

REPORT
ON
AMBIENT MERCURY
MONITORING
NEAR ERCO WORLDWIDE,
PORT EDWARDS, WISCONSIN
DECEMBER 1, 2008

—

MARCH 31, 2011

CONDUCTED BY WISCONSIN DNR

Natural Resources Board

Jonathon P. Ela, Chair, Madison

John W. Welter, Vice-Chair, Eau Claire

David Clausen, Secretary, Amery

Preston D. Cole, Milwaukee

Gary E. Rhode, River Falls

Christine L. Thomas, Stevens Point

Jane Wiley, Wausau

Wisconsin Department of Natural Resources

Cathy Stepp, Secretary

Matt Moroney, Deputy Secretary

Scott Gunderson, Executive Assistant

Air and Waste Division

Patrick Stevens, Division Administrator

Suzanne Bangert, Deputy Administrator

Bureau of Air Management

John Melby, Director

Bart Sponseller, Air Monitoring Section Chief

Author

David (Vid) Grande, Air Toxics Chemist, Air Monitoring Section

Executive Summary

Mercury cell chlor-alkali plants are recognized as significant mercury sources to the environment. Most of these plants have either closed or converted to non-mercury using technologies, so that now only a handful of these plants remain in the United States.

ERCO Worldwide owns and operates a chlor-alkali plant in Port Edwards, Wisconsin, which, until 2009, used the mercury cell technology. Prior to this time, the facility was responsible for about 20% of the annual mercury emissions reported in Wisconsin. In August 2007, ERCO's parent company, Superior Plus, approved a capital investment to replace the mercury cell technology with membrane cell technology. This \$135MM project was intended to eliminate process-based mercury emissions to the environment, expand production capability, strengthen the business for the future and secure jobs in southern Wood County.

The Wisconsin Department of Natural Resources (the department) regulates mercury emissions under NR446, which prohibits mercury emissions significant enough to cause the ambient concentration to exceed $1 \mu\text{g}/\text{m}^3$ averaged over a 30 day period. In part to observe the facility's compliance with NR446 and to assure the mercury cell demolition project was conducted in a manner that would not endanger human health or the environment, DNR's Air Monitoring Section requested and was granted permission from the facility's management to conduct monitoring for mercury before, during and after the conversion project. Results obtained during this project are contained herein.

In summary:

- Monitoring was conducted from 12/01/2008 through 03/31/2011, beginning about 6 months prior to the conversion project start, and ending about 11 months after the conversion was complete.
- Average monthly mercury concentrations observed during monitoring decreased more than 10-fold from prior to conversion.
- Maximum monthly concentrations decreased by approximately 100-fold over the course of the project.
- At no time during monitoring was the daily average greater than the NR446 standard level.
- While there are still some elevated values, monthly average concentrations are approaching the global background concentration for mercury observed in rural and remote sites.

Table of Contents

Executive Summary	iii
Table of Contents	iv
Acknowledgements	iv
Project Overview	1
Equipment and Methodology	5
Ambient Data, Mercury Results	7
Average	8
Ambient Data, Meteorological Evaluation	10
Ambient Data, Gaseous Oxidized Mercury	15
Ambient Data, Meteorological Evaluation	17
Quality Control	20
Daily Calibration Reports	21
Data Qualifiers	24
Channel Consistency	25
Co-Located Analyzer Comparisons	28
Primary	28
Co-Located	28
Primary	28
Co-Located	28
Depletion Events	30
Conclusions	31

Acknowledgements

We would like to extend our appreciation to the following for their support, involvement and guidance for this project and the report you are reading.

Many thanks to the management of ERCO Worldwide for voluntarily converting their process from mercury cell to membrane cell technology, thereby significantly reducing mercury emissions in the state of Wisconsin, and for allowing this study to proceed on their property while they did so.

United State Geological Service Mercury Research Lab – David Krabbenhoft

This lab studies mercury issues in the air and water, and graciously loaned us the speciation analyzer, allowing for the exploration of Gaseous Oxidized Mercury from the mercury cell process.

National Atmospheric Deposition Network, Mercury Deposition Network – Mark Olson

This individual is the Atmospheric Mercury Network Site Liaison, and provided technical support at times throughout the project, as well as help setting up the speciation system.

DNR Staff – Mark Allen, Bruce Rodger, Bart Sponseller, Tom Woletz, Mike Ross, and Don Grasser

These individuals provided material support, study design advice, on-going moral support and/or report review.

Project Overview

Reducing mercury emissions from manufacturing processes is an essential part of reducing the overall mercury load to the atmosphere. While many mercury-containing consumer items are being discontinued (thermometers, thermostats, mercury switches, etc), a number of antiquated manufacturing processes continue to persist, one of which is chlor-alkali production. The traditional production of chlor-alkali compounds [chlorine, caustic soda (NaOH), and caustic potash (KOH)] involves passing a heated brine solution through electrochemical cells containing large quantities of mercury. Electricity passes through the cells to convert the brine to chlor-alkali compounds. Hydrogen is produced as a byproduct.

ERCO Worldwide's Port Edwards plant (formerly owned by Vulcan Materials Company, Chemical Division) produced chlor-alkali compounds using mercury cells until 2009. While technically mercury is not consumed in the process, conditions allow significant quantities of mercury to evaporate, much of which escapes as fugitive emissions. Estimated mercury emissions – reported to the DNR between 1992 and 2008 – are listed in Table I-1 below. During this time, ERCO Worldwide's Port Edwards plant was the largest single source of mercury to the atmosphere in Wisconsin, responsible for approximately 20% of the annual total reported emissions statewide.

Table I-1: Reported Mercury Emissions

Year	Hg (lbs)						
1992	1092	1997	1082	2002	1082	2007	1093
1993	1097	1998	1082	2003	1074	2008	1092
1994	1141	1999	1111	2004	1072	2009	1089
1995	1114	2000	1111	2005	1094	2010	414
1996	1100	2001	1082	2006	1092		

In 2002, the Wisconsin DNR Air Monitoring section received permission from the facility (then Vulcan Materials Company) to conduct a pair of short term air monitoring deployments in a trailer located across Highway 73 to the east of the facility, in an auxiliary parking lot for employees and contractors. Results from this monitoring were previously reported in 2003 as “Ambient Mercury Monitoring Near Vulcan Materials Company” and are available on the DNR website (<http://dnr.wi.gov/air/pdf/vulcanhgmon.pdf>). This monitoring showed that extremely high mercury concentrations were present in the ambient air, with maximum observed concentrations greater than 3000 ng/m³, more than 2000 times the general background levels observed at rural and remote monitoring sites worldwide. These results are provided in a summary herein, to provide additional comparison values.

Efforts to reduce and control mercury emissions from this and other Chlor-alkali facilities have been ongoing. From 2000 to 2004, the prior ownership of the Port Edwards facility invested \$2.6MM in mercury cell technology improvements intended to reduce mercury emissions. These improvements included such things as sealed endboxes, welded plate hydrogen coolers, seal-less mercury pumps, and the elimination of the decomposer circuit breakers.

On December 19, 2003, US EPA published the National Emission Standard for Hazardous Air Pollutants (NESHAP) for Mercury Emissions from Mercury Chlor-Alkali Plants. From 2005 to 2007, ERCO Worldwide invested another \$2.9MM in modifications for compliance with the mercury cell NESHAP requirements. These improvements included such things as the installation of carbon beds on the point source air emissions, purchase of a mercury cell MACT recordkeeping database, installation of

continuous monitoring on the point sources and installation of continuous cell room fugitive monitoring. The air pollution control operation permit that DNR Air issued to ERCO in 2006 required ERCO to begin meeting NESHAP requirements to control mercury emissions by December 19, 2007.

During this time frame (2000 – 2007), several of the other remaining mercury cell chlor-alkali plants in the United States closed or converted to membrane cell technology. In August 2007, ERCO’s parent company, Superior Plus, approved a capital investment to replace the mercury cell technology with membrane cell technology. This \$135MM project was intended to eliminate process based mercury emissions to the environment, expand production capability, strengthen the business for the future and secure jobs in South Wood County. On April 13, 2009, DNR Air issued an air pollution control construction permit authorizing ERCO to construct and operate a process associated with decommissioning and decontaminating mercury-contaminated equipment.

Within that construction permit ERCO was required to not allow mercury emissions in such quantities and duration as to cause the mercury concentration in the ambient air to exceed 1 microgram per cubic meter, averaged over any 30-day period, as required in s. NR 446.03(1), Wis. Adm. Code. To meet that ambient concentration limit, the construction permit required ERCO to follow certain work practice standards specified in the NESHAP for Mercury Emissions from Mercury Chlor-Alkali Plants, to conduct decommissioning and decontamination activities indoors, and to open and decontaminate no more than two mercury cells at any one time.

In 2009 and 2010, ERCO removed the mercury cells and replaced them with membrane cells. Table I-2 below documents highlights of the construction process involved. All mercury was removed and the primary mercury-contaminated equipment was decontaminated and removed during this time, with the plant thereby moving from Wisconsin’s largest mercury source to a minor one, with only residual mercury now coming from the site. Removing this mercury has reduced point source mercury emissions in Wisconsin by about 20%.

Table I-2: Process Conversion and Monitoring Timeline

Date	Action
December 1, 2008	Monitoring Starts
June 8, 2009	Mercury Cell Process Decommissioning Starts
June 30, 2009	Hydrochloric Acid Plant Construction Starts
July 7, 2009	Chlorine Drying and Liquefaction Plant Construction Starts
July 23, 2009	Membrane Cell Process Construction Starts
November 18, 2009	Initial Membrane Cell Process Startup
November 18, 2009	Chlorine Drying and Liquefaction Process Startup
December 1, 2009	Membrane Cell Process Operational
December 5, 2009	Hydrochloric Acid Plant Startup
April 27, 2010	Mercury Cell Process Decommissioning Completed

Due to the importance of ambient mercury emissions, the department desired to quantify the before, during and after effects of the mercury removal, and requested permission to conduct a monitoring study during this time. The facility graciously agreed to host a monitoring trailer, not only providing a secure location, but also power for operations. The trailer was located in the same spot as the 2002 monitoring short-term study, and monitoring occurred between December 1, 2008 and March 31, 2011. This timing allowed for collection of several months of data prior to any change to the process, throughout the entire switch from mercury cell to membrane cell technology, and for about a year following the completion of the conversion.

The department alerted ERCO whenever the measured hourly mercury concentrations exceeded 0.5 micrograms per cubic meter for 12 hours during any 24 consecutive hour periods. The intent of these alerts was to allow ERCO sufficient time to alter decommissioning and decontamination activities to ensure that the allowable mercury concentration in the ambient air did not exceed 1 microgram per cubic meter, averaged over any 30-day period. These alerts were issued twice within the project, both times during the early phases of decommissioning of the mercury cells. At no time was this standard violated.

In addition to the elemental form of mercury measured by standard instrumentation, process conditions can lead to an unknown, but potentially significant percentage of the mercury being converted from the relatively benign elemental form to more highly reactive forms which can deposit out of the atmosphere much more quickly than the elemental form. These forms are collectively known as Gaseous Oxidized Mercury, or GOM. This led to an interest in determining the reactive mercury present in the process stream. A specialized analyzer, known as a speciation analyzer, was borrowed from US Geological Survey's Mercury Laboratory in Middleton, Wisconsin, and configured for the expected higher range of concentrations it might encounter. This analyzer was on site between January 21, 2009 and April 21, 2009. Reactive mercury sampling was discontinued on March 16, 2009 because the high concentrations observed rendered further sampling too difficult.

