (65.7% Hg^0) of the total Hg measured. These results were well-matched by the CMM as shown in Figure 6-1.

Table 6-1
Stack Ontario Hydro Mercury Speciation Results

Date	Particulate-Bound Hg, µg/Nm^3	Hg^{2+}, µg/Nm^3*	Hg^0, µg/Nm^3	Hg (total), µg/Nm^3	Hg^0 as a % of Total Hg	Hg^{2+} as a % of Total Hg
08/27/03	0.00	3.30	6.70	10.00	67.0	33.0
08/29/03	0.00	3.43	6.06	9.49	63.9	36.1
08/30/03	0.00	3.02	6.63	9.65	68.7	31.3
08/31/03	0.00	4.01	5.10	9.11	56.0	44.0
09/02/03	0.00	2.51	5.66	8.17	69.3	30.7
09/04/03	0.00	3.07	6.83	9.90	69.0	31.0
Average	0.00	3.22	6.16	9.39	65.7	34.3
Std. Dev.	0.00	0.50	0.68	0.67	5.1	5.1

* All concentrations (µg/Nm^3) are based on 1 atmosphere pressure and 20°C

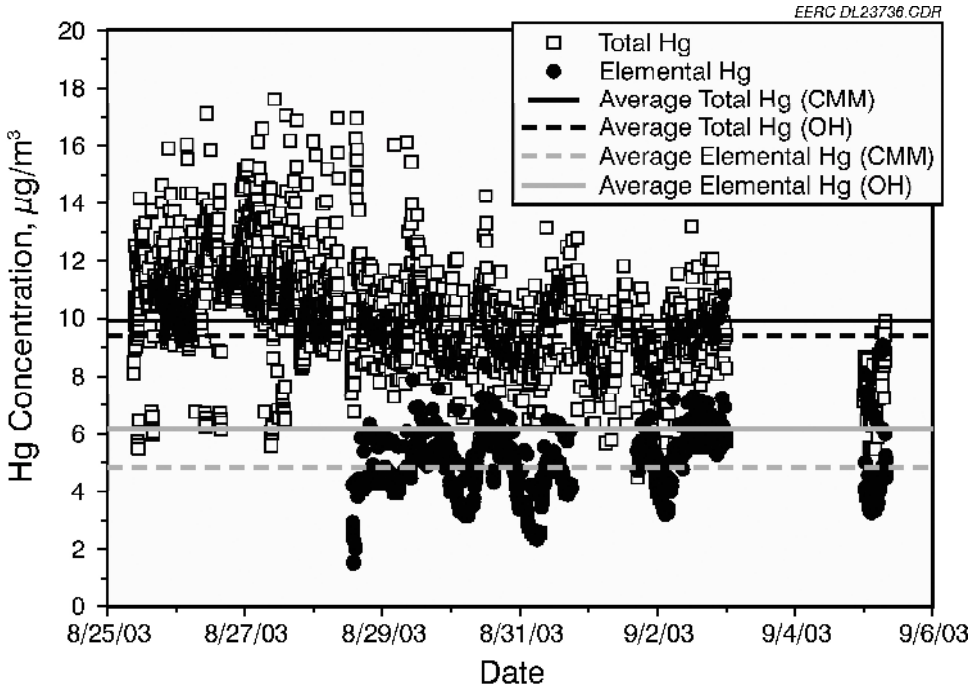

Figure 6-1
Stack CMM Mercury Speciation Results

6.2 Plume Results at Pleasant Prairie

A summary of the results from the plume sampling at the Pleasant Prairie Plant are presented in Table 6-2, with the average presented in Table 6-3. The plume Hg concentrations have been converted to equivalent stack concentrations and are presented as such. The complete data set is presented in Appendix A, and an explanation of the data reduction procedure is presented in Appendix B.

Table 6-2
Plume Mercury Speciation Data

Hg^0 Sample No.	Sample Point Nearest the Stack, µg/Nm^3							Sample Point Nominally 5 miles from Stack, µg/Nm^3					Sample Point Nominally 10 miles from Stack, µg/Nm^3			
	8-27	8-30	8-31	9-2	9-4	9-4	Avg.	8-27	8-30	8-31	9-2	Avg.	8-27	8-30	9-2	Avg.
1	6.0	6.4	1.6	5.5	-16.2*			2.8	9.2	5.6	7.6		1.2	4.1	1.6	
2	42.0	7.5	6.3	9.2	5.0	16.2		28.3	10.2	13.9	10.0		5.3	13.2	8.6	
3	10.6		4.7	5.7	4.0	16.5		33.5	12.0	15.7	24.4		7.8	12.8	7.6	
4	9.8	4.7	8.0	-13.1	2.3	157.7		36.1	7.9	11.7	10.9		15.7	28.3	5.9	
5	11.9	9.0	15.6	15.4		18.0		11.8	16.3	25.9	10.3		7.9	13.0	16.9	
6	37.8	6.5	7.4	3.9	17.5			75.5	14.8	14.5	9.1		27.7	27.3	3.7	
7	12.9	14.5	18.2		15.0	43.9		56.1	12.5	49.8	16.4		17.2	21.0	14.0	
8	14.0	7.9	10.1	7.2	10.6	12.8		8.3	13.6	25.0	80.6		19.9	11.6	6.1	
9	15.5	5.8	10.2		9.8	19.2		17.8	15.7	21.6	5.3		14.8	22.7	17.4	
10	12.5	24.2	8.9	7.6	9.9	28.7		28.5	17.0	89.3	16.0		19.2	16.3	19.5	
Avg. Hg^0	11.7	9.6	9.1	6.5	10.0	18.6	***11.4***	13.8	12.0	19.8	8.9	***13.6***	14.4	15.7	6.8	***12.3***
Std. Dev	2.9	6.2	3.9	1.9	5.3	5.4	4.1	9.8	2.7	13.6	2.1	4.6	5.8	7.4	4.0	4.8
Hg (part.)	0.04	0.05	0.06	0.03	0.05	0.15	***0.06***	0.07	0.11	0.18	0.05	***0.10***	0.10	0.17	0.01	***0.09***
Std. Dev.	–	–	–	–	–	–	0.04					0.06				0.08
RGM	1.8	2.5	2.6	1.3	2.0	1.7	***2.0***	1.2	2.3	2.4	0.9	***1.7***	1.4	2.4	1.0	***1.6***
Std. Dev.	–	–	–	–	–	–	0.5	–	–	–	–	0.8	–	–	–	0.7
Total Hg	13.5	12.2	11.8	7.8	12.1	20.4	***13.5***	15.1	14.4	22.3	9.8	***15.4***	15.9	18.3	7.8	***14.0***
Std. Dev.	–	–	–	–	–	–	4.1	–	–	–	–	5.2	–	–	–	5.5
% Hg^0	86.4	78.8	77.4	83.0	83.0	91.0	***84.7***	91.6	83.3	88.5	90.4	***88.3***	90.6	85.9	87.1	***87.9***
% Hg(part)	0.3	0.5	0.5	0.4	0.4	0.7	***0.4***	0.5	0.8	0.8	0.5	***0.6***	0.6	0.9	0.1	***0.6***
% RGM	13.3	20.7	22.1	16.6	16.6	8.3	***14.9***	8.0	16.0	10.7	9.1	***11.0***	8.8	13.1	12.8	***11.4***

* The highlighted data were not used in calculating the averages or standard deviations.

Table 6-3
Average Mercury Speciation Results for Each Location (from Table 6-2)*

	Hg_p, µg/Nm^3	Hg^0, µg/Nm^3	RGM, µg/Nm^3	Total Hg, µg/Nm^3	% Hg^0
In the Stack					
Average	0.00	3.2	6.2	9.4	65.7
Std. Dev.	0.00	0.5	0.7	0.7	5.1
Location Nearest the Stack (~1500 ft)					
Average	0.06	11.4	2.0	13.5	84.7
Std. Dev.	0.04	4.1	0.5	4.1	5.0
Location Nominally 5 miles from Stack					
Average	0.10	13.6	1.7	15.4	88.3
Std. Dev.	0.06	4.6	0.8	5.2	4.0
Location Nominally 10 miles from Stack					
Average	0.09	12.3	1.6	14.0	87.9
Std. Dev.	0.08	4.8	0.7	5.5	2.6

* All concentrations are based on normal (N) conditions defined as 1 atmosphere pressure, 20°C, and 3% O_2.