Figure A: Satellite Overview of ERCO Worldwide Port Edwards Facility

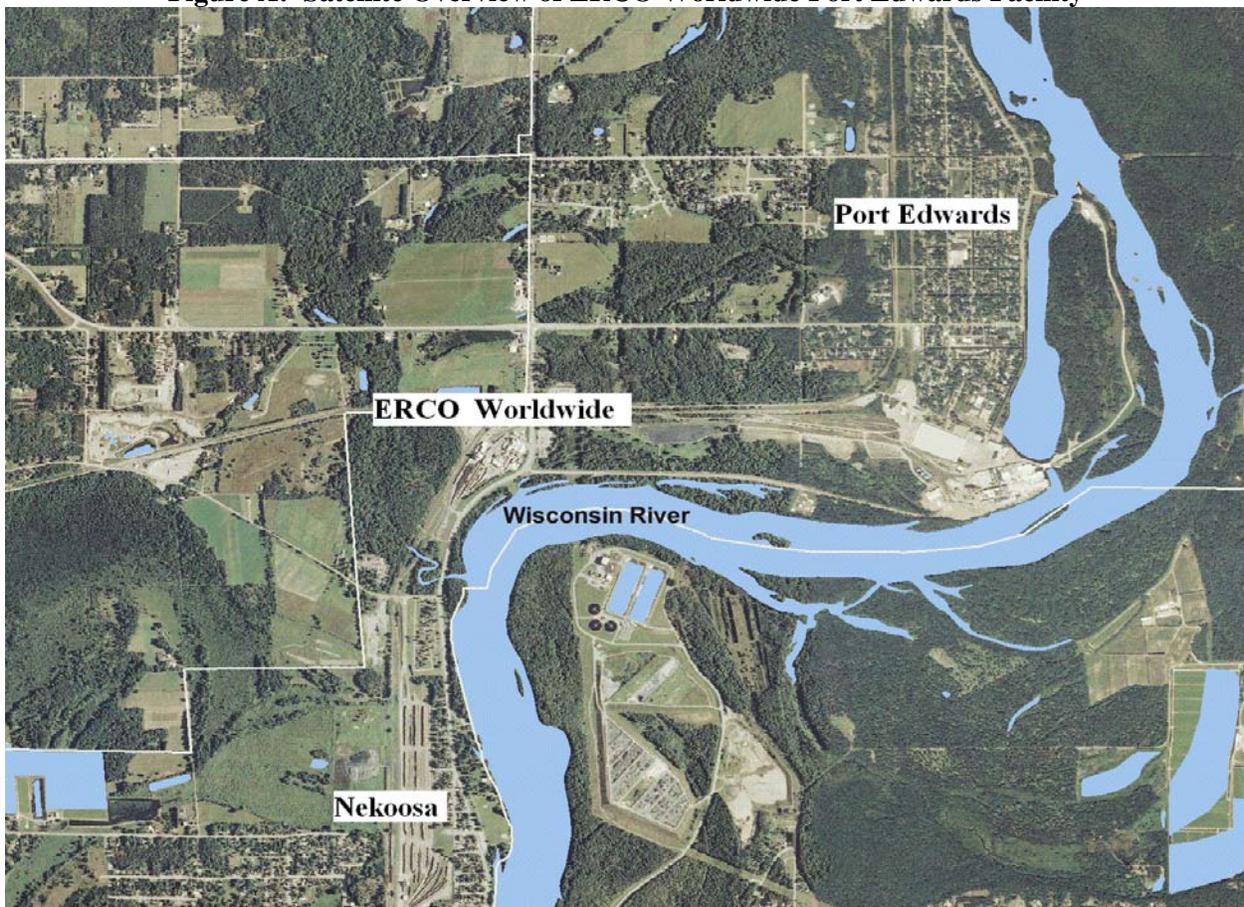


Figure B: Aerial View of ERCO Worldwide (monitoring trailer in lower right)



Equipment and Methodology

Elemental mercury measurements conducted from December 1, 2008 through the present were obtained through the use of a Tekran 2537B Mercury Vapour Analyzer. This instrument collects mercury by drawing ambient air through a cartridge containing a gold adsorbent. The collected mercury is then thermally desorbed and detected using Cold Vapour Atomic Fluorescence Spectrometry (CVAFS). The use of two adsorbent cartridges in parallel allows for continuous sampling of ambient air. The instrument deployed to this site was less than 6 months old at the time of deployment.

The sampling cycle consists of drawing ambient air over the adsorbent cartridge for 5 minutes, after which a valve switches the sample flow to the second cartridge. The first cartridge is then flushed to remove any unabsorbed mercury in the cartridge and airways, after which it is heated to drive off the mercury and send it to the detector. This protocol therefore provides 5 minute average concentrations. Typical operation calls for a sampling rate of 1 liter per minute; however the high concentrations encountered during the first two phases of the project led to a decision to sample at 0.5 liters per minute to avoid overloading the detector as much as possible. The sampler was returned to 1 liter per minute following the majority of the mercury removal work, on February 1, 2010.

An internal Mercury permeation source allows for an automated calibration of the analyzer. The calibration cycle includes a cleaning cycle intended to remove any residual mercury on the cartridges; zero determinations during which clean cylinder air is sampled for the same period as ambient determinations; and span determinations during which air is sampled from over the permeation source. The instrument performs another cleaning cycle before returning to ambient air sampling. The calibration cycle takes 40 minutes to perform in its entirety.

Instrument performance is monitored by the response during the clean and zero cycles, and the changes in the response factor calculated from the span values. Major residual concentrations in the zero or clean cycles may be an indicator of instrumental contamination requiring corrective action. Sudden major changes in a response factor or major differences between the two channels may also be indications of instrumental malfunctions.

In addition to the automatic internal calibration, manual calibration checks can be performed. Ideally, this is accomplished by switching the zero cylinder air and ambient sample lines, therefore providing a clean baseline response, and injecting known quantities of mercury vapor during the sampling cycle. The known quantities of mercury vapor are provided by a mercury source, which contains a small quantity of elemental mercury held at a constant temperature in a closed space. A syringe is used to extract an aliquot of air from the device, and vapor pressure calculations are used to quantify the amount of mercury injected into the analyzer.

Manual calibration checks were performed as described several times throughout the monitoring period. The general rule for acceptable results from this check is $\pm 20\%$ of the calculated value. A summary of internal calibrations and manual calibration checks is included in the Quality Control Data section. Calculations used for this procedure are included in Appendix A: Verification Protocols following the main body of this report.

The speciation sampler deployed consists of a Tekran 2537A Mercury Vapour Analyzer, and a Tekran 1130 Mercury Speciation Unit which consists of a pump unit and a denuder module. The 1130 serves to trap the reactive mercury forms on a coated denuder during the sampling phase, following which the denuder is desorbed and analyzed. The 2537A serves as the mercury detecting instrument both during the

sampling phase, where elemental mercury is determined, and during the desorption phase, when the trapped reactive mercury is driven off of the denuder in elemental form. Because the concentrations of reactive forms of mercury are significantly lower than the elemental form, an auxiliary pump unit is required, and a sampling rate of 10 liters per minute employed instead of the usual 1 liter per minute for elemental only applications.

Typical operation of a speciation sampler involves a sampling period of 1 – 2 hours, followed by an analysis phase which lasts an hour. However, with the concentrations we were likely to encounter at the ERCO site, a sampling period of 20 minutes followed by an analysis phase of 40 minutes was employed. The overall sampling scheme included 4 elemental determinations; 3 zero air flush cycles to drive any free elemental mercury in the sampling train out; 3 GOM cycles where the denuder was heated to 500°C; and then 2 zero air flush cycles following the analysis while the denuder was cooled back to 50°C.

In addition to the performance checks on the 2537A (which are the same for elemental only or speciated operations), the multiple analysis cycles of each phase of the analysis provide a mechanism for checking and correcting the observed GOM data. Ideally, the second and third analysis cycles of both the initial zero air flush and the GOM determination will be zero or close to it, thus indicating that the system is clean before heating begins, and that all mercury was driven off the denuder in the initial heating. Also, the post-analysis flush cycles will ideally be zero.

However, it is recognized that this will not always be the case, and standard protocol developed by the National Atmospheric Deposition Program's Mercury Deposition Network (MDN) for operation of these samplers calls for subtraction of a blank value from the determined GOM result. Total GOM is evaluated as the sum of the three cycles during which the denuder was heated, minus three times the third flush cycle value (three times that value because it is assumed that this value represents an instrumental background which will be present in all three of the GOM cycles).

Indeed, the concentrations of both elemental and reactive mercury were significant enough that we frequently did not see the speciation flush cycles return to zero. Our denuders were frequently overloaded and continued to emit high levels of mercury into analytical cycles following a return to low ambient levels of mercury, and a significant portion of our data has had to be invalidated because of this and other issues.

Meteorological data for the project was collected using a roof mounted wind vane and cup anemometer. Data from the sensors was logged continuously throughout the project as minute average values, from which 5 minute average vectors were calculated for comparison with the mercury data.

All data for the project was routinely downloaded from the trailer computer and stored in computers at the DNR's central office. The data was imported to database and spreadsheet formats for processing and analysis.

Ambient Data, Mercury Results

Data from each phase (before, during and after) of the mercury cell to membrane cell conversion project is considered separately. The pre-conversion monitoring period includes all values obtained before major work began on the project on June 8, 2009. The second phase of the project, during which the mercury cells were drained and removed, and the membrane cells installed lasted until April 27, 2010, with most mercury removal work finished by December, 2009. The operation of the facility after all major mercury contamination was removed includes all remaining data. Data from the 2002 monitoring conducted when Vulcan Materials owned and operated the facility are included for comparison.

The 5-minute average values are consolidated to provide overall, as well as hourly and daily averages. The first table (R-1) below presents the overall average, maximum and minimum five minute average values observed. The second table (R-2) presents the hourly average values, while the third table (R-3) presents the daily average values. It should be noted that the "Count" values represent the number of 5-minute averages incorporated into each of the calculations. All hours and days with less than 75% completeness have been disregarded in Tables R-2 and R-3, thus resulting in reduced counts. Data was not disregarded in these tables for any other reason.

Note that values observed during the 2002 monitoring deployments are generally somewhat higher than those observed during the conversion period deployment, with about 17% of the days monitored having daily averages in excess of 100 ng/m³. While this may in part be due to seasonal effects (see the monthly average values following), it may also be a measure of the success of ERCO's efforts to tighten up the mercury cell process and reduce emissions.

The highest daily average concentrations were observed during the construction in the summer of 2009, with three days having averages close to or in excess of 500 ng/m³, and four exceeding the maximum observed in 2002. It was predicted before the project began that mercury losses to the atmosphere would be higher during the conversion process because of the need to open all of the mercury containing equipment to remove it, as well as removing part of the cell room wall to allow access. Instead, the highest 5 minute and hourly average mercury concentrations were observed in 2002. Again, this may be a result of ERCO's efforts to tighten up the process to reduce emissions, as well as the care taken during demolition to minimize mercury emissions,

It is important to note that the minimum 5-minute average values observed during all portions of the monitoring were zero. This is unusual as the global background concentration averages around 1.3 ng/m³. (This concentration is equivalent to approximately one drop in 100 full sized Olympic swimming pools) Periods where concentrations drop significantly below 1.0 ng/m³ are known as depletions. The implication of seeing values go to zero is that something is removing the global background mercury from the air. During the first month of monitoring in 2008, a significant depletion event lasting almost 6 consecutive hours occurred. Further discussion on this topic is included the Conclusions section of this report.

Also note the significant reduction in concentrations observed during the Post-Conversion monitoring. While it is true that some mercury contamination remains associated with the facility from years of use, converting from the mercury cell process to the membrane cell technology has indeed been accompanied by a large reduction in ambient mercury concentrations around the facility. The tables below (R-4 and R-6) show that measured mercury concentrations in December 2010 were 90% lower than those measured in December 2008.

Table R-1: Summation of 5 Minute Average Values, ng/m³

Period	Average	Max	Min	Count
April/May 2002	51.4	2638	0.0	8591
August/Sept 2002	60.4	3047	0.0	11735
Pre-Conversion: 2008/2009	23.2	2195	0.0	53553
Conversion: 2009/2010	31.9	2702	0.0	89995
Post-Conversion thru 2010	4.6	316.9	0.0	95673

Table R-2: Summation of Hourly Average Values, ng/m³

Period	Average	Max	Min	Hours	Count
April/May 2002	50.8	2102.9	2.2	701	8399
August/Sept 2002	60.8	1003.6	2.8	960	11479
Pre-Conversion: 2008/2009	23.2	820.3	0.0	4439	53249
Conversion: 2009/2010	31.8	1964	0.9	7456	89428
Post-Conversion thru 2010	4.6	117.6	0.7	7923	95040

Table R-3: Summation of Daily Average Values, ng/m³

Period	Average	Max	Min	Days	Count
April/May 2002	44.0	394.6	4.3	29	8132
August/Sept 2002	61.0	277.8	7.8	41	11498
Pre-Conversion: 2008/2009	23.1	270.4	1.5	188	53481
Conversion: 2009/2010	31.8	675.1	1.1	316	89719
Post-Conversion thru 2010	4.6	37.4	0.8	335	95202

In addition to the overall project phase values reported in Tables R-1 through R-3, an attempt to evaluate seasonality in the data is included in Tables R-4 through R-6 following. In these tables, monthly average, maximum and minimum values are displayed. These values may be more comparable to the short term deployments in 2002 in the Table R-1 above.

Highest monthly averages are observed in July and August, 2009, in the middle of the conversion process, while by December 2009, when the membrane cell process began operating, and the vast majority of the mercury already removed, monthly average concentrations dropped to single digits where they have remained since.

In Table R-6, note that the maximum concentrations observed have been decreasing following a peak in August, 2010. Whether this is evidence of a seasonal effect (cooler weather reducing volatilization), or indication of a continued decrease of residual contamination, is not known.

The data in these tables is presented in Figure 1 following. Note that each phase is separated on the graph. The graph is logarithmically scaled to allow easy comparison of the wide range of values observed. Note that average values beginning in December 2009 have all been less than 10 ng/m³, and that maximum values, since the conversion process was completed, have been distinctly lower than those beforehand.

Figure 2 compares the daily average concentrations and calculated rolling 30-day average concentrations with the NR446 standard of 1 µg/m³ (1000 ng/m³). Note that the standard was not exceeded on any day.

Table R-4: Summary of Monthly Values, Pre-Conversion, ng/m³

Month	Year	Average	Maximum	Minimum	Values
December	2008	23.5	2195	0.0	8628
January	2009	17.0	2121	1.8	8821
February	2009	19.2	468.2	0.9	7991
March	2009	18.2	702.6	1.0	8812
April	2009	18.8	1020	0.9	8493
May	2009	40.4	1730	0.6	8808
June	2009	29.5	550.4	0.8	2000

Table R-5: Summary of Monthly Values, During Conversion, ng/m³

Month	Year	Average	Maximum	Minimum	Values
June	2009	48.4	1269	0.0	6549
July	2009	82.2	2702	0.7	8819
August	2009	112.6	2140	0.7	8748
September	2009	24.6	1223	0.9	8529
October	2009	37.4	673.3	0.9	8838
November	2009	10.4	481.8	0.0	8518
December	2009	4.9	282.5	0.8	8791
January	2010	5.3	270.4	0.0	8821
February	2010	2.5	438.9	0.0	6199
March	2010	5.2	391.4	0.9	8806
April	2010	6.8	1081	0.9	7377

Table R-6: Summary of Monthly Values, Post-Conversion, ng/m³

Month	Year	Average	Maximum	Minimum	Values
April	2010	2.0	32.7	0.9	1136
May	2010	6.4	209.6	0.8	8836
June	2010	8.0	172.6	0.9	8560
July	2010	7.4	155.2	0.9	8822
August	2010	8.0	316.9	0.7	8845
September	2010	5.0	97.4	0.9	8518
October	2010	4.7	69.0	1.1	8816
November	2010	3.5	51.9	1.1	8357
December	2010	2.3	38.3	0.0	8770
January	2011	1.8	17.6	0.9	8431
February	2011	2.0	95.1	0.7	7984
March	2011	1.4	29.9	0.6	8598

Figure 1: Monthly Max/Min/Average Chart, December, 2008 – March, 2011

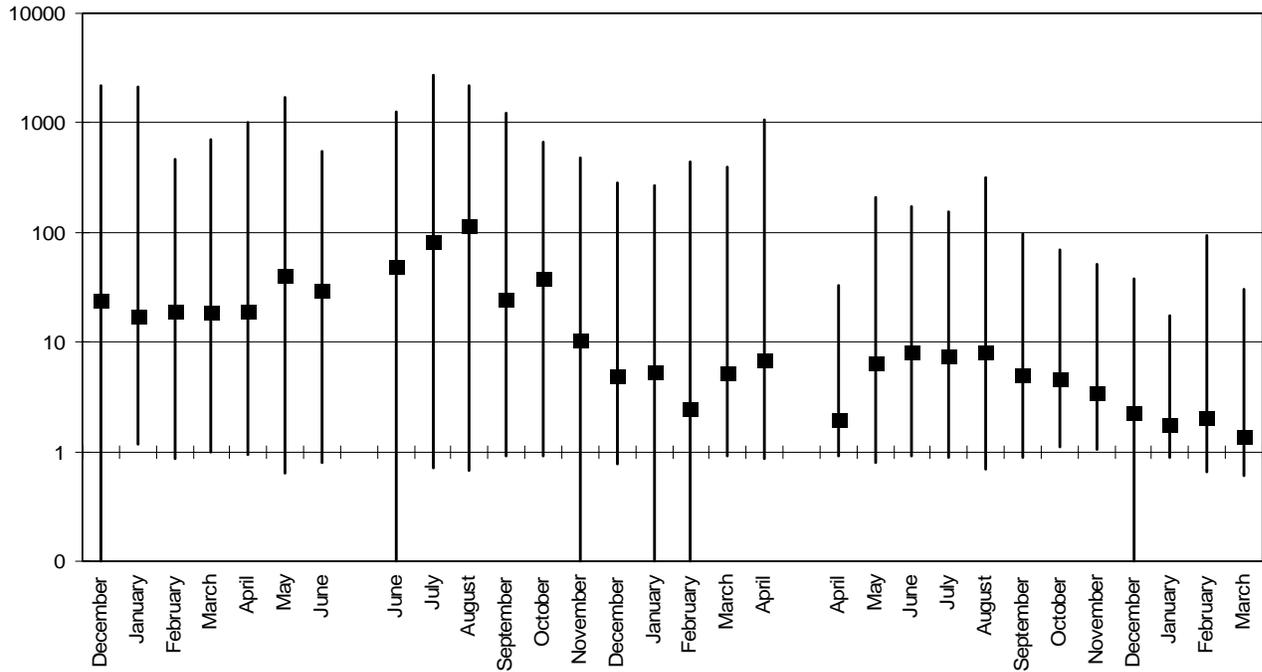
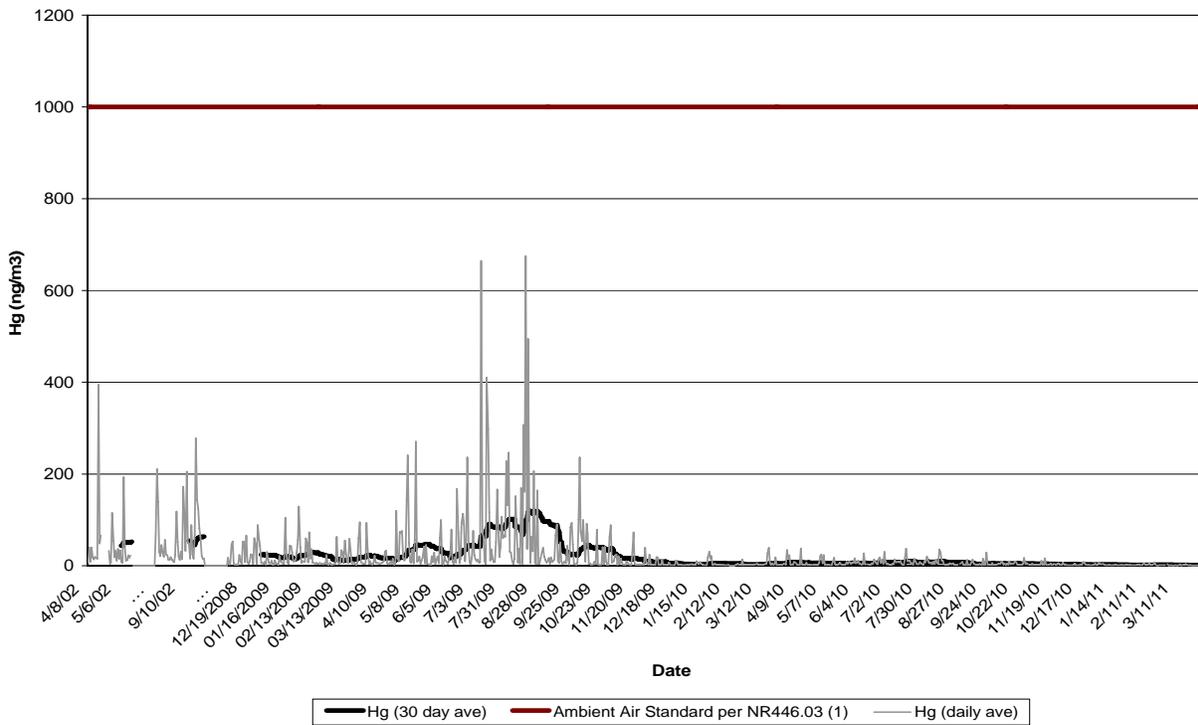


Figure 2: Results in Comparison with NR446 Standard (ng/m³)



Ambient Data, Meteorological Evaluation

Meteorological data obtained from tripod mounted sensors on the roof of the monitoring trailer were incorporated to evaluate the differences between winds coming from the direction of the facility and those coming from other directions. The facility was directly west (270°) of the monitoring trailer, covering an arc of about 90 – 100° from that location. Tables R-7, R-8 and R-9 present a meteorological evaluation of the data. The tables present data evaluated on a cardinal direction basis, with each octant based on ±22.5° of the true direction. For example, the octant labeled “northeast” incorporates all values observed when the winds were between 22.5° and 67.5°.

In addition to including the average, maximum and minimum average mercury values observed from each direction, the number of values observed and the percentage of the total values from each direction are included. It should be noted that the total values reported in these tables is less than the total number of values reported in Table R-1. The reason for this is that there are periods of invalid meteorological data. The most significant of these was between 12/29/2008 and 01/23/2009, during which the wind vane was frozen most of the time. The second portion of the table tallies the number of values occurring in different data ranges. Finally, a percentage of the total values in each of the data ranges is provided.

Table R-7: Evaluation of Results by Wind Direction, Pre-Conversion Monitoring Period, ng/m3

Octant	Average	Max	Min	Count	Sector %	>100	>50	>25	>10	>5	<5	Total
North	5.0	1074	0.8	6341	14.0%	9	11	46	486	1077	4712	6341
NorthEast	6.3	216.1	0.8	2560	5.7%	1	11	53	307	714	1474	2560
East	6.4	207.4	1.1	3979	8.8%	3	36	101	371	921	2547	3979
SouthEast	4.7	524.3	1.2	4727	10.5%	3	8	60	332	586	3738	4727
South	16.2	1129	0.6	11517	25.5%	397	178	269	1180	2343	7150	11517
SouthWest	78.7	2195	0.6	4119	9.1%	1086	460	359	556	739	919	4119
West	117.5	1532	0.0	2677	5.9%	1002	640	444	277	130	184	2677
NorthWest	21.0	1730	0.5	9167	20.3%	439	451	665	1208	1548	4856	9167
All	24.7	2195	0.0	45087	100.0%	2940	1795	1997	4717	8058	25580	45087
Percentage of Total Hourly Observations						6.5%	4.0%	4.4%	10.5%	17.9%	56.7%	100.0%

Table R-8: Evaluation of Results by Wind Direction, Conversion Monitoring Period, ng/m3

Octant	Average	Max	Min	Count	Sector %	>100	>50	>25	>10	>5	<5	Total
North	5.1	1971	0.6	15979	17.8%	55	81	228	1051	2042	12522	15979
NorthEast	6.0	1000	0.7	8261	9.2%	57	59	125	649	1075	6296	8261
East	3.6	513.3	0.7	13103	14.5%	34	35	120	402	922	11590	13103
SouthEast	3.4	527.1	0.8	8611	9.6%	13	17	40	200	760	7581	8611
South	8.8	1644	0.0	9490	10.5%	164	125	178	603	1357	7063	9490
SouthWest	142.2	2702	0.0	5582	6.2%	1457	497	743	869	651	1365	5582
West	209.8	2160	0.0	6672	7.4%	3082	998	1056	929	315	292	6672
NorthWest	16.5	1398	0.0	22283	24.8%	797	633	1035	3079	3320	13419	22283
All	31.9	2702	0.0	89981	100.0%	5659	2445	3525	7782	10442	60128	89981
Percentage of Total Observations						6.3%	2.7%	3.9%	8.6%	11.6%	66.8%	100.0%

Table R-9: Evaluation of Results by Wind Direction, Post-Conversion Monitoring, ng/m3

Octant	Average	Max	Min	Count	Sector %	>100	>50	>25	>10	>5	<5	Total
North	2.7	115.9	0.6	16206	16.9%	1	5	39	478	1208	14475	16206
NorthEast	3.0	75.6	0.7	7176	7.5%	0	2	6	212	830	6126	7176
East	2.1	49.5	0.6	10974	11.5%	0	0	10	89	447	10428	10974
SouthEast	1.7	25.5	0.6	10876	11.4%	0	0	1	20	86	10769	10876
South	2.4	99.6	0.6	13168	13.7%	0	30	85	207	261	12585	13168
SouthWest	12.7	209.6	0.7	8674	9.1%	57	436	838	1458	1234	4651	8674
West	19.2	316.9	0.0	7075	7.4%	44	593	1301	1869	1441	1827	7075
NorthWest	2.6	83.5	0.2	21513	22.5%	0	11	171	582	889	19860	21513
All	4.6	316.9	0.0	95662	100.0%	102	1077	2451	4915	6396	80721	95662
Percentage of Total Observations						0.1%	1.1%	2.6%	5.1%	6.7%	84.4%	100.0%

Table R-10: Evaluation of Results by Wind Direction, 2002 Monitoring, ng/m3

Octant	Average	Max	Min	Count	Sector %	>100	>50	>25	>10	>5	<5	Totals
North	20.3	343.7	2.5	1228	12.4%	23	85	172	409	388	151	1228
NorthEast	23.5	167.8	3.8	644	6.5%	4	41	208	204	118	69	644
East	16.5	123.6	3.5	877	8.9%	1	18	175	283	280	120	877
SouthEast	15.5	313.8	3.0	1420	14.4%	14	27	183	447	563	186	1420
South	37.2	765.4	0.0	2506	25.4%	189	275	606	1030	336	70	2506
SouthWest	265.7	3047.0	0.0	801	8.1%	480	106	133	71	8	3	801
West	245.6	1657.0	0.0	885	9.0%	615	145	86	27	5	7	885
NorthWest	37.1	573.3	2.0	1503	15.2%	110	195	328	463	293	114	1503
All	66.5	3047.0	0	9864	100.0%	1436	892	1891	2934	1991	720	9864
Percentage of Total Observations						14.6%	9.0%	19.2%	29.7%	20.2%	7.3%	100.0%

This information in Tables R-7, R-8, R-9 and R-10 is shown graphically in Figures 3, 4, 5 and 6, respectively, on the following pages, which illustrate the concentration versus the wind direction in each respective monitoring period. The graphs are based on average concentrations for particular 20 degree wind segments. For Example, the wind direction of 320 degrees on the x-axis contains all values associated with wind directions between 301 and 320 degrees.