6.2.1 Data Outliers

After the data were reduced, examination revealed a number of high Hg^0 concentrations that corresponded to very high dilution ratios, as shown by the highlighted data in Appendix A (a high dilution ratio is defined as one >3 times the average without that point). The high dilution ratios occurred during intermittent aircraft transit of smaller plume eddies separated from the main body of the plume. These areas had relatively high proportions of ambient air sampled in short times and are not statistically characteristic of the plume material at that distance from the stack. Even with relatively stable winds, turbulent eddies would result in complex plume structure, causing some passes through the plume to only intersect edges of the plume rather than the cross-center line transects that were sought. The peripheral intersects would capture relatively large proportions of ambient air with markedly lower NO_x values than the main body of the plume. During these sampling episodes, the NO_x concentration would be just high enough to trigger the zero-air inlet valve to shut off and begin the sampling process. Once the valve was triggered, the valve was set with a delay to stay off for 5 seconds once the NO_x level again fell below the trigger point. This was done to prevent rapid cycling of the valve, which would make the data nearly impossible to resolve. Since the NO_x concentration was near ambient levels in these segments of the plume, the resulting dilution ratios were artificially high. In retrospect, it would have been better to have set the NO_x trigger point a bit higher (i.e., 10–12 rather than 8–

9 ppb). In addition, the delay could have been reduced to 3 rather than 5 seconds. The highlighted data shown in Table 6-2 are those data points that were calculated based on high dilution ratios and were not used in the averages or determining the mass balances.

Several sets of data were also not used because wind conditions did not allow proper plume formation for sampling, for example, the data for Sample Point 3 on August 31. It was difficult to locate the plume at the 10-mile sampling point. The same was true on September 4 where the winds were variable and light, making it difficult to locate the plume even near the stack. The plume was very spotty at the 5-mile sample point and could not be found at the 10-mile sample point. Instead of trying to sample at 10 miles, it was decided to return to the stack to get more data at that sample point. The winds eventually deteriorated to the point where the plume could not consistently be found even near the stack, and there was no usable data generated for this sample point. Also, none of the negative Hg concentrations was included in the averages. Negative values occurred when the measured Hg concentration in the plume was less than the average background concentration.

6.2.2 Mass Balance Calculations

The stack Hg concentration data were normalized to 3% O_2, 0°C, and 1 atmosphere. The plume data are also reported at 0°C and 1 atmosphere for comparison on an equal basis. The plume data were reduced by first correcting for the amount of sampling time in the plume. This allows a Hg concentration in the plume to be calculated. The plume concentrations were then converted to an equivalent stack concentration by applying dilution factors which were based on the plume and stack NO_x concentrations (shown previously in Equation 1). A complete explanation and examples of the data reduction procedures are presented in Appendix B. A mass balance was calculated using the average total Hg data from each sampling point each day and the corresponding stack data. The results are presented in Table 6-4. Although many of the mass balance closures are somewhat high, they are quite reasonable considering the variability of the data and the difficult nature of the sampling. The most likely causes for the high Hg concentration are underreported NO_x concentration or Hg offgassing from the soda-lime traps used in the aircraft Hg analyzer when exposed to plume gas. These will be discussed in detail in Section 6.2.3.

Table 6-4
Total Hg Mass Balance: Plume Hg Compared to Stack Hg

Sample Point Nearest the Stack			Sample Point 5 miles Out			Sample Point 10 miles Out		
Total Hg in Plume, µg/Nm^3	Total Hg in Stack, µg/Nm^3	Balance, %	Total Hg in Plume, µg/Nm^3	Total Hg in Stack, µg/Nm^3	Balance, %	Total Hg in Plume, µg/Nm^3	Total Hg in Stack, µg/Nm^3	Balance, %
13.5	9.3	145	15.1	9.3	162	15.9	9.3	171
12.2	8.5	144	14.4	8.5	169	18.3	8.5	215
11.8	7.6	155	22.3	7.6	293	7.8	9.2	85
7.8	9.2	85	9.8	9.2	105			
12.1	9.2	131						
20.4	9.2	221						

6.2.3 Plume Hg Speciation Results

Figure 6-2 is a plot of the average percentage of Hg^0 in the plume as it moves from the stack to 10 miles downwind of the stack. There is a substantial increase in the concentration of Hg^0 from the stack to the first sample point, a smaller increase from the first to the second sample point, and then no change to the last sample location (10 miles). Overall, the Hg^0 increases from 67% of the total Hg to 88% by the time it reaches the 5-mile sample point. This is clearly seen in Figure 6-3. The question arises, is this increase real or does it represent a high bias in the Hg^0 concentration measurements in the plume? Figure 6-4 plots the average total plume Hg concentrations (as equivalent stack concentrations) at each location for each day of sampling. The graph shows that the total Hg concentration increased (4 of the 5 days) from the stack to the location nearest the stack and then remains relatively constant as the plume moves downwind. Figure 6-5 plots the RGM concentrations for each sampling point each day and shows that the RGM fraction decreases as the plume moves from the stack downwind. Overall, several factors could cause the Hg^0 concentration (and total Hg) to be reported higher in the plume than in the stack including:

- Low background Hg readings
- Inefficient trapping of the RGM in the Tekran denuder system
- Underreported plume NO_x concentrations
- Integration errors of the NO_x data
- Problems with the soda-lime traps

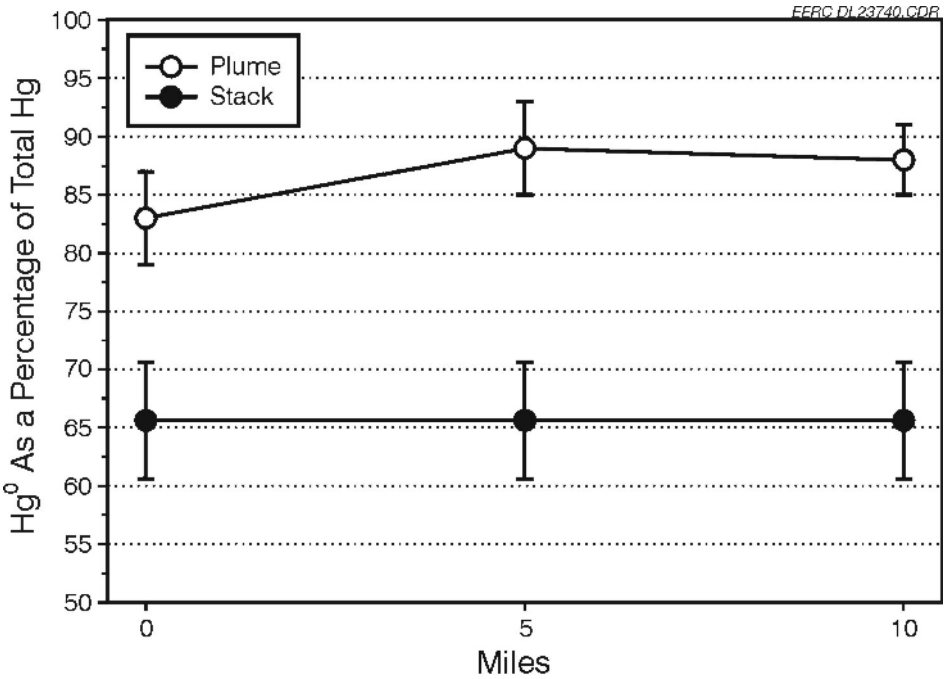

Figure 6-2
Plot of the Concentration of Hg^0 in the Plume As It Moves from the Stack to 10 miles Downwind of the Stack