The bars in the graphs show the number of values averaged into the concentration value, while the line shows the average concentration. The left Y-axis provides the range for the number of values while the right Y-axis provides the range for the concentrations. Note that the scale of the Y-axes is consistent between the graphs. Even though the shape of each graph is similar, showing significantly higher concentrations with westerly winds, the magnitude of the peak values is an order of magnitude lower following conversion to the membrane cell process.

Both the numerical and graphical representations indicate a clear and significant influence of ERCO Worldwide - Port Edwards plant on local ambient mercury concentrations, as well as the reduction of this impact following conversion. In addition to the current monitoring period results displayed this way, Figure 6 documents the 2002 monitoring results in the same format.

Figure 3: Ambient Mercury Concentration versus Wind Direction, Pre-Conversion

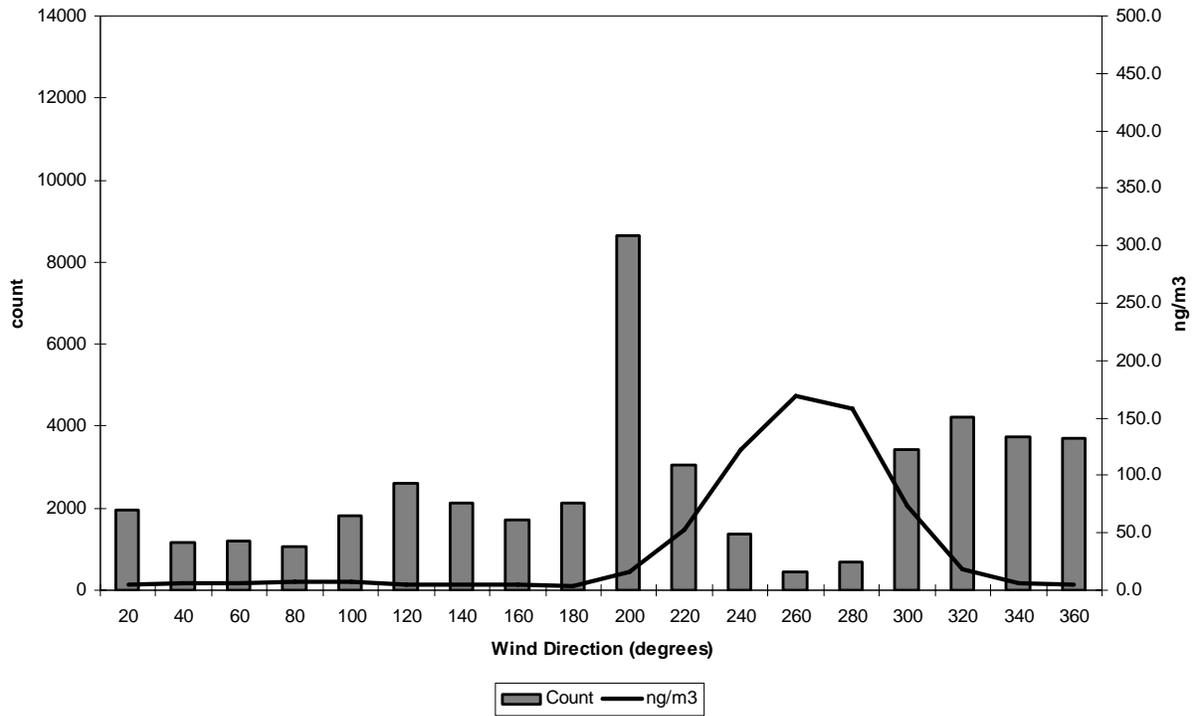


Figure 4: Ambient Mercury Concentration versus Wind Direction, Conversion

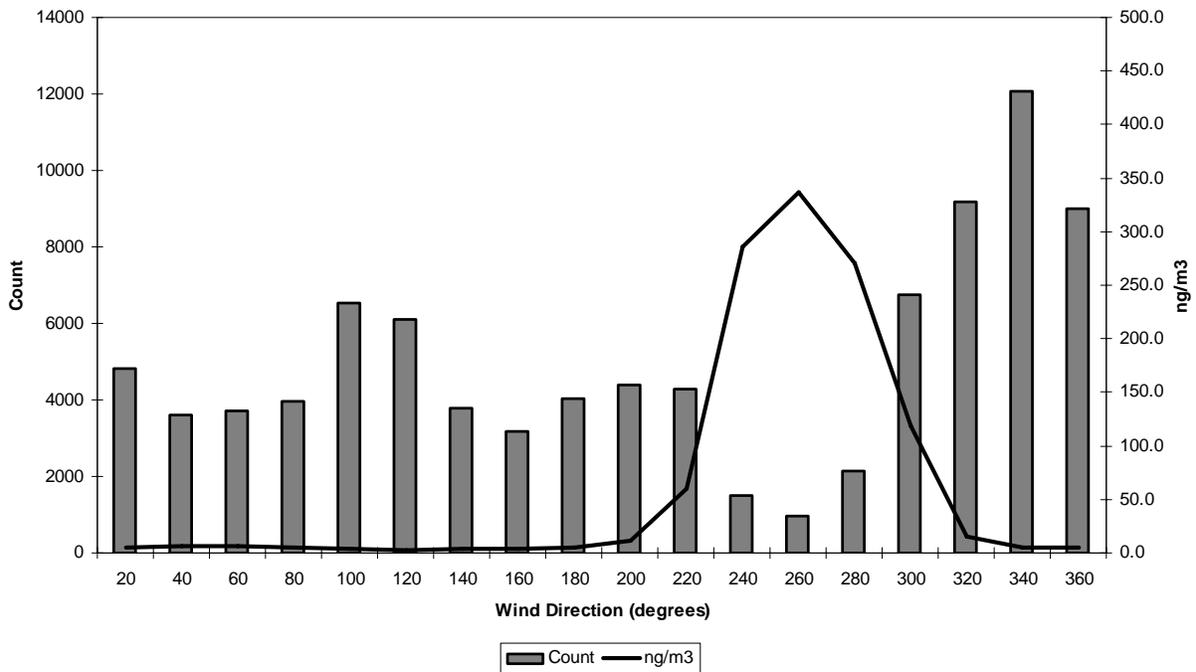


Figure 5: Ambient Mercury Concentration versus Wind Direction, Post-Conversion

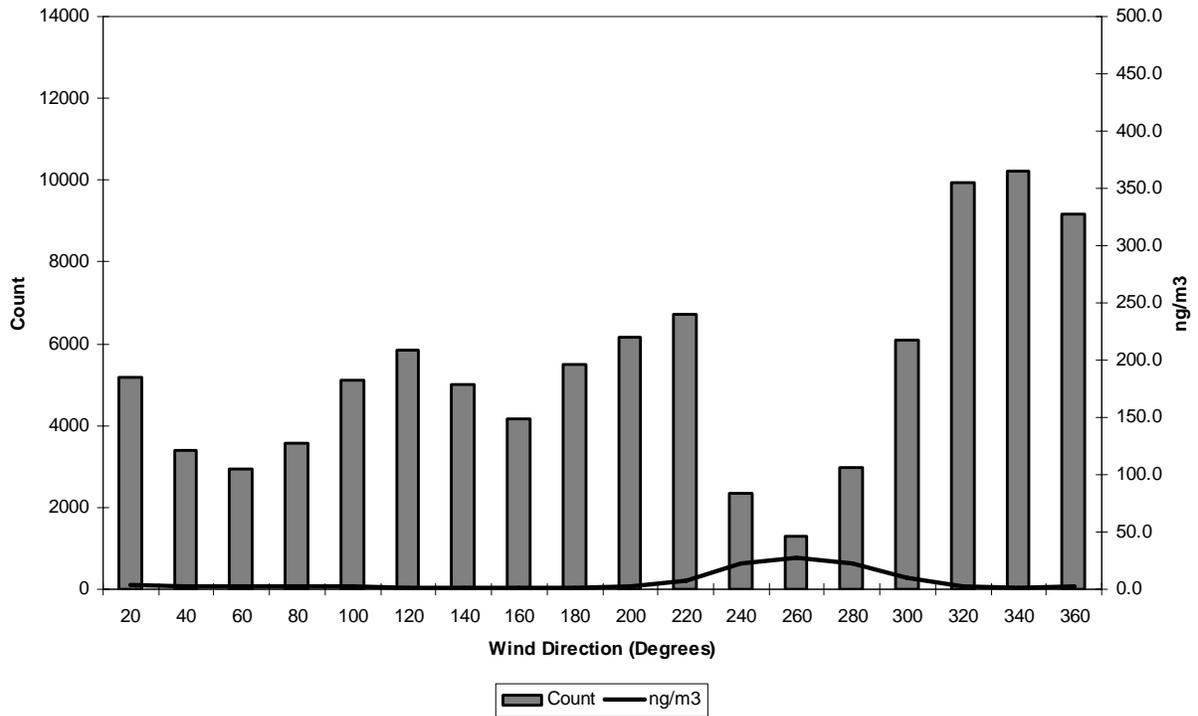
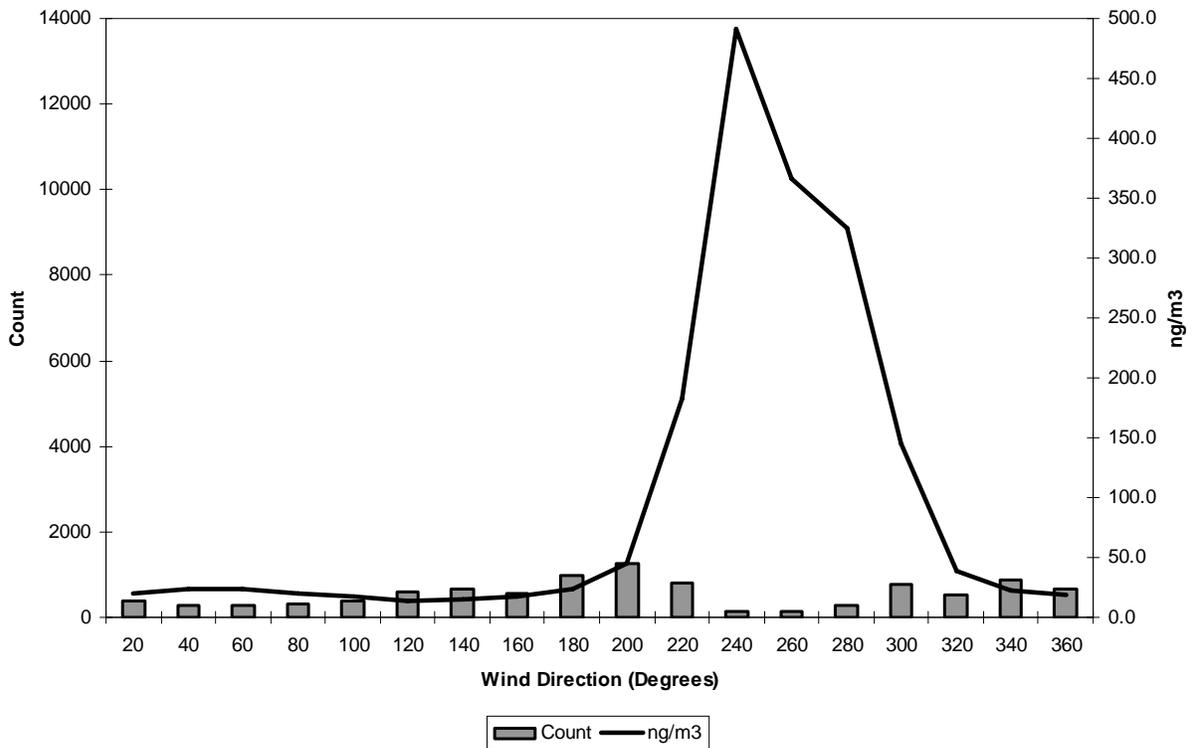


Figure 6: Ambient Mercury Concentration versus Wind Direction, 2002



Ambient Data, Gaseous Oxidized Mercury

GOM data was collected between January and March, 2009 only and thus is representative of the pre-conversion phase only. Significant difficulties were experienced in collecting this data, as the concentrations observed far exceeded the typical conditions to which speciation samplers are exposed. In spite of our efforts to reduce the exposure and obtain consistently usable data, the instrument experienced significant overload at times. This situation required us to change glassware more frequently than anticipated, and led to some loss of data.

These difficulties also extended into qualifying what is valid data. Ideally, the final zero air flush, the final GOM reading, and the final post analysis zero air flush will all equal zero. This state represents a condition in which the system has removed successfully all mercury collected during the analysis. However, in the case of our data, these cycles frequently did not return to zero, which indicates either contamination of the system, or that the analysis cycle did not remove all mercury from the system.

This situation makes evaluation of the data difficult, and there is a temptation to simply invalidate the entire GOM data set. However, the quantity of these reactive forms of mercury coming from the facility is important, and a less stringent set of standards for residual mercury in the system was adopted for this work. Invalidated data fits into one or more of several categories, outlined below.