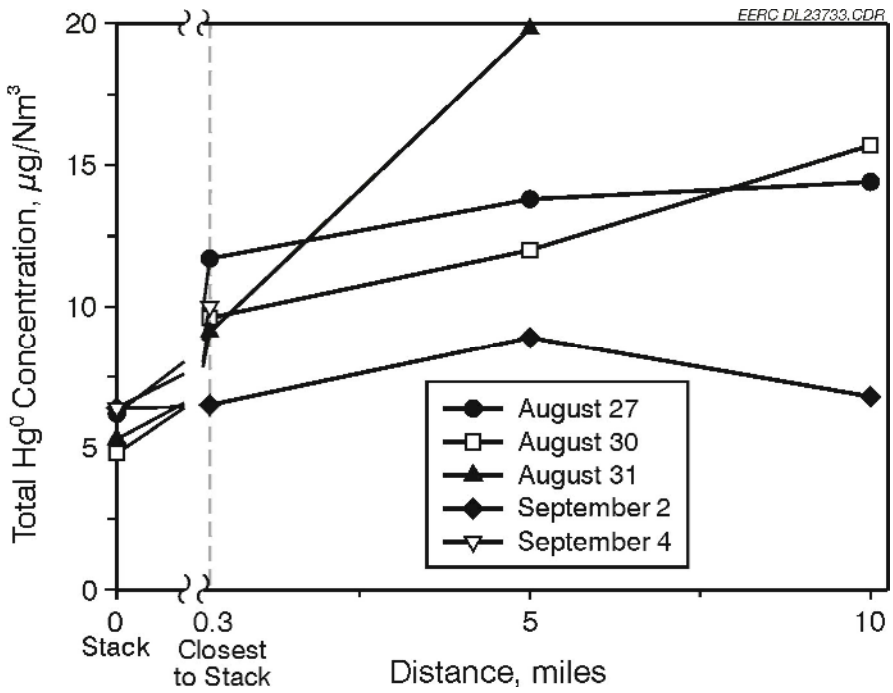

Figure 6-3
Plot of the % Hg^0 in the Plume Compared to the Stack Hg Concentration As a Function of Distance from the Stack

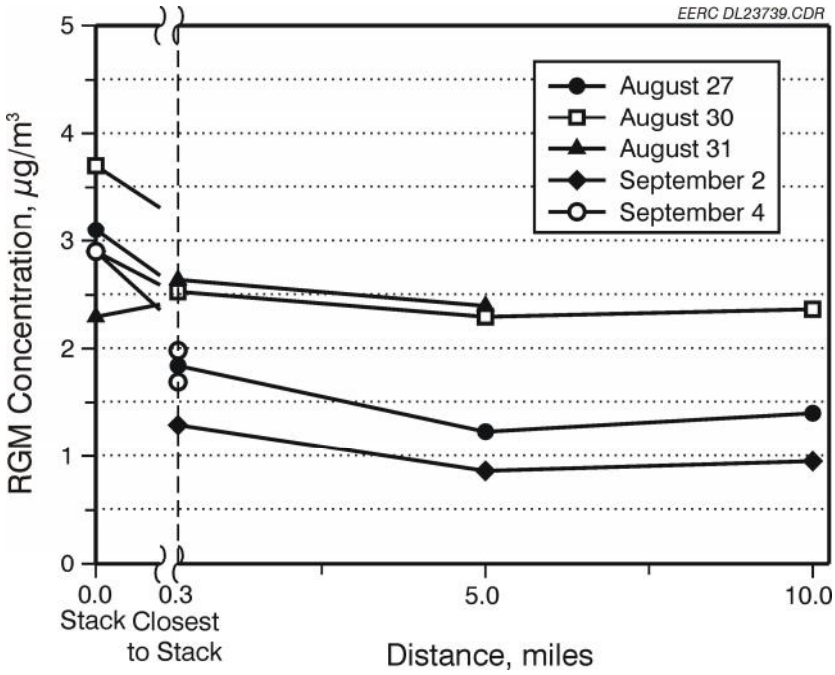

Figure 6-4
Plot of the Concentration of Total Mercury in the Plume As It Moves from the Stack to 10 miles Downwind of the Stack

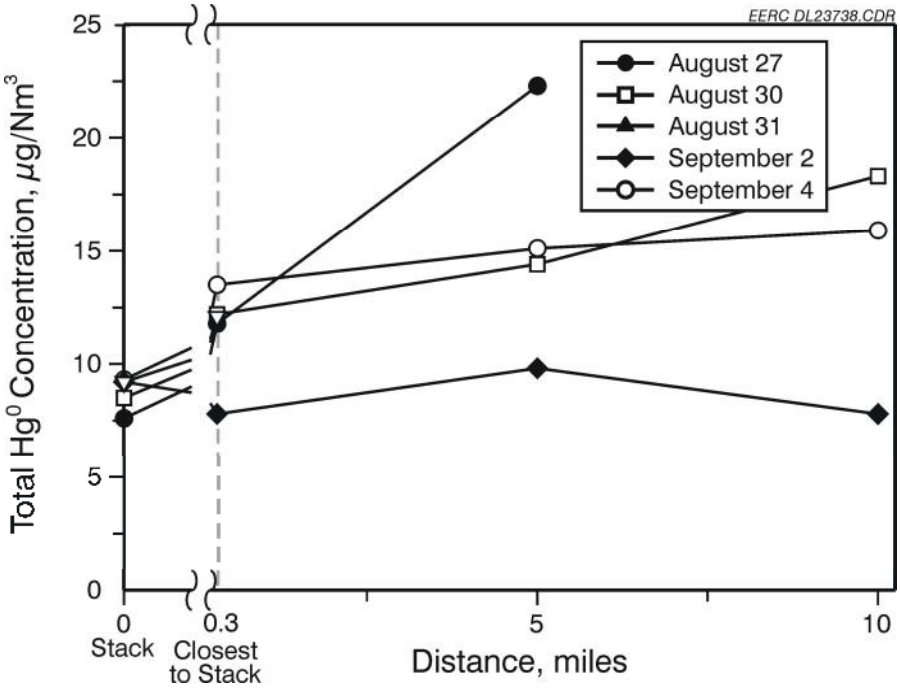

Figure 6-5
Plot of the Concentration of RGM in the Plume As It Moves from the Stack to 10 miles Downwind of the Stack

Each of these possibilities are discussed below.

Low Background Mercury Readings

The subtraction of low background concentrations from the measured plume concentrations would result in higher concentrations when they are converted to equivalent stack concentrations. However, this does not appear to be true because the measured background concentrations were fairly consistent and in the expected range. Also, low background RGM concentrations would have caused those values to be higher as well, and this is not the case. The background Hg concentrations for each day are presented in Table 6-5. On September 2, an additional background sample was taken at the end of the plume-sampling period at a point 10 miles from the plant, but out of the plume. This sample was taken to determine if there was residual Hg in the sampling system after completing the plume sampling. The results from the two background samples on September 2 show there was no residual Hg in the system. It also indicates there were no sampling artifacts when the background Hg concentrations were sampled.

Table 6-5
Background Mercury Concentrations

	Hg^0 Sample, ng/Nm^3											RGM, pg/Nm^3
	1	2	3	4	5	6	7	8	9	10	Avg.	
Aug 27	NS	NS	2.10	1.95	1.90	2.02	1.90	2.07	2.01	1.93	1.99	9.80
Aug 30	NS	1.37	1.53	1.50	1.61	1.51	1.70	NS	NS	NS	1.54	7.18
Aug 31	1.25	1.88	1.97	2.08	2.12	2.16	2.11	2.35	2.16	2.24	2.03	16.20
Sep 2	1.97	2.70	2.32	2.24	2.36	2.23	2.39	2.15	2.00	1.90	2.23	13.16
Sep 2	1.74	1.90	2.25	2.32	2.35	2.26	2.24	2.16	2.19	2.34	2.18	28.89
Sep 4	2.01	2.05	2.32	1.89	1.73	1.71	2.00	1.78	1.74	1.62	1.89	5.52

Inefficient Trapping of the RGM in the Annular Denuder

If the RGM were not trapped in the denuder but passed through to the analyzer, it would be reported as Hg^0. However, if the RGM were to pass through the annular denuder, it would most likely be trapped on the particulate filter and be reported instead as particulate-bound Hg. The data for the particulate-bound Hg concentrations do not suggest this was the case.

Underreported Plume NO_x Concentrations

This would result in larger dilution ratios and higher equivalent stack concentrations, but it would affect both the Hg^0 and the RGM concentrations. As shown in Figure 6-5, the RGM

concentrations show a definite decrease in concentration from the stack to the downwind sampling locations. Even if the plume NO_x concentrations were underreported, it would affect both the Hg^0 and RGM concentrations in the same way and would not affect the ratio of the Hg^0 to RGM. Clearly, the ratio of Hg^0 to RGM does show an evolution as the plume moves downwind from the stack, implying a change in speciation occurring solely within the plume itself between the stack exit and full dispersion into the ambient atmosphere. Similarly, if the stack NO_x concentrations were over-reported, it would result in higher concentrations for both the Hg^0 and the RGM.

Integration Errors of the NO_x Data

This could also result in low average plume NO_x concentrations, but was not likely. At the closest sampling point, sample gas was flowing through the system at all times; zero air was not used. Even though the plane was in the plume for only a few seconds each pass, NO_x and Hg were sampled all of the time. At the 5- and 10-mile sampling points, the plane was in the plume for much longer periods of time, and being off by 1 or 2 seconds in the integration interval would have a negligible effect on the Hg concentration.

Problems with the Soda-Lime Traps

Modified soda-lime traps were used to scrub acid gases from the sample gas stream before it reached the Hg analyzer. At Plant Bowen, it was observed that Hg desorbed from these traps when they were exposed to ambient air rather than when exposed to the scrubbed zero air. There did not appear to be any offgassing of Hg when ambient air was sampled at the Pleasant Prairie Plant, but a different type of soda-lime trap (supplied by Frontier Geosciences) was used. It was not determined during the Bowen sampling if the soda lime would also desorb Hg in the presence of the plume gas. If a small amount of Hg did desorb from the soda-lime trap when exposed to the plume gas, this could be the source of the higher Hg^0 concentrations at the Pleasant Prairie Plant. However, there does not appear to be any way to determine if this was the case or not.

6.3 Vertical Mercury Profile

In addition to plume sampling, a flight was completed to measure Hg concentration as a function of altitude. The first sample was collected 10 miles from the plant at an approximate altitude of 2500 feet in the plume. The second sample point was at an approximate altitude of 500 feet and may have been in the plume. The NO_x concentrations at the 500-foot elevation were higher than at the 2500-foot elevation. These higher levels may have been caused by ground traffic or the plume. There was a major highway running north–south to the east of the sampling point and a lake with heavy boat traffic directly below the sampling point. The third sampling point was at an approximate altitude of 16,500 feet, and the final sample point was at 8500 feet. A correction factor provided by Banic et al. [8] was applied to the data from the last two sample points as shown in Equation 2:

$$GEM_{real} = GEM_{meas} \div [(0.765 \times P_d) + 0.250] \qquad \text{[Eq. 2]}$$

Where: GEM_{real} is the equivalent value at 1 atm pressure
GEM_{meas} is the output of the analyzer at the pressure P_d (expressed in atm) at the detection cell vent

This is a general correction, and Banic et al. suggest the pressure dependence be determined for the specific operating conditions used in an experiment. The results from this flight are presented in Table 6-6. The Hg concentrations at the two lower elevations are presented as measured. Any Hg contributed by the plume has not been subtracted, and no time compensation has been made. The results show there is a significant increase in particulate-bound Hg above the boundary layer and the RGM remains elevated above the background concentrations measured in the boundary layer.

Table 6-6
Vertical Profile Data

	@ 500 ft	@ 2500 ft	@ 8500 ft	@ 16,500 ft	Background
Hg^0 Sample No.			**Hg^0 Concentration, ng/Nm^3**		
1	1.142	1.292	1.151	0.687	0.961
2	1.400	1.616	0.968	0.547	1.369
3	1.650	1.824	0.814	0.437	1.533
4	1.795	1.686	0.881	0.493	1.503
5	1.516	1.748	0.828	0.428	1.613
6	1.532	1.791	0.704	0.370	1.514
7	1.567	1.590	0.873	0.312	1.701
8	1.636	1.625	0.812	0.329	0.659
9	1.903	1.322	0.753	0.288	0.313
10	1.409	1.678	0.751	0.322	0.890
Average	1.555	1.617	0.853	0.421	1.539
			Non-Hg^0 Concentrations, pg/Nm^3		
Hg(part.)	6.812	3.478	29.99	120.2	3.772
RGM	70.968	63.12	55.80	86.05	7.178

7
CONCLUSIONS AND RECOMMENDATIONS

Based on the testing at Pleasant Prairie, the following conclusion can be made:

- Hg can be measured in plumes with reasonable accuracy. However, great care must be taken to prevent contamination.
- Using a dilution factor based on the plume and stack NO_x, a reasonable Hg mass balance can be obtained when the Hg in the stack is compared to the Hg in the plume.
- There appeared to be a reduction in RGM at Pleasant Prairie when the RGM in the plume is compared to the RGM in the stack (with a corresponding increase in Hg^0). There was a 44% reduction of RGM from the stack to the first sample point and a 66% reduction of RGM from the stack to the 5-mile sample point, with no additional reduction between the 5- and 10-mile locations.
- There does appear to be an elevated concentration of particulate-bound Hg and RGM above the boundary layer. However, the Hg^0 concentration does not change.

Although the results from this test along with the work done by Frontier Geosciences and Atmospheric Research & Analysis, Inc., tend to show a reduction in RGM and a corresponding increase in Hg^0 in the plume, it is still inconclusive. The first recommendation is that a mechanism be developed that can logically explain the results. In addition, more testing of this type needs to be done. Ideally, the tests would be conducted at a facility with the following characteristics:

- Fires a coal that generates >70% Hg^{2+} at the stack.
- Has a single stack.
- Does not employee SCR technology.
- Is relatively isolated.

It is clear from the testing done to date that the approach to doing this type of work is sound. However, better methods of finding the plume need to be investigated. A fair number of the data points generated at Pleasant Prairie had to thrown out due to “skimming of the plume” resulting in very high dilution ratios.

8
REFERENCES

1. Toxicological Effects of Methylmercury. *National Academies Press*, Washington, D.C., 2000.

2. Lindqvist, O.; Rodhe, H. Atmospheric Mercury—A Review. *Tellus* **1995**, 37B, 136–159.

3. Danilchik, P; Imhoff, R.; Liang, L.; Valente, R.; Dismukes, E.; Brown, C.; Spurling, D.; Huang, Z.; Prestbo, E. A Comparison of the Fate of Mercury in Flues and Plumes of Coal-Fired Boilers. Presented at the Mercury as a Global Pollutant Conference, July 10–14, 1994, Whistler, British Columbia.

4. Imhoff, R.E. *Preliminary Report on Measurements of Gas- and Particle-Phase Mercury in the Plumes of Coal-Fired Boilers*; Atmospheric Sciences Department, Environmental Research Center, Tennessee Valley Authority, March 15, 1995

5. Prestbo, E.M.; Calhoun, J.A.; Brunette, R.C.; Paladini, M. Hg Speciation in a Simulated Coal Combustion Plume. In *Proceedings of Air Quality: Mercury, Trace Elements, and Particulate Matter Conference*; McLean, VA, Dec 1–4, 1998.

6. Laudal, D.L; Prestbo, E. *Investigation of the Fate of Mercury in a Coal Combustion Plume Using a Static Plume Dilution Chamber*; Final Report for U.S. Department of Energy Contract No. DE-FC-26-95FT40321; Energy & Environmental Research Center: Grand Forks, ND, Oct 2001.