1. Known operator error
2. Issues with the instrument
3. Mercury in flush cycle exceeds that in denuder heating cycle

The final phase of data validation involved an in-depth evaluation of all cycles involved in the determination, plus a comparison of the data with the elemental mercury observed during the same time period. The data shows that higher elemental values associated with the facility are expected to correspond with higher GOM values. Likewise, lower elemental values are expected to correspond with lower GOM values. An effect of instrumental carryover can be seen in high GOM values associated with low elemental values following facility impacted high values. This is likely representative of an overloaded denuder which is no longer functioning properly.

A significant stretch of data in the latter category was observed following a massive GOM peak on 3/10/2009. Much of the data following this event is questionable, however not all data has been invalidated because the denuder appeared to track changes, and eventually recovered. Values during this time period which have been invalidated are those which show an increase in GOM even though elemental values decreased, or which indicate that more than 50% of the mercury present is in a reactive form even though elemental values are very low.

It should be noted that in spite of our efforts to reduce our data to only the most valid possible values, significant irregularities remain, including significant zero flush cycle values. As such, our data can not be considered truly quantitative, although we do believe that it represents general ambient conditions before the conversion to membrane cell technology. Most of the problems with our data are relatively insignificant at the higher concentrations observed, with the residual mercury in the system representing typically less than 15% of the GOM values greater than 1000 pg/m³.

It should also be noted that while the tables and evaluations of the data following are based on what we chose to consider valid data, the difficulties associated with making this determination have led to the decision to include the raw data, both valid and invalidated, as Appendix E for others to evaluate on their own basis.

Table R-10 below summarizes the data with respect to completeness, the quantity of potentially valid data collected. Note that this table does not reveal the effort involved in obtaining the valid data, nor does it address periods where results pass the loosened criteria we used to evaluate contamination and yet are actually biasing results significantly. The work load associated with maintaining the instrument in operating condition was a prime consideration in removing the speciation aspect of the sampler, and simply running the instrument as a co-located elemental analyzer between March 16 and April 21, 2010.

Table R-10: GOM Completeness

Time Period	Hours	Valid	Completeness	Comments
1/21/2009 - 1/29/2009	191	185	96.9%	
1/29/2009 - 2/2/2009	99	0	0.0%	Operator Error/Overloaded Denuder
2/2/2009 - 2/18/2009	382	379	99.2%	
2/18/2009 - 2/23/2009	125	0	0.0%	Internal Leak in Instrument
2/23/2009 - 3/16/2009	494	425	86.0%	
Overall	1291	989	76.6%	

Data presented in Tables R-11 through R-13 on the following page summarize the results associated with the GOM determinations. Results in Table R-11 represent the GOM present during the 20 minutes of atmospheric sampling performed each hour during the day, with average, maximum and minimum values shown, as well as the total number of determinations and the numbers associated with different concentration limits. The reactive forms of mercury are typically present in much smaller concentrations than those of elemental mercury, and as such are reported in pg/m^3 , while GEM is reported in ng/m^3 .

Table R-12 presents the elemental mercury determinations made while the speciation analyzer was collecting the GOM, showing again, the average, maximum and minimum as well as counts. An additional factor associated with these results is the percentage of GOM (GOM%) detected during each determination. This percentage serves as an important indicator of normalcy. Typical background conditions rarely show greater than 2% GEM. Table R-13 presents the GOM% observed during this study. Note that conditions in which mercury carryover between samples is present may bias the GOM% high.

Table R-11: Summary of Observed GOM Values (in pg/m^3)

Average	Max	Min	Count	>5000	>1000	>500	>100	<100
1775.0	63124.5	-0.4	989	72	97	54	263	503

Table R-12: Summary of Observed Concurrent GEM Values (in ng/m^3)

Average	Max	Min	Values	>75	>25	>10	>3.5	<3.5
18.2	415.5	1.2	989	76	64	76	299	474

Table R-13: Summary of Percent GOM Values (in percent)

Average	Max	Min	Values	>20%	>10%	>5%	>2%	<2%
4.6%	38.8%	0.0%	989	38	72	153	311	415

Two important facts should be noted about these results. One is that many of the higher GOM values observed around this facility are much higher than values typically observed, even around other industrial processes where values in excess of 1,000 pg/m³ are unusual. Secondly, the maximum GEM value observed during the sampling for reactive mercury is significantly lower than the maximum observed overall. The implication of the second point is that the upper bound of reactive forms of mercury associated with this type of facility has not been determined.

Ambient Data, Meteorological Evaluation

Meteorological data was incorporated to evaluate the differences between winds coming from the facility and those coming from elsewhere. The facility was directly west (270°) of the monitoring trailer, covering an arc of about 90 – 100° from that location. Tables R-14, R-15 and R-16 present a meteorological evaluation of the data. The tables present data evaluated on a cardinal direction basis, with each octant based on ±22.5° of the true direction. For example, the octant labeled “northeast” incorporates all values observed when the winds were between 22.5° and 67.5°.

In addition to including the average, maximum and minimum observed from each direction, the number of hourly values observed and the percentage of the total hourly values from each direction are included. The second portion of the table tallies the number of values occurring in different data ranges. Finally, a percentage of the total values in each of the data ranges is provided.

Note that while there are 989 hours of GOM data in consideration overall, there are only 947 hours of data which is matched with valid meteorological data. Also, the wind speed and wind directions used in these evaluations were based solely on the 20 minute sampling period.

Table R-14: Evaluation of GOM Data by Wind Direction, pg/m³

Octant	Average	Max	Min	Count	Sector %	>1000	>500	>250	>100	>50	<50	Total
North	93	1110	0	195	20.6%	1	7	8	26	37	116	195
NorthEast	123	640	4	63	6.7%	0	1	6	21	13	22	63
East	98	571	5	62	6.5%	0	2	5	7	22	26	62
SouthEast	135	1250	4	111	11.7%	1	3	13	26	41	27	111
South	264	11867	19	140	14.8%	3	11	12	40	55	19	140
SouthWest	8790	61870	24	74	7.8%	49	8	3	6	5	3	74
West	13194	63125	510	59	6.2%	56	3	0	0	0	0	59
NorthWest	973	32129	0	243	25.7%	58	18	36	47	38	46	243
All	1847	63125	0	947	100.0%	168	53	83	173	211	259	947
Percentage of Total Hourly Observations						17.7%	5.6%	8.8%	18.3%	22.3%	27.3%	100.0%

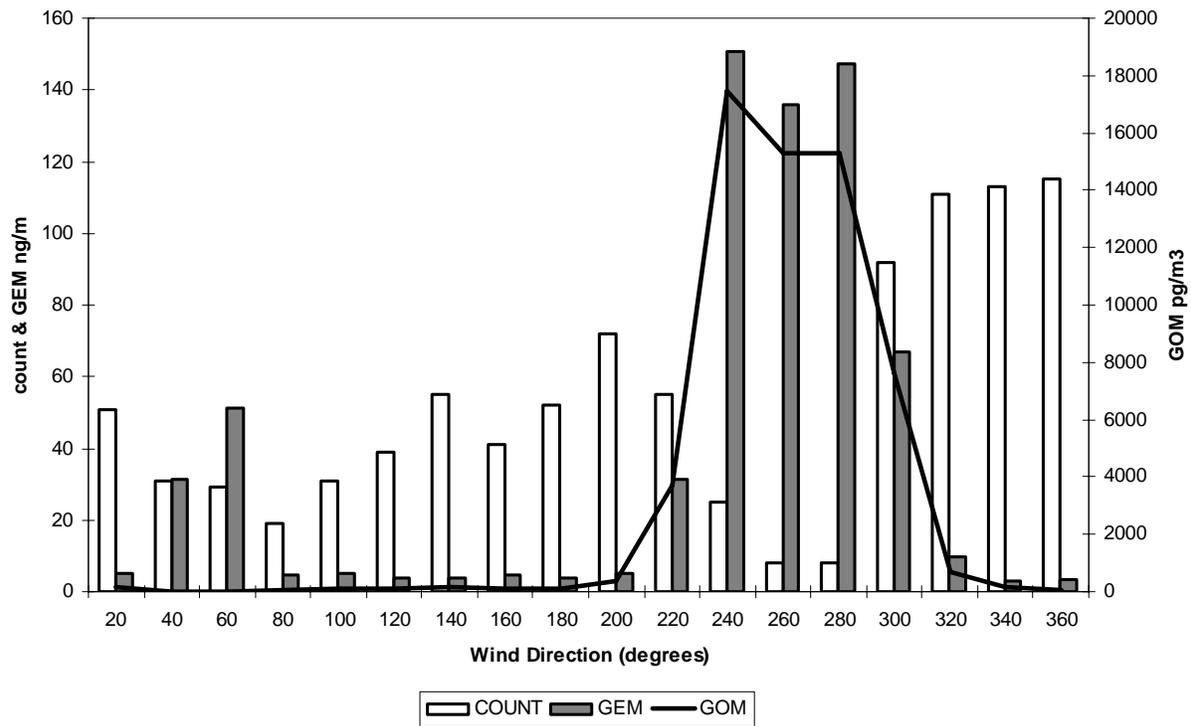
Table R-15: Evaluation of GEM Data by Wind Direction, ng/m³

Octant	Average	Max	Min	Count	Sector %	>100	>50	>25	>10	>5	<5	Total
North	3.8	18.2	1.2	195	20.6%	0	0	0	13	19	163	195
NorthEast	5.5	20.2	1.7	63	6.7%	0	0	0	7	21	35	63
East	4.4	13.8	2.6	62	6.5%	0	0	0	3	11	48	62
SouthEast	4.2	21.6	2.0	111	11.7%	0	0	0	3	12	96	111
South	4.6	34.0	2.0	140	14.8%	0	0	1	5	30	104	140
SouthWest	77.6	415.5	3.0	74	7.8%	21	15	12	3	12	11	74
West	108.7	319.6	17.7	59	6.2%	27	20	10	2	0	0	59
NorthWest	12.5	129.2	1.6	243	25.7%	3	13	17	35	33	142	243
All	18.6	415.5	1.2	947	100.0%	51	48	40	71	138	599	947
Percentage of Total Hourly Observations						5.4%	5.1%	4.2%	7.5%	14.6%	63.3%	100.0%

Table R-16: Evaluation of GOM % Data by Wind Direction, %

Octant	Average	Max	Min	Count	Sector %	>20	<20	<10	<5	<2	<1	Total
North	2.2%	14.9%	0.0%	195	20.6%	0	8	8	48	74	57	195
NorthEast	2.1%	5.7%	0.2%	63	6.7%	0	0	2	27	19	15	63
East	2.0%	8.4%	0.1%	62	6.5%	0	0	4	17	21	20	62
SouthEast	3.1%	11.9%	0.1%	111	11.7%	0	1	18	44	31	17	111
South	4.2%	34.9%	0.3%	140	14.8%	2	7	28	59	34	10	140
SouthWest	10.6%	38.8%	0.8%	74	7.8%	17	8	20	12	13	4	74
West	10.1%	34.2%	1.2%	59	6.2%	7	15	21	13	3	0	59
NorthWest	6.0%	34.0%	0.0%	243	25.7%	12	33	52	82	31	33	243
All	4.7%	38.8%	0.0%	947	100.0%	38	72	153	302	226	156	947
Percentage of Total Hourly Observations						4.0%	7.6%	16.2%	31.9%	23.9%	16.5%	100.0%

Figure 7: Ambient Elemental and Oxidized Mercury Concentration versus Wind Direction



Quality Control

Missing data is listed in Tables Q-1 through Q-3. Not included in these tables is the time off-line for internal calibrations. The calibration procedure requires the analyzer to be off-line for 40 minutes for each cycle, which is about 2.8% of the data for the day of calibration. During the majority of the project, calibrations were conducted every 71 hours (just less than every three days).

Generally, all systems functioned well through the majority of the testing program. The most significant issues which arose include the freezing of the wind vane in December 2008 and January 2009, the malfunction of the data logger in February 2010, the unstable calibrations in October and November 2010, and an excess of low values starting in February, 2011 and continuing through the end of the project. The first issue led to the loss of all meteorological data, but no mercury data. The second issue led to the loss of all data when the logger locked up. The third issue led to the direct loss of no data, but all mercury data during this period is potentially suspect. Further discussion is included in the calibration section following. The final issue led to the deployment of a second analyzer to the site to verify readings. Further discussion is included in the co-location and depletion event sections.