7. Edgerton, E.; Hartsell, B.; Jansen, J. Field Observations of Mercury Partitioning in Power Plant Plumes. In *Proceedings of the International Conference on Air Quality III: Mercury, Trace Elements, and Particulate Matter*; Arlington, VA, Sept 2002

8. Banic, C.M.; Beauchamp, S.T.; Tordon, R.J.; Schroeder, W.H.; Steffen, A.; Anlauf, K.A.; Wong, H.K.T. Vertical Distribution of Gaseous Elemental Mercury in Canada. *J. Geophys. Res.* **2003**, *108* (D9), 4264.

A.II
MERCURY WORKSHEETS

On all tables, highlighted area indicates data suspect because of high dilution ratios.

Mercury Worksheets

Table A.I-1
Complete Data Mercury Worksheet: August 27, 2003

SAMPLE POINT 1, Hg^0					
Tekran Sample No.	Dilution Ratio	Sample Time, sec	Plume Hg^0 Conc., ng/Nm^3	Contribution to Stack Conc., µg/Nm^3	Stack Hg^0 Conc., µg/Nm^3
1	663	12		4.3	
	218	14	14.2	1.7	6.0
2	2685	9	15.6	42.0	42.0
3	1019	13		8.0	
	444	10	13.8	2.7	10.6
4	1039	11		3.3	
	409	12		1.4	
	1080	16	11.4	5.0	9.8
5	343	7		1.0	
	1158	22	12.4	10.9	11.9
6	694	8		3.6	
	11,722	4		30.5	
	1135	5	11.1	3.7	37.8
7	1304	5		5.1	
	826	12	13.3	7.8	12.9
8	275	9		2.8	
	774	13	24.6	11.2	14.0
9	372	8		1.7	
	1251	19	15.7	13.8	15.5
10	778	8		3.3	
	1742	8		7.3	
	335	11	14.2	1.9	12.5

Tekran Sample No.	Sample Time, sec	Plume Conc., pg/Nm^3	Stack Conc., µg/Nm^3
Hg_p	236	47.8	0.04
RGM	236	2455.9	1.84
Total Hg			19.2

SAMPLE POINT 2, Hg^0					
Tekran Sample No.	Dilution Ratio	Sample Time, sec	Plume Hg^0 Conc., ng/Nm^3	Contribution to Stack Conc., µg/Nm^3	Stack Hg^0 Conc., µg/Nm^3
1	15,763	131	0.2	2.8	2.8
2	24,956	17		6.0	
	20,579	76	1.3	22.3	28.3
3	61,132	63		25.1	
	25,085	51	0.7	8.4	33.5
4	6441	71		8.6	
	90,934	16	1.6	27.5	36.1
5	17,117	141	0.7	11.8	11.8
6	96,996	17		13.9	
	727,465	7		43.0	
	24,453	90	1.0	18.6	75.5
7	16,421	50		19.1	
	111,918	13		33.8	
	15,478	9	1.7	3.2	56.1
8	19,985	138	0.4	8.3	8.3
9	24,660	133	0.7	17.8	17.8
10	83,617	30		13.6	
	76,576	9		4.9	
	24,249	85	0.7	11.2	28.5

Tekran Sample No.	Sample Time, sec	Plume Conc., pg/Nm^3	Stack Conc., µg/Nm^3
Hg_p	1147	4.6927	0.07
RGM	1147	81.3864	1.23
Total Hg			31.2

SAMPLE POINT 3					
Tekran Sample No.	Dilution Ratio	Sample Time, sec	Plume Hg^0 Conc., ng/Nm^3	Contribution to Stack Conc., µg/Nm^3	Stack Hg^0 Conc., µg/Nm^3
1	31,488	150	0.04	1.2	1.2
2	17,011	41		0.9	
	32,887	106	0.19	4.4	5.3
3	28,460	115		5.8	
	31,488	35	0.27	2.0	7.8
4	32,887	132		10.9	
	87,055	12		2.6	
	147,993	6	0.38	2.2	15.7
5	24,261	150	0.33	7.9	7.9
6	37,947	14		4.1	
	61,664	14		6.6	
	27,406	81	0.84	17.0	27.7
7	26,427	150	0.65	17.2	17.2
8	18,499	59		6.8	
	56,921	22		7.8	
	23,124	37	0.73	5.3	19.9
9	23,870	110		12.2	
	23,870	24	0.62	2.7	14.8
10	24,666	107		17.7	
	44,846	5	0.75	1.5	19.2

Tekran Sample No.	Sample Time, sec	Plume Conc., pg/Nm^3	Stack Conc., µg/Nm^3
Hg_p	1370	3.62	0.10
RGM	1370	50.35	1.40
Total Hg		54.0	14.9

Table A.I-2
Complete Data Mercury Worksheet: August 30, 2003

SAMPLE POINT 1, Hg^0						SAMPLE POINT 2, Hg^0						SAMPLE POINT 3, Hg^0					
Tekran Sample No.	Dilution Ratio	Sample Time, sec	Plume Hg^0 Conc., ng/Nm^3	Contribution to Stack Conc., µg/Nm^3	Stack Hg^0 Conc., µg/Nm^3	Tekran Sample No.	Dilution Ratio	Sample Time, sec	Plume Hg^0 Conc., ng/Nm^3	Contribution to Stack Conc., µg/Nm^3	Stack Hg^0 Conc., µg/Nm^3	Tekran Sample No.	Dilution Ratio	Sample Time, sec	Plume Hg^0 Conc., ng/Nm^3	Contribution to Stack Conc., µg/Nm^3	Stack Hg^0 Conc., µg/Nm^3
1	207	8		1.0		1	27,424	34		4.2		1	19,532	63		2.5	
	1060	8	10.1	5.3	6.4		10,528	103	0.6	4.9	9.2		15,666	51	0.23	1.6	4.1
2	377	11	20.0	7.5	7.5	2	35,746	15		2.8		2	28,270	53		6.0	
							16,630	86	0.5	7.4	10.2		59,680	11		2.6	
													53,331	13		2.8	
													16,171	27	0.42	1.8	13.2
3					NS	3	45,071	14		3.7		3	17,862	54		5.2	
							18,986	14		1.6			16,312	88	0.76	7.7	12.8
							11,044	104	0.8	6.7	12.0						
4	646	4	7.2	4.7	4.7	4	20,677	80		5.1		4	21,123	38		8.7	
							40,812	21		2.6			74,452	15		12.1	
							36,760	2	0.3	0.2	7.9		26,385	26	0.86	7.4	28.3
5	1912	5	4.7	9.0	9.0	5	58,456	7		2.5		5	18,296	55		5.1	
							20,487	111	0.7	13.9	16.3		25,066	62	0.59	7.9	13.0
6	344	13	19.0	6.5	6.5	6	7331	55		5.1		6	26,761	81	1.02	27.3	27.3
							34,325	10		4.3							
							35,994	12	1.0	5.4	14.8						
7	1315	11	11.1	14.5	14.5	7	13,012	84	1.0	12.5	12.5	7	20,602	93		15.1	
													105,911	7	0.79	5.9	21.0
8	435	11		2.6		8	10,535	73	1.3	13.6	13.6	8	27,245	96	0.43	11.6	11.6
	685	14	13.8	5.3	7.9												
9	442	12		4.3		9	46,004	11		4.3		9	24,257	88	0.94	22.7	22.7
	309	6	14.5	1.5	5.8		16,454	83	0.8	11.5	15.7						
10	1138	3		16.1		10	13,155	90		8.0		10	30,079	95		10.1	
	429	4	33.1	8.1	24.2		88,854	7		4.2			88,467	11		3.4	
							49,998	14	0.8	4.7	17.0		59,680	13	0.42	2.7	16.3

Tekran Sample No.	Sample Time, sec	Plume Conc., pg/Nm^3	Stack Conc., µg/Nm^3	Tekran Sample No.	Sample Time, sec	Plume Conc., pg/Nm^3	Stack Conc., µg/Nm^3	Tekran Sample No.	Sample Time, sec	Plume Conc., pg/Nm^3	Stack Conc., µg/Nm^3
Hg_p	110	70.5	0.05	**Hg_p**	1030	6.80227	0.11	**Hg_p**	1040	8.11	0.17
RGM	110	3869.0	2.53	**RGM**	1030	141.277	2.33	**RGM**	1040	111.29	2.37
Total Hg			12.2	**Total Hg**			15.4	**Total Hg**		119.4	19.6

Mercury Worksheets

Table A.I-3
Complete Data Mercury Worksheet: August 31, 2003

SAMPLE POINT 1, Hg^0					
Tekran Sample No.	Dilution Ratio	Sample Time, sec	Plume Hg^0 Conc., ng/Nm^3	Contribution to Stack Conc., µg/Nm^3	Stack Hg^0 Conc., µg/Nm^3
1	338	7	4.7	1.6	1.6
2	153	8		2.8	
	263	6	31.6	3.6	6.3
3	196	9	24.1	4.7	4.7
4	345	6		4.7	
	284	5	25.2	3.3	8.0
5	612	3	25.5	15.6	15.6
6	245	8		3.3	
	273	9	28.4	4.1	7.4
7	908	9		8.8	
	8760	1	10.8	9.4	18.2
8	468	4		4.5	
	389	6	24.1	5.6	10.1
9	516	8		6.9	
	275	7	25.2	3.2	10.2
10	256	7		4.6	
	333	5	30.9	4.3	8.9

SAMPLE POINT 2, Hg^0					
Tekran Sample No.	Dilution Ratio	Sample Time, sec	Plume Hg^0 Conc., ng/Nm^3	Contribution to Stack Conc., µg/Nm^3	Stack Hg^0 Conc., µg/Nm^3
1	27,536	15		2.0	
	11,023	68	0.4	3.6	5.6
2	6656	68	2.1	13.9	13.9
3	12,485	81	1.3	15.7	15.7
4	28,486	13		6.0	
	7999	32		4.2	
5	15,251	12		5.9	
	17,111	24		13.2	
	12,412	17	1.7	6.8	25.9
6	8526	35		4.5	
	10,283	65	1.5	10.0	14.5
7	15,603	40	3.2	49.8	49.8
8	13,642	52		9.7	
	56,324	8		6.2	
	94,710	7	0.9	9.1	25.0
9	10,227	22		2.6	
	15,142	33		5.8	
	45,059	25	0.9	13.2	21.6
10	38,522	26	2.3	89.3	89.3

SAMPLE POINT 3, Hg^0					
Tekran Sample No.	Dilution Ratio	Sample Time, sec	Plume Hg^0 Conc., ng/Nm^3	Contribution to Stack Conc., µg/Nm^3	Stack Hg^0 Conc., µg/Nm^3
1	755,473	3		8.0	
	30,219	68	0.3	7.3	15.3
2	33,577	62		-5.5	
	137,359	11	-0.2	-4.0	-9.4
3	755,471	2		3.7	
4	54,944	71	0.4	23.2	23.2
5	60,438	30		-0.9	
	137,359	25		-1.7	
	107,924	50		-2.7	
	83,942	22	0.1	0.9	6.4
6	70,277	25		9.0	
	44,440	45	0.4	10.2	19.2
7	100,730	16		5.3	
	45,787	13		2.0	
	137,359	16		7.3	
	137,359	14		6.4	
	232,454	7		5.4	
	62,956	32	0.3	6.7	31.8
8	177,759	13		100.2	
	52,102	17		38.4	
	73,705	11	1.8	35.2	173.8
9	125,912	11		18.0	
	79,524	18		18.7	
	39,762	27		14.0	
	81,673	11	0.9	11.7	60.6
10	83,942	13		10.1	
	62,956	16		9.3	
	167,883	7	0.3	10.8	30.2

Tekran Sample No.	Sample Time, sec	Plume Conc., pg/Nm^3	Stack Conc., µg/Nm^3
Hg_p	108	160.9	0.06
RGM	108	7397.0	2.64
Total Hg			

Tekran Sample No.	Sample Time, sec	Plume Conc., pg/Nm^3	Stack Conc., µg/Nm^3
Hg_p	662	11.2507	0.18
RGM	662	153.611	2.42
Total Hg			

Tekran Sample No.	Sample Time, sec	Plume Conc., pg/Nm^3	Stack Conc., µg/Nm^3
Hg_p	742	9.1	
RGM	742	15.1	
Total Hg			

Table A.I-4
Complete Data Mercury Worksheet: September 2, 2003

SAMPLE POINT 1, Hg^0						SAMPLE POINT 2, Hg^0						SAMPLE POINT 3, Hg^0					
Tekran Sample No.	Dilution Ratio	Sample Time, sec	Plume Hg^0 Conc., ng/Nm^3	Contribution to Stack Conc., µg/Nm^3	Stack Hg^0 Conc., µg/Nm^3	Tekran Sample No.	Dilution Ratio	Sample Time, sec	Plume Hg^0 Conc., ng/Nm^3	Contribution to Stack Conc., µg/Nm^3	Stack Hg^0 Conc., µg/Nm^3	Tekran Sample No.	Dilution Ratio	Sample Time, sec	Plume Hg^0 Conc., ng/Nm^3	Contribution to Stack Conc., µg/Nm^3	Stack Hg^0 Conc., µg/Nm^3
1	276	9		3.4		1	10,431	51		2.6		1	16,022	101		1.5	
	186	8	23.5	2.1	5.5		69,450	12		4.0			21,205	7	0.1	0.1	1.6
							6332	35	0.5	1.1	7.6						
2	143	8		2.5		2	16,192	26		3.8		2	20,599	119	0.4	8.6	8.6
	608	5	28.7	6.7	9.2		8495	80	1.0	6.2	10.0						
3	196	7	28.9	5.7	5.7	3	57,174	9		12.8		3	16,022	111	0.5	7.6	7.6
							6650	62		10.3							
							49,606	1	1.8	1.2	24.4						
4	2274	4	-5.8	-13.1	-13.1	4	66,414	6		3.0		4	18,493	105		5.0	
							10,682	71		5.7			57,958	6	0.3	0.9	5.9
5	4771	4	3.2	15.4	15.4	5	9892	74		8.4		5	57,958	11		3.8	
							7672	21	1.1	1.9	10.3		18,520	92		10.2	
													60,391	8	0.7	2.9	16.9
6	343	5		2.5		6	10,322	53		4.1		6	21,522	124	0.2	3.7	3.7
	186	5	14.9	1.4	3.9		10,222	65	0.9	5.0	9.1						
7					NS*	7	80,183	11		6.2		7	37,946	35		5.8	
							43,659	11		3.4			18,973	100	0.6	8.2	14.0
							11,606	84	0.7	6.8	16.4						
8	492	4		3.4		8	22,221	7		4.0		8	21,205	123	0.3	6.1	6.1
	369	6	17.2	3.8	7.2		65,124	46	1.4	76.6	80.6						
9					NS	9	17,398	90		4.6		9	86,813	13		5.9	
							23,923	9	0.3	0.6	5.3		17,756	122		11.3	
													46,300	1	0.7	0.2	17.4
10	188	6		2.9		10	124,057	10		9.7		10	106,846	6		4.0	
	226	8	36.1	4.7	7.6		8539	67		4.5			19,507	129	0.8	15.5	19.5
							9500	24	0.8	1.8	16.0						

Tekran Sample No.	Sample Time, sec	Plume Conc., pg/Nm^3	Stack Conc., µg/Nm^3	Tekran Sample No.	Sample Time, sec	Plume Conc., pg/Nm^3	Stack Conc., µg/Nm^3	Tekran Sample No.	Sample Time, sec	Plume Conc., pg/Nm^3	Stack Conc., µg/Nm^3
Hg_p	79	115.6	0.03	**Hg_p**	943	4.98017	0.05	**Hg_p**	1213	0.6	0.01
RGM	79	5300.7	1.29	**RGM**	943	86.4234	0.86	**RGM**	1213	50.4	0.95
Total Hg			2.6	**Total Hg**			20.0	**Total Hg**			11.1

* No sample.