Table Q-1: Missing or Suspect Data Periods, Pre-Conversion

Date	Missing	Reasons for Invalidation
12/29/2008 – 01/23/2009	All Met	Wind Vane Frozen
01/21/2009 12:35 – 13:25	11	Installing Speciation Instrument
01/21/2009 14:00 – 15:15	16	Instrument Comparisons/Checks
03/16/2009 12:30 – 13:40	18	Maintenance
04/03/2009 08:50 – 12:15	42	Verification Check
04/03/2009 12:25 – 13:45	19	Maintenance
05/07/2009 13:00 – 13:15	2	Valve Mis-fires?
05/29/2009 20:00 – 20:40	7	Maintenance

Table Q-2: Missing or Suspect Data Periods, Conversion

Date	Missing	Reasons for Invalidation
06/08/2009 10:00 – 10:15	3	Maintenance
07/05/2009 17:30 – 18:40	16	Maintenance
08/06/2009 09:50 – 14:30	56	Verification Check
08/25/2009 10:20 – 11:20	12	Maintenance
09/15/2009 11:15 – 12:05	10	Maintenance
10/14/2009 12:30 – 12:40	2	Maintenance
11/06/2009 11:50 – 14:00	26	Verification Check
12/03/2009 11:00 – 15:10	50	Injection Port Issues
12/10/2009 00:50 – 01:30	4	Valve Mis-Fires?
01/05/2010 11:00 – 12:10	11	Maintenance
02/01/2010 10:55 – 15:00	55	Maintenance
02/11/2010 09:35 – 02/17/2010 10:05	1732	Data Logger Malfunction
03/06/2010 22:25 – 22:55	6	Data Transmission Error, No Backup
03/09/2010 22:10 – 22:25	2	Data Transmission Error, No Backup
03/15/2010 08:25 – 10:25	25	New Data Logger Installed
04/02/2010 09:55 – 13:50	45	Injection Port/Verifications

Table Q-3: Missing or Suspect Data Periods, Post-Conversion

Date	Missing	Reasons for Invalidation
05/06/2010 08:50 – 09:50	12	Maintenance
07/08/2010 09:10 – 12:00	18	Maintenance
08/12/2010 11:00 – 11:30	3	Maintenance
09/16/2010 11:00 – 11:30	3	Maintenance
09/29/2010 10:30 – 14:00	39	Verifications
10/06/2010 14:20 – 17:00	8	Maintenance
11/04/2010 10:00 – 14:30	29	Verifications
11/17/2010 10:50 – 11:30	6	Maintenance
12/01/2010 10:00 – 17:00	47	Maintenance and Verifications
10/01/2010 – 11/17/2010		Unstable Calibrations (see text)
01/25/2011 00:50 – 01/26/2011 11:00	399	Argon Tank Issues
01/26/2011 10:05 – 10:50	8	Maintenance
03/01/2011 11:20 – 12:15	12	Maintenance
03/08/2011 09:25 – 11:30	26	Maintenance and Evaluations
03/08/2011 15:40 – 16:20	9	Maintenance
03/31/2011 09:10 – 11:00	23	Final Verifications
01/31/2011 – 03/31/2011		Excessive Low Values (see text)

Daily Calibration Reports

Daily calibrations of the analyzer were automatically conducted at 01:00. The calibration consists of three sample runs on each channel of the analyzer. Runs include a trap cleaning, a zero gas, and a span gas. Following the calibration the instrument prints a report that includes the instrument response factor for each sampling trap. The response factor is then used for the calculation of all results until the next calibration cycle. After the calibration and prior to the start of ambient sampling the analyzer performs a second cleaning run on each trap.

Parameters examined on the calibrations were the clean and zero values, and the span and calculated response factor. In general, these parameters indicate an overall excellent performance by the instrument. Very few of the more than 600 zero cycles returned results greater than zero (6 of 142 during the pre-conversion phase; 5 of 242 during the conversion process; and 0 of 224 during the post-conversion phase), which is a good indicator that instrument contamination was not a factor during this project.

The response factor, however, did indicate some difficulties, particularly during October and November of 2010. In general, the response factor is not expected to change much between calibrations. Exceptions to this arise when maintenance such as adjusting the lamp voltage is performed, but generally a gradual change over time is expected, as illustrated with Figures 8 and 9 on the following pages, which show the calculated response factors for each channel of the instrument for the pre-conversion and during conversion monitoring periods. Note that response factors are in units of area per nanogram.

One quirk of the instrument in use is that it initially had a tendency towards increasing response factors over time. This is unusual for these instruments, as most we have had experience with tend to show a gradual decay of response factor over time. During the higher concentration phases of the work around ERCO there were numerous attempts to decrease the sensitivity of the instrument to reduce the number of overloads experienced. This is illustrated in the figures by the sudden shifts of response factor downwards. Shifts up tend to represent lamp adjustments where no effort was made to reduce sensitivity.

Most often, the two channels generate response factors which are very close to each other. Sometimes, however, differences begin to arise (as seen when the traces begin to separate significantly in the figures). These situations require intervention, typically involving cleaning or replacing the cartridges to restore uniform response.

Figure 8: Pre-Conversion Monitoring Period Response Factors, A & B Channels, Area/ng

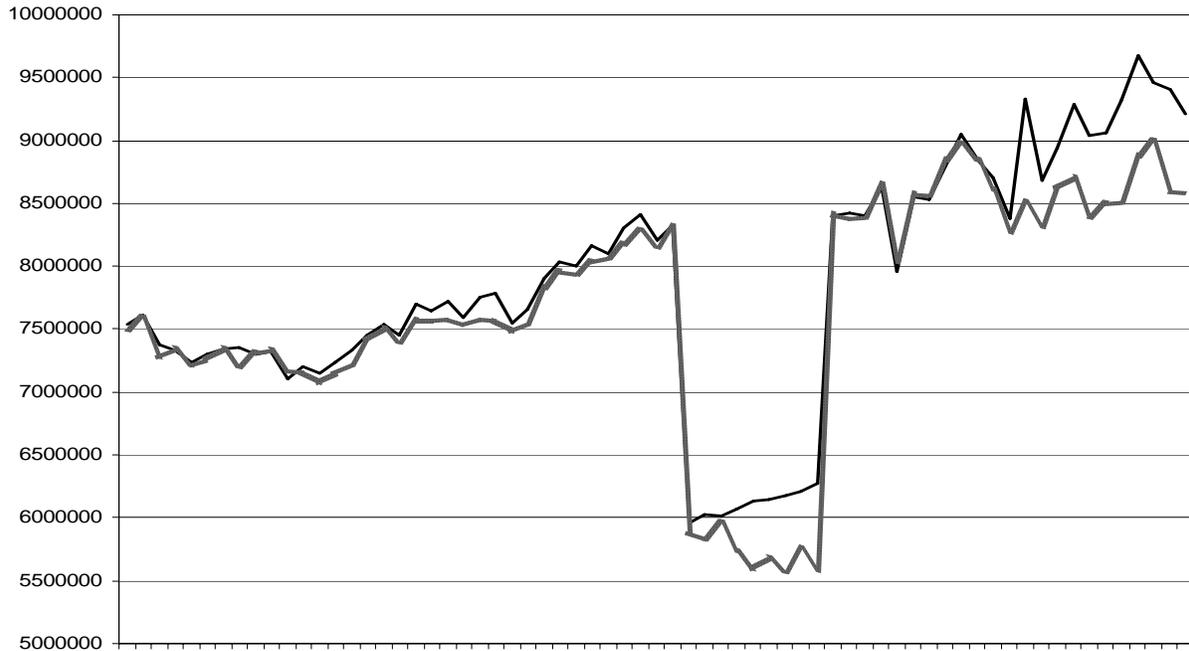
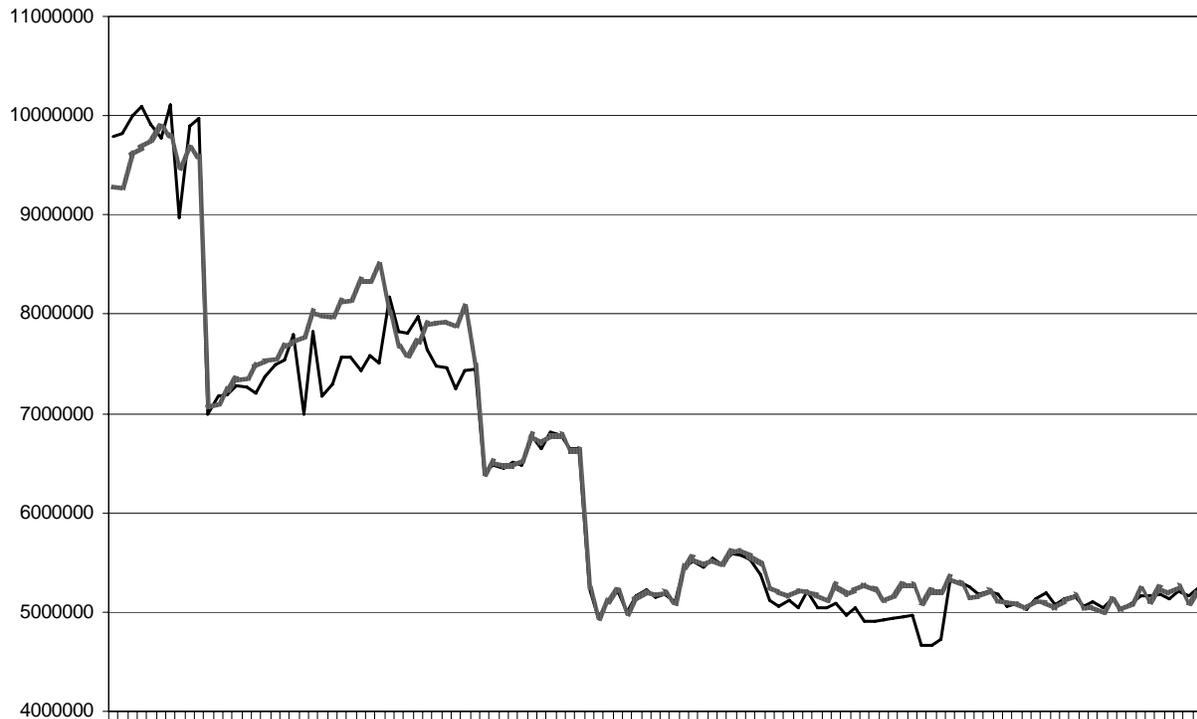


Figure 9: Conversion Monitoring Period Response Factors, A & B Channels, Area/ng



Another quirk of the instrument is that the injection port, through which manual injections of mercury are made to verify the calibrations, is slightly defective. Most of the time the instrument has been on site, this port has been capped. Periodic repair efforts, intended so that the port would function properly at all times (holding together and not leaking), have been made throughout the monitoring project. On September 29, 2010, such an effort was made in conjunction with verification injections. Following the injections, instead of replacing the plug, the injection port was left in place, as it appeared to have no leaks.

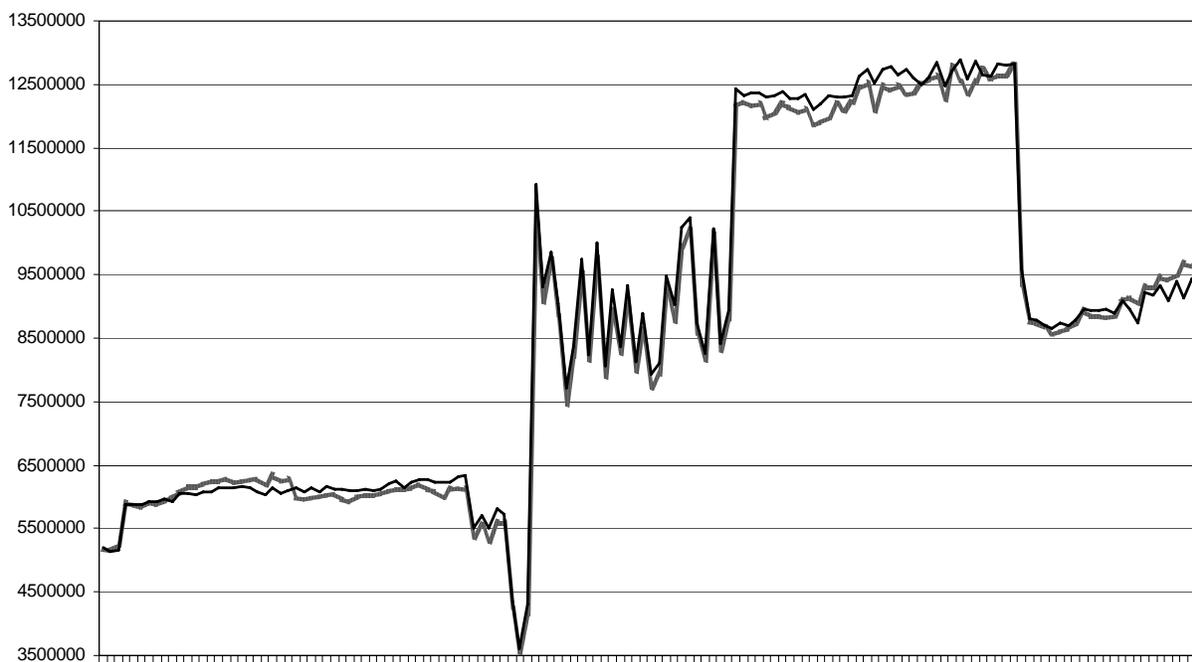
Beginning with the next calibration, a significant shift in response factor was observed. When responding to this shift, the lamp indicator light was on, and the lamp would not adjust properly. A new lamp was then installed, a good calibration was obtained, and it was assumed that the response factor issue was related solely to the lamp. During the month of October following the installation of the lamp, however, each calibration was significantly different from the previous.

Troubleshooting at the beginning of November did not reveal the problem. Under sampling conditions, no leaks were observed, and an electronic lamp control issue was considered likely. This type of problem would have led to the need to remove the instrument and the likely in-validation of the data obtained since the calibration instability began. The instrument was set to calibrate on a 23 hour interval in an effort to keep a closer track on the supposed electronic drift. During the next site visit, on November 17th, the actual problem was revealed to be the injection port, which had shifted internally in a way which allowed the system to leak when it was under pressure (during the zero air mediated calibration cycles). Repairs were made, and the instrument left on the daily calibration cycle to ensure the problem was solved.

Because of the nature of the problem, it is believed that ambient data during this time was only affected to the extent that the actual instrument response differed from the response factor in effect that day. A calculation was made using an average response factor obtained following stabilization of the calibration cycles, wherein the ambient data was found to be over-estimated between October 6th and November 17th, 2010 by up to about 25%. The decision was made to keep the data as it is in the database rather than incorporating the re-calculated values largely for conservative reasons: it is better to over-estimate the concentration of toxic chemicals in the environment than to under-estimate them, and we can not guarantee that the response observed following stabilization in the middle of November would be the same right after changing the lamp at the beginning of October.

Figure 10 documents the changes in response factor during the post-construction phase. The period in question is apparent, as the section of the graph with significant daily changes. Note how before and after this period, the response factors are particularly stable.

Figure 10: Post-Conversion Monitoring Period Response Factors, A & B Channels, Area/ng



Data Qualifiers

Each measurement made by the Tekran instrument includes a qualifier called the “desorption flag”. The desorption flag notes any irregularities in the operation of the analyzer during the analysis cycle. Most measurements are assigned an “OK” code. Other significant codes reported in the study were “NP”, “Mx”, and “OL”.

The “NP” designation indicates that no peak was observed. An “NP” designation during an ambient sample may indicate that there is a problem with the instrument (such as excessive noise leading to the inability to determine whether or not a peak was present), or that a depletion event is in progress. How to evaluate the difference is explored further in the “Depletion” section following.

The “Mx” designation (where “x” is a digit from 2 – 9) is an indicator that more than a single peak was observed during the analysis phase of the cycle. Typically this is an indicator of decreased adsorption trap efficiency. A significant quantity of these indicators requires action, such as cleaning or replacing the traps.

The “OL” designation indicates that sufficient mercury was present in the sample to exceed the maximum detector voltage. While the detector peaks at 5.2 volts, anything with a peak height greater than 5.0 volts is flagged. The presence of this flag may indicate that the resulting concentration is an under-estimate of the actual ambient conditions. However, verification tests generating “OL” peaks by introducing known quantities of mercury generally lead to acceptable results, so no effort to remove or otherwise flag any OL peaks from this dataset was made. Knowing that high concentrations during the initial parts of this project were inevitable, efforts to decrease both the instrument sensitivity and the mercury exposure were incorporated throughout the initial phases of the project.

Table Q-4 below summarizes the codes assigned to the ambient data in this project. The number of ambient readings assigned to each of the different codes is shown. It is important to note that of the over 214,000 ambient measurements included in the data for this report, a total of only 837 of them, representing less than 0.4%, are flagged any way other than “OK”.

Table Q-4: Description Flag Summary, Pre-Conversion/Conversion/Post-Conversion

Code	Pre-Conversion	Conversion	Post-Conversion
NP	69	10	1
Mx	16	25	20
OL	79	623	0

Channel Consistency

The final data examined here is the channel consistency. The Tekran analyzer uses two gold traps that sample alternately. While one trap is sampling air, the alternate trap is undergoing desorption and analysis. This arrangement allows continuous sampling of the ambient air. While each trap collects independent samples for analysis, the daily average will summarize all measurements on each channel and these average values should be similar.

Channel similarity is expressed as a ratio of the difference between the channels to the average of the readings. The criterion for a well functioning instrument in a relatively stable ambient environment is for the ratio to be between 0.8 and 1.2 on most days. Multiple days in a row which are outside of these limits are an indicator that maintenance is required. In areas with fluctuating mercury concentrations, staying within these limits is more difficult.

We examined the daily averages for all sampling days of the project. The results are shown in Figures 11, 12 and 13 on the following pages. These graphs display the daily channel difference as a ratio, along with the control limits of +/- 0.2. Note that while most days are within the control limit range, each of the monitoring periods does show some days outside of the limits.

Table Q-5 below documents the number of days outside of the +/- 0.2 limits. While both the absolute number and the percentage of days which fall outside of the control limits are higher than desirable, much of the difference is found to be associated with days of fluctuating mercury levels, which can skew these ratios (note that since August 1st, 2010, there has been only one day which does not meet this criterion).

It is not felt that the less than ideal channel consistency shown here greatly impacts the data. Interventions were made several times throughout the project.

Table Q-5: Channel Consistency Out of Limits

Days	Pre-Conversion	Conversion	Post-Conversion
Out of Limit	41	47	40
Total	189	318	339
Percentage	21.7%	14.8%	11.8%

Figure 11: Daily Channel Average Ratio, Pre-Conversion

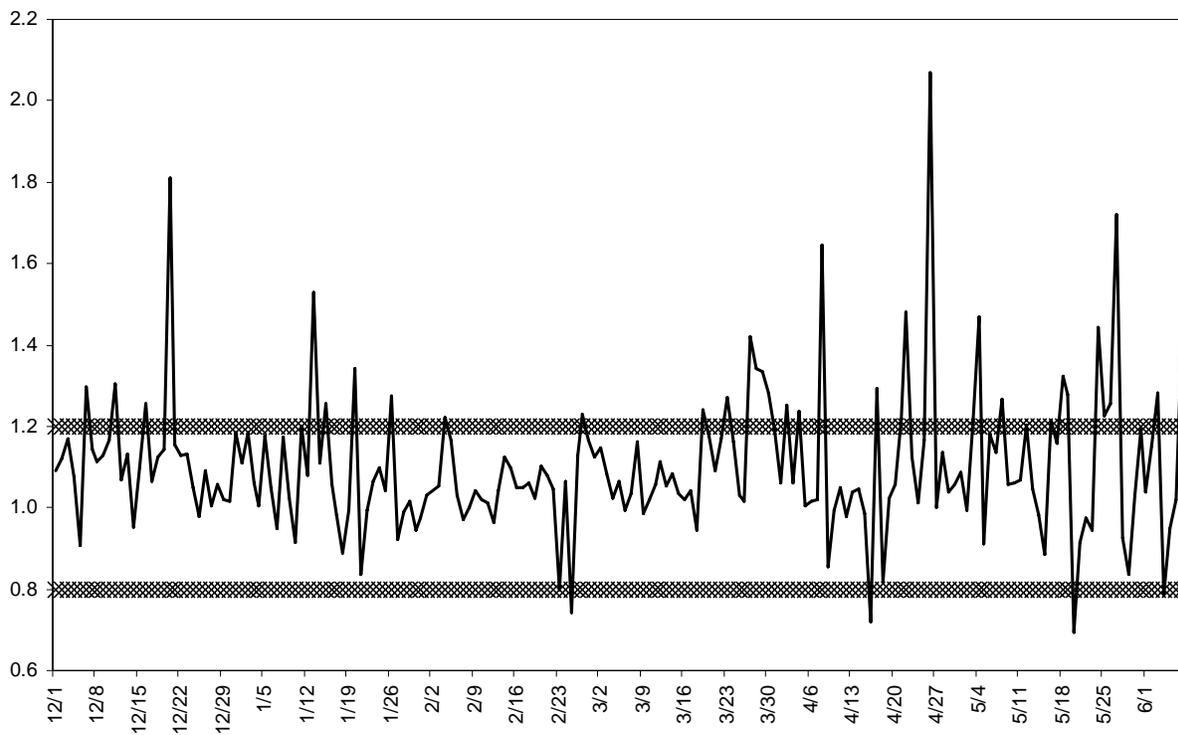


Figure 12: Daily Channel Average Ratio, Conversion

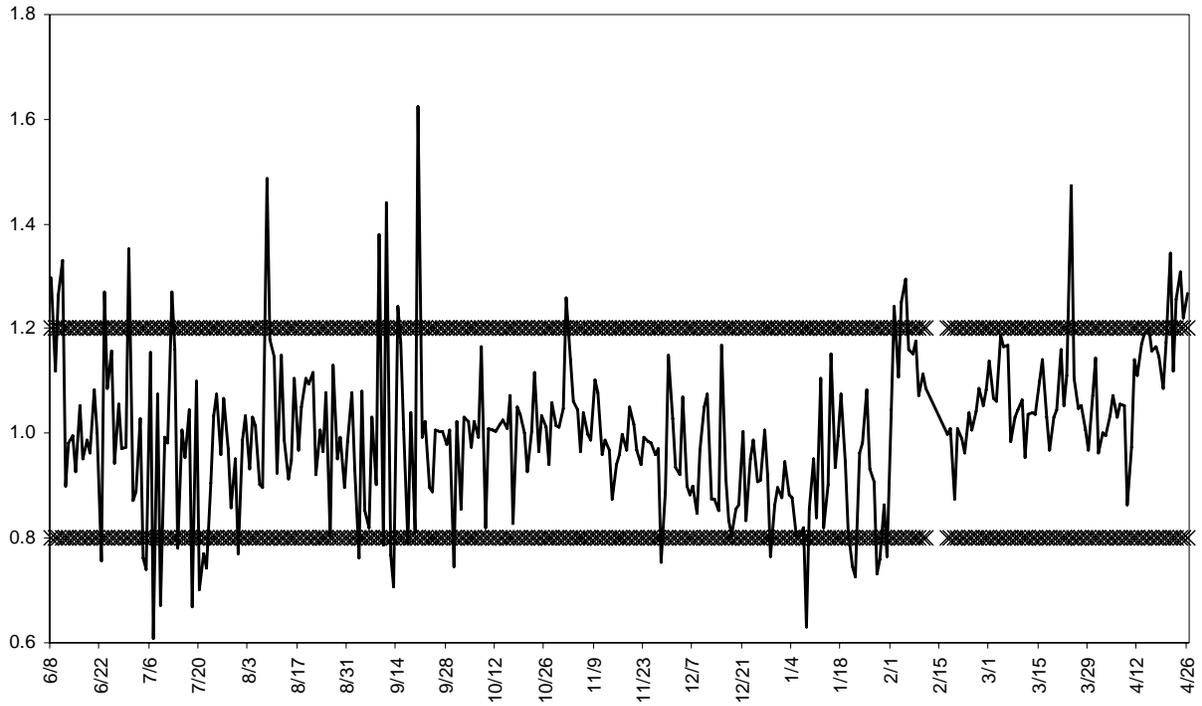
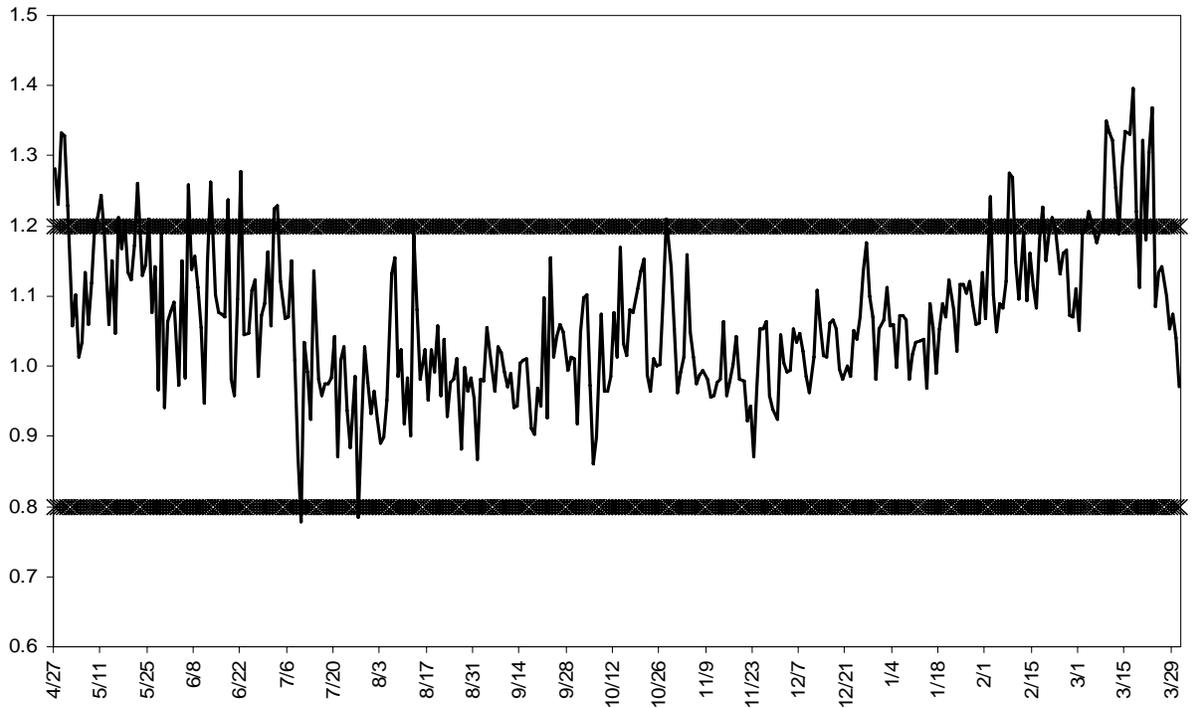


Figure 13: Daily Channel Average Ratio, Post-Conversion



Co-Located Analyzer Comparisons

Comparing the results from two separate analyzers operated side by side is an important means to verify the data collected from the primary analyzer. There were two periods in which such comparisons were made. The first of these was between March 16th and April 21st, 2009. This was after speciation sampling had been discontinued because of the difficulties associated with maintaining reliable results, but before the analyzer was removed. During this time, the instrument was run on an elemental only cycle, permitting a co-location comparison.