Mercury Worksheets

Table A.I-5
Complete Data Mercury Worksheet: September 4, 2003

SAMPLE POINT 1, Hg^0						SAMPLE POINT 1, Hg^0						SAMPLE POINT 2, Hg^0					
Tekran Sample No.	Dilution Ratio	Sample Time, sec	Plume Hg^0 Conc., ng/Nm^3	Contribution to Stack Conc. µg/Nm^3	Stack Hg^0 Conc., µg/Nm^3	Tekran Sample No.	Dilution Ratio	Sample Time, sec	Plume Hg^0 Conc., ng/Nm^3	Contribution to Stack Conc. µg/Nm^3	Stack Hg^0 Conc., µg/Nm^3	Tekran Sample No.	Dilution Ratio	Sample Time, sec	Plume Hg^0 Conc., ng/Nm^3	Contribution to Stack Conc. µg/Nm^3	Stack Hg^0 Conc., µg/Nm^3
1	596	6		-0.5		1					NS	1	86,954	7		86.6	
	117,182	1	-0.9	-15.7	-16.2								53,975	18		138.2	
													34,577	12	5.3	59.0	283.7
2	713	8	7.1	5.0	5.0	2	731	4		10.2		2	43,180	12		140.5	
							249	7	38.2	6.1	16.2		80,196	20	8.7	434.8	575.3
3	6163	2	0.6	4.0	4.0	3	334	8	49.5	16.5	16.5	3	34,841	28		130.6	
													79,424	7		74.4	
													22,258	5	5.4	14.9	220.0
4	675	4	3.4	2.3	2.3	4	4596.55	7	34.3	157.7	157.7	4	22,322	19		5.3	
													70,053	13		11.4	
													50,304	11		6.9	
													20,938	36		9.4	
													65,850	7		5.7	
													40,275	6	1.1	3.0	50.4
5					NS	5	455	10	39.6	18.0	18.0	5	45,103	23		43.7	
													14,063	44	2.8	26.1	69.7
6	713	6	24.5	17.5	17.5	6					NS	6	20,076	16		4.0	
													42,873	11		5.9	
													36,682	15		6.9	
													26,660	70	1.4	23.2	44.6
7	301	3	49.9	15.0	15.0	7	1218.58	8	36.0	43.9	43.9	7	36,381	9		128.7	
													65,198	7		179.4	
													78,862	10	10.2	309.9	618.0
8	347	5	30.4	10.6	10.6	8	390	10		7.6		8	136,073	10		259.4	
							535	5	29.3	5.2	12.8		44,939	17	5.1	145.7	405.1
9	369	7	26.6	9.8	9.8	9	647	12	29.7	19.2	19.2	9	30,178	48		69.8	
													182,699	7	2.7	61.6	131.4
10	292	4		4.0		10	806	8	35.7	28.7	28.7	10	41,849	8		411.7	
	437	4	27.2	6.0	9.9								71,576	7	18.4	616.1	1027.8

Tekran Sample No.	Sample Time, sec	Plume Conc., pg/Nm^3	Stack Conc., µg/Nm^3	Tekran Sample No.	Sample Time, sec	Plume Conc., pg/Nm^3	Stack Conc., µg/Nm^3	Tekran Sample No.	Sample Time, sec	Plume Conc., pg/Nm^3	Stack Conc., µg/Nm^3
Hg_p	50	108.3	0.05	**Hg_p**	79	277.8	0.15	**Hg_p**	503	5.79	
RGM	50	4051.0	1.98	**RGM**	79	3155.8	1.69	**RGM**	503	23.42	
Total Hg			7.6	**Total Hg**			41.0	**Total Hg**			

A.II
DATA REDUCTION PROCEDURES

The Tekran mercury (Hg) sampling system was set up so that the Model 2537A ran continuously providing an Hg^0 reading every 2.5 minutes regardless of the sample source. The Model 1130 and Model 1135 (particulate-bound Hg and reactive gas mercury [RGM], respectively) were synchronized with the Model 2537A and completed a sample/desorb cycle in 1 hour. There were 24 Model 2537A sample cycles in 1 hour and are as follows:

- For Cycles 1–10, sample gas was pulled through the denuder and particulate filter removing the RGM and particulate-bound Hg. The readings for Cycles 1–10 are then the elemental mercury (Hg^0) concentration in the sample gas.
- For Cycle 11, the sampling system is flooded with zero air, and the pyrolizer in the Model 1135 is heated.
- For Cycles 12–16, the particulate filter is heated and desorbed. The total concentration of Hg on the particulate filter is the sum of the five values for Cycles 12–16.
- For Cycles 17–21, the denuder is heated and desorbed. Again, the total RGM concentration is the sum of the five values for Cycles 17–21.
- For Cycles 22–24, zero-air flow is maintained through the system, and cooling air for the components is initiated.

In this appendix, each Hg^0 reading from the Model 2537A is called a "Tekran Sample" basically denoting which 2.5-minute sampling cycle a sampling event occurred in. In addition, for each 2.5-minute sampling cycle (Cycles 1–10 only), there were several sampling "events." These events included a pass through the plume (Sample Point 1) or a cycling of the zero air off and on (Sample Points 2 and 3).

The following is a description of the data reduction procedure used to convert the raw Hg data to an equivalent stack Hg concentration. Examples are given for Sample Point 1, which was the closest to the plant. In some instances where the procedure is different, examples are also given for Sample Point 2.

1. Import raw NO_x data for a given flight to a worksheet labeled "NO_x data."

2. Import raw valve data for a given flight to a "Time data" worksheet.

3. Import raw Hg data for a given flight to a worksheet labeled "Raw Hg data."

4. Set up the "NO_x data" page for each sampling point in the format shown in Table A.II-1.

Data Reduction Procedures

Table A.II-1
Data Format for Converting Plume Hg Data to Equivalent Stack Hg Data

SAMPLE POINT 1

Average Stack NO_x = ppm

Time	NO_x Conc., ppb	Average Conc., ppb	Tekran Sample	Average Background NO_x, ppb	Average Plume NO_x, ppb	Dilution Ratio

Where: "Average Stack NO_x, ppm" = stack concentration averaged over sampling period. For further test points, the time of plume travel must also be taken into account. This value is used in the calculation of the dilution ratio.

"Time" = time of the airplane NO_x sample, taken from raw data file. Concentrations were recorded once every second.

"NO_x Conc., ppb" = plume NO_x concentration which is taken from the raw data.

"Average Conc., ppb" = column used to calculate either the average background or average plume NO_x concentrations. The average plume concentrations are calculated for either a given pass through the plume (Sample Point 1), or a period of time when the zero air was off (Sample Points 2 and 3). The average background concentration is calculated when the plane was not in the plume.

"Tekran Sample" = the plane passed through the plume 2–3 times during each 2.5-minute Tekran sampling cycle for Sample Point 1, or the zero air was turned off and on several times for Sample Points 2 and 3. Therefore, "Tekran Sample" denotes which of the ten sample cycles each pass through the plume or zero air off occurred.

"Average Background NO_x, ppb" = average NO_x concentration when not in the plume.

"Average Plume NO_x, ppb" = average NO_x concentration when in the plume. Transferred from the "Average Conc., ppb" column. There is a value for each pass through the plume (Sample Point 1) or each time the zero air was turned off (Sample Points 2 and 3).

"Dilution Ratio" is defined as shown in Equation A.II-1:

$$\text{Dilution Ratio} = \frac{[(\text{average stack } NO_x) \times 1000 - (\text{average background } NO_x)]}{[(\text{average plume } NO_x) - (\text{average background } NO_x)]} \quad \text{[Eq. A.II-1]}$$

5. Set up the "Time data" worksheet for each sample point in the format shown in Table A.II-2.

Table A.II 2
Format for Sample Time

SAMPLE POINT 1

Sample No.	Time On	Time Off	Sample Time, sec	Time On	Time Off	Sample Time, sec	Time On	Time Off	Sample Time, sec	Total Time, sec

Where: "Sample" denotes during which of the ten Hg^0 Tekran sample cycles an "event" occurred.