The second period of co-location was between March 8th and March 31st, 2011. During this period a different analyzer was brought to the site because of the dramatic increase in low values observed on the primary analyzer beginning on January 31, 2011. Between this time and the end of the project, over 76% of all values below 1 ng/m³ observed during the entire project were collected. It is not clear what caused the instrument's difficulties, but the difference before and after this date is clear.

Prior to January 31, 2011, values below 1 ng/m³ were observed on 150 out of 791 days (19%), with an average occurrence of less than 12 results per day with at least one low value. A significant portion of these values were associated with apparent depletion events, although many were associated with other periods of instrumental issues.

Beginning on that day, values below 1 ng/m³ were observed on 54 out of 60 days (90%), with an average occurrence of more than 100 values per day with at least one low value. In spite of maintenance interventions on March 1 and March 8, instrumental response improved only in the immediate aftermath of the intervention.

Results of the instrument comparisons are reported in Tables Q-6 and Q-7 below. Figures 14 and 15 document both periods of comparison, and show that the instruments follow the same trends. During both periods the primary instrument proved to read lower than the co-located instrument, with the difference being approximately 19.6% lower in 2009, and approximately 36.8% lower in 2011.

While both of these differences are significant, they do not alter the overall character of the results observed around the facility, which is that at no time was the NR446 standard exceeded, and by the end of the monitoring, results were approaching the average global background concentration.

Table Q-6: Co-Location Results, March – April, 2009

Analyzer	Average	Max	Min	Count
Primary	16.6	702.6	1.0	9948
Co-Located	19.2	765.5	1.6	10264

Table Q-7: Co-Location Results, March, 2011

Analyzer	Average	Max	Min	Count
Primary	1.4	29.9	0.6	6378
Co-Located	2.0	33.9	0.8	6538

Figure 14: Co-location Results, March 16 – April 21, 2009

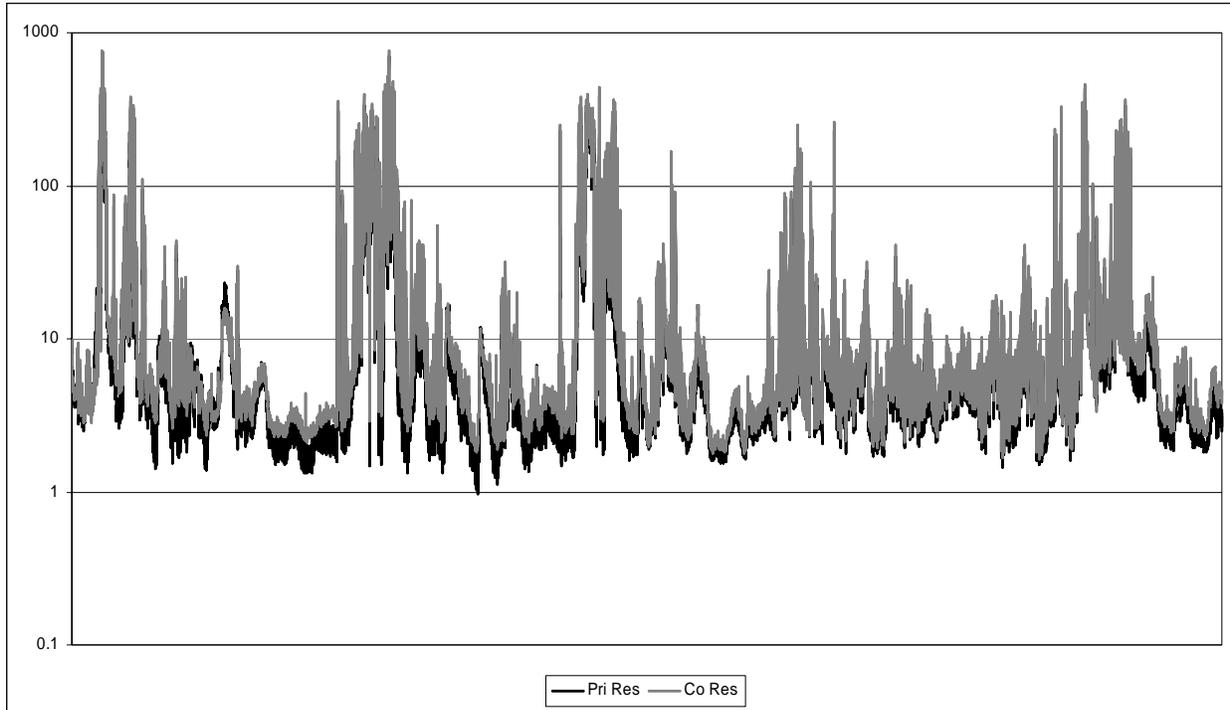
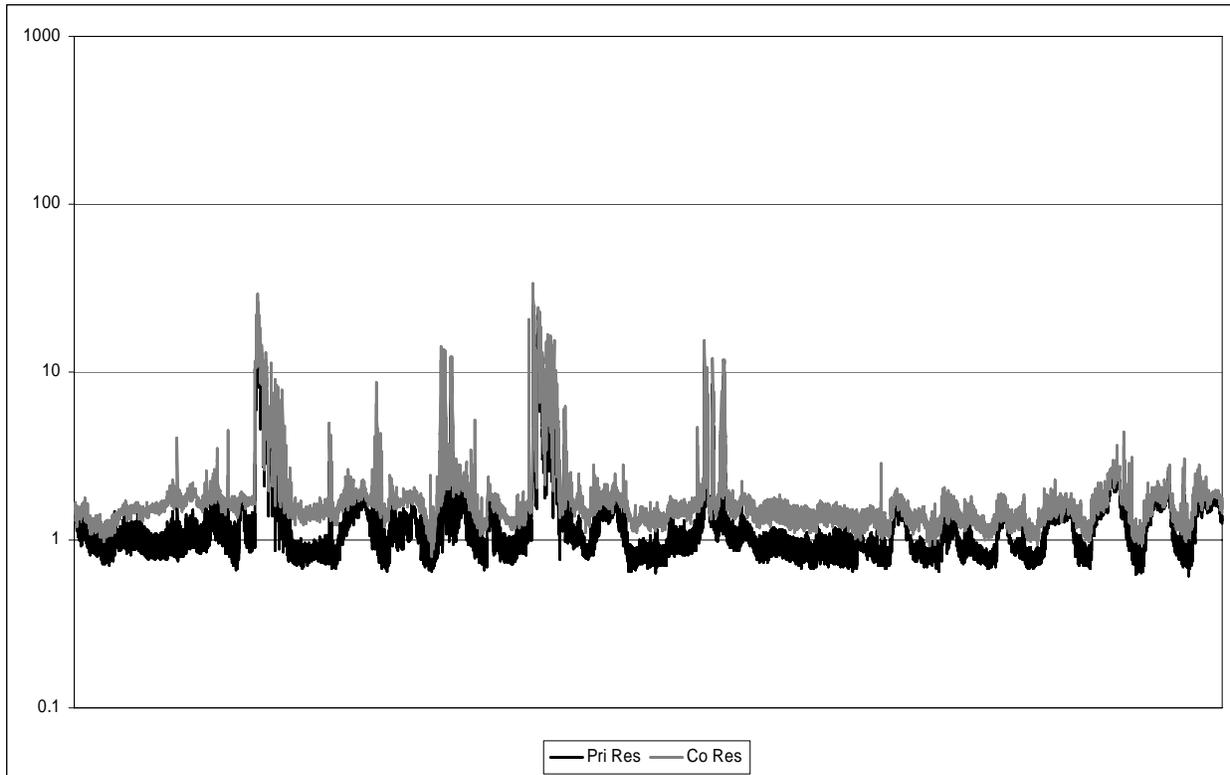


Figure 15: Co-location Results, March 8 –31, 2011



Depletion Events

There is a generally recognized global background concentration of mercury in the atmosphere of about 1.3 ng/m^3 . As this is an average, values below this level can and do occur. The National Atmospheric Deposition Monitoring Program (NADP) which is attempting to standardize procedures for mercury monitoring flags all data below 1 ng/m^3 for review, as low values can be an indicator of instrument malfunction, as discussed in the previous section.

In spite of these factors, events where mercury concentrations are reduced well below the global background are observed, and referred to as depletions. The most well known depletion event is associated with the polar sunrise. It occurs both in the Arctic and the Antarctic when the sun first returns in spring. During these events, elemental mercury values drop to zero, while reactive forms of mercury increase in concentration.

It is believed that these depletion events occur because halogen ions (chlorine, bromine and iodine) generated by the action of sea water have an extended atmospheric residence time in the dark and cold conditions of a polar winter. When the sun light reaches these areas, it catalyzes photosynthetic reactions between the background mercury present and the halogens, which converts the elemental mercury to reactive forms which can then be deposited in the snow.

During the monitoring around Vulcan in 2002, several periods of zero elemental mercury concentrations were observed. Some of these zero readings were deemed suspect because of slight instrumental irregularities associated with them, however the remainder of the values were left with no reason to invalidate them, and no real explanation, except as possible depletion events associated with the chlorine in the facility.

Again during this monitoring, several periods of zero elemental mercury concentrations have been observed. A few of these are considered suspect, because they occur in only one of the two channels, or because unusually high noise was associated with the reading. The majority of these zero values, however, are associated with instrumental parameters indicating the values are valid, and thus associated with depletion events.

In addition to the zero values, which are the most obvious indicators of a depletion event, numerous values less than 1.0 ng/m^3 have been observed through the project. The majority of these values occurred during the final 2 months of the project, and is associated with an instrumental malfunction. The remainder does not appear to be associated directly with clear depletion events. Table Q-6 below documents all zero values, and all values greater than zero but less than 1.0 observed during each phase of the monitoring. Results from 2011 are segregated from the remainder of the Post-Conversion portion of the project as they are the result of a known instrument problem.

Table Q-8: Low Values

Days	Pre-Conversion	Conversion	Post-Conversion	2011
Zero Values	69	12	1	0
Percentage	0.13%	0.01%	0.001%	0.0%
Values <1	200	1143	299	5509
Percentage	0.37%	1.27%	0.42%	22.0%

The most significant of the depletion events began on December 27th and continued into December 29th, 2008. During this time, 68 of the 69 pre-conversion monitoring period zero values were recorded. Two

other events are of note, on June 28th, 2009 during which time 6 of the 12 zero values observed during the conversion process were observed, and on December 1st, 2010, during which the only post-conversion zero value was observed.

While the detailed chemistry of mercury cycling in the atmosphere is not fully understood, non-elemental forms of mercury, which are not captured by the elemental mercury analyzer, are highly reactive and easily washed out of the atmosphere. Normally, the reactive forms of mercury are present as only a small percentage of the total gaseous mercury. Contrary to normal conditions, EPA emission estimates of reactive and elemental mercury from chlor-alkali plants indicate that a significant percentage of the emissions could be in the reactive form, and our work with the speciation analyzer examining Gaseous Oxidized Mercury appears to support this. It is possible that the proper conditions (mostly reactive forms of mercury emissions at a particular point in time, combined with rain or fog to wash the mercury out of the atmosphere) could lead to the observed depletion events.

At this point, there is no real way to verify whether or not the observed low elemental mercury values represent actual depletion events, although it seems likely. While the mechanism leading to the depletions is unclear, and beyond the scope of this study, the data does provide interesting information about mercury chemistry. Unfortunately, the speciation analyzer was not on site during any of these events, and so whether the decrease in elemental mercury was accompanied by a rise in the gaseous oxidized forms is unknown.

Conclusions

This report presents a unique study, measuring atmospheric mercury concentrations before, during and after the conversion of a mercury cell chlor-alkali plant to a membrane cell chlor-alkali plant that does not use mercury. The data clearly shows high concentrations of ambient mercury associated with the original mercury cell process. In addition, the speciation analyzer, even though it proved operationally too difficult to continue beyond a relatively short period, demonstrated that a relatively high percentage of the total mercury coming from the facility at that time was in the gaseous oxidized form, and thus readily deposited in the immediate environment.

Following the conversion, a dramatic decrease in the mercury concentrations measured around the facility was observed. While somewhat elevated levels still occur near the facility, these levels likely represent residual contamination both in the facility itself and in the near by areas, as a result of decades of mercury use and deposition. It is anticipated that over time these levels will gradually decrease to a point approaching the global background on a consistent basis.

Overall, converting the mercury cells to membrane cells at ERCO Worldwide- Port Edwards has significantly reduced mercury emissions in Wisconsin, and should eliminate any additional local mercury contamination.