"Time On" denotes when the plume was entered and the sample gas was turned on (corresponds to the zero air being turned off).

"Time Off" denotes when the plane left the plume (sample off, zero air on).

Note: There needs to be a "Time On" and "Time Off" column for each time the zero-air valve is actuated.

"Sample Time, sec" is the time in the plume (Time off - Time on). This is repeated for each time the zero air valve is cycled during a 2.5-minute sample cycle.

"Total Time" = sum of "Sample Time" for each 2.5-minute sample cycle.

6. Set up the "Hg data" worksheet with the following columns (Table A.II-3) for each sample point (the columns that need to be set up for the background sample point will also be noted):

Data Reduction Procedures

Table A.II 3
Sample Data Format

SAMPLE POINT 1			
Tekran Cycle Time		2.5	Min
Denuder Absorb Time		25	Min
Hg^0 Sample No.	Sample Time, min	Hg^0 Conc., ng/Nm^3	Hg Conc., ng/Nm^3
1	0.43	4.445	14.19
2	0.15	2.922	15.62
3	0.38	4.104	13.82
4	0.65	4.936	11.35
5	0.48	4.377	12.37
6	0.28	3.238	11.06
7	0.28	3.496	13.34
8	0.37	5.587	24.56
9	0.45	4.809	15.69
10	0.45	4.532	14.15
Hg(part) Sample No.		Hg^0 Conc., pg/Nm^3	Total, pg/Nm^3
1	3.93	3.15	47.8
2		2.53	
3		4.18	
4		2.60	
5		2.49	
RGM Sample No.		Hg^0 Conc., pg/Nm^3	Total, pg/Nm^3
1	3.93	302.183	2455.9
2		80.976	
3		5.777	
4		4.519	
5		2.762	

Where: The "Tekran Cycle Time" and "Denuder Absorb Time" were potential variables, but did not vary during the testing program.

"Hg^0 Sample No." denotes which of the Tekran Cycles 1–10 the Hg^0 concentration corresponds to. Also make a column with this heading for the Background sample point.

"Sample Time, min" = total time in the plume taken from the "NO_x data" page for the given sample Cycle 1–10.

"Hg^0 Conc., Ng/Nm^3" = Hg^0 concentration from the "raw Hg data" worksheet for the corresponding sample Cycle 1–10. Also make a column with this heading for the Background sample point, and average the values in this column for the average background concentration.

"Hg^0 Conc., ng/Nm^3" = the average Hg^0 concentration in the plume.

Example: Using the values from the first sample cycle for (Sample Point 1) in Table A.II-3, the Hg^0 concentration is calculated as shown in Equation A.II-2:

$$Hg^0\ \text{Conc.} = (4.445 - 2.0) \times \frac{2.5}{0.43} = 14.19\,\text{ng/Nm}^3 \qquad \text{[Eq. A.II-2]}$$

The first term in Equation A.II-2 is the Hg^0 concentration measurement for the first sampling cycle. The second term is the average background Hg^0 concentration which is found elsewhere on the worksheet. The third term is the ratio of Tekran cycle time to time in the plume. For Sample Point 1, no zero air was used. The system sampled outside air at all times. Therefore, to get a plume concentration of Hg^0, first the average background concentration is subtracted from each Tekran Hg^0 sample data point. The remainder is the plume contribution to the Tekran Hg^0 sample concentration. This number needs to be corrected for time. The contribution from the plume was not collected over the entire Tekran sampling cycle. The correction factor is the ratio of the Tekran sample time (2.5 minutes) to the actual sample time (less than 2.5 minutes). This gives the average plume Hg^0 concentration for each Tekran sample Cycle 1–10.

For Sample Points 2 and 3, the system is purged with zero gas when the aircraft was not in the plume. The measured value is the sum of the background and plume concentrations for the sample period. The time correction is applied to the measured value first. The background concentration is then subtracted to give the flue gas Hg concentration in the plume. The calculations for Hg^0, particulate-bound Hg, and RGM are shown in Equations A.II-3 through A.II-5.

$$Hg^0\ \text{Conc.} = \left(1.887 \times \frac{2.5}{2.18}\right) - 2.0 = 0.16\,\text{ng/Nm}^3 \qquad \text{[Eq. A.II-3]}$$

The first term is the measured Hg concentration for the Tekran sampling cycle. The second term is the ratio of sampling cycle time to the total time in the plume. The third term is the background Hg^0 concentration.

$$\mathrm{Hg_{part}\ Conc.} = \mathrm{sum}(3.15 \ldots 2.493) - 7.5 \times \frac{25}{3.93} \qquad \text{[Eq. A.II-4]}$$

The first term is the sum of the measurements for Cycles 12–16. The second term is the average background particulate-bound Hg concentration taken from elsewhere on the worksheet. The third term is the ratio of cycle time to total time in the plume. The calculations are similar for the RGM concentration.

An example for data from Sample Point 2:

$$\mathrm{Hg_{RGM}\ Conc.} = \mathrm{sum}(1.639 \ldots 1.651) \times \frac{25}{19.12} - 7.5 \qquad \text{[Eq. A.II-5]}$$

7. Set up a “Sample Integration” worksheet with the following columns for each sample point (Table A.II-4):

Table A.II-4
Sample Integration

SAMPLE POINT 1, Hg^0

Tekran Sample No.	Dilution Ratio	Sample Time, sec	Plume Hg^0 Conc., ng/Nm^3	Contribution to Stack Conc., µg/Nm^3	Stack Hg^0 Conc., µg/Nm^3
1	663	12		4.3	
	218	14	14.2	1.7	6.0
2	2685	9	15.6	42.0	42.0
3	1019	13		8.0	
	444	10	13.8	2.7	10.6
4	1039	11		3.3	
	409	12		1.4	
	1080	16	11.4	5.0	9.8
5	343	7		1.0	
	1158	22	12.4	10.9	11.9
6	694	8		3.6	
	11,722	4		30.5	
	1135	5	11.1	3.7	37.8
7	1304	5		5.1	
	826	12	13.3	7.8	12.9
8	275	9		2.8	
	774	13	24.6	11.2	14.0
9	372	8		1.7	
	1251	19	15.7	13.8	15.5
10	778	8		3.3	
	1742	8		7.3	
	335	11	14.2	1.9	12.5

	Sample Time, sec	Plume Conc., pg/Nm^3	Stack Conc. Equiv., µg/Nm^3
Hg(part)	236	47.8	0.04
RGM	236	2455.9	1.84
Total Hg			19.2
% RGM			9.6%
% Hg^0			90.2%
% Hg(part)			0.2%

Where: "Tekran Sample No." again notates which Hg^0 sample cycle.

"Dilution Ratio" is taken from the "NO_x data" worksheet (Table A.II-1). For each pass through the plume, there is a corresponding average dilution ratio. In the above example, the dilution ratio for the first pass through the plume during the first Tekran Hg^0 sampling cycle at Sample Point 1 was 629 ppb.

"Sample Time, sec" = the time in the plume during each pass or when the zero-air valve is deactivated, taken from the "Time data" worksheet (Table A.II-2).

"Plume Hg^0 Conc., ng/Nm^3" = the average Hg^0 concentration in the plume for the corresponding Tekran sample no., taken from the "Hg data" worksheet (Table A.II-3).

"Contribution to Stack Conc., µg/Nm^3" = the plume concentration for each pass converted to a stack concentration as shown in the example in Equation A.II-6:

$$\frac{12}{(12+14)} \times \frac{629 \times 14.2}{1000} = 4.1 \mu g / Nm^3 \qquad \text{[Eq. A.II-6]}$$

The first term is the time for the first pass through the plume divided by the total time in the plume for the Tekran sample Cycle 1. The second term is the dilution ratio for the first pass times the average plume concentration for the first Tekran sample cycle (divided by 1000 to convert to µg/Nm^3). A similar calculation is made to convert the particulate-bound and RGM concentrations to stack equivalent values.

"Stack Hg^0 Conc., µg/Nm^3" = sum of the "Contribution to Stack Conc., µg/Nm^3" values.