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Environmental Sampling FY-03 Annual Report –Understanding the Movement of Mercury at the INEEL

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Idaho National Engineering and Environmental Laboratory
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ABSTRACT

Environmental mercury measurements were started in Fy-01 at the Idaho National Engineering Laboratory (INEEL) to monitor downwind impacts from on-going waste treatment operations at the Idaho Nuclear Technology and Engineering Center (INTEC) and to improve our scientific understanding of mercury fate and transport in this region. This document provides a summary of the sampling done in FY04. Continuous total gaseous mercury (TGM) measurements were made using a Tekran® Model 2537A mercury vapor analyzer during October 2002 and from February through July 2003. The equipment was deployed in a self-contained field trailer at the Experimental Field Station (EFS) four kilometers downwind (northeast) of INTEC. Mercury surface-to-air flux measurements were made in October 2002 and from February through May 2003 to better understand the fate of the estimated 1500 kg of mercury emitted from 36 years of calciner operations at INTEC and to improve our scientific understanding of mercury environmental cycling in this region. Flux was measured using an INEEL-designed dynamic flux chamber system with a Tekran® automated dual sampling (TADS) unit. Diel flux was positively correlated with solar radiation ($r = 0.65$), air temperature ($r = 0.64$), and wind speed ($r = 0.38$), and a general linear model for flux prediction at the INEEL was developed. Reactive gaseous mercury (RGM) was measured at EFS in July using a Tekran® Model 1130 mercury speciation unit. Based on comparisons with other published data around the U.S., mercury air concentrations and surface flux rates directly downwind from INTEC were not distinguishable from remote area (non-industrial) background levels during the monitoring period.

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INTRODUCTION

Mercury (Hg) is a high priority toxic air pollutant that is of concern at the Idaho National Engineering and Environmental Laboratory (INEEL), across the U.S., and globally. Mercury atmospheric deposition rates across the U.S. have increased by factors of three to five in the last 100 years, and by factors of five to six around the INEEL, based on a Mud Lake sediment studies performed in 2001. These increases are thought to be due to global buildup of Hg in the atmosphere from worldwide industrial emission sources and long-range atmospheric transport. However, local source impacts may also be significant, and it has been difficult to partition and quantify the fractional contribution from the different source locations.

Significant on-going research is being performed to better understand mercury's complex environmental cycling in an effort to better quantify contributing sources.[1,2] At the INEEL's Idaho Nuclear Technology and Engineering Center (INTEC), significant quantities (est. 40 kg/year) of Hg were released to the atmosphere during high-level waste (HLW) calcining operations, and Hg is the risk-driving toxic air pollutant currently being released from operations of the Liquid Effluent Treatment and Disposal (LET&D), Process Equipment Waste Evaporator (PEWE), and the New Waste Calcining Facility (NWCF) Evaporator Tank System (NWCF ETS – formerly HLLWE).

The HLW Environmental Sampling work reported here is: 1) providing defensible atmospheric and surface measurements of Hg downwind from INTEC to monitor on-going process emissions and 2) increasing our scientific understanding of Hg fate and transport in this region. Both of these goals will facilitate the HLW Program's path forward decisions and regulatory permitting of existing and future waste treatment operations.

SUMMARY

FY-03 sampling activities included air sampling of total gaseous mercury (TGM) air concentrations and surface-to-air flux rates, installation and operation of a new mercury speciation unit, and presentation of these results at a national conference. A summary of the sampling activities is as follows:

- Continuous measurements were made for TGM using a Tekran® Model 2537A mercury vapor analyzer during October 2002 and from February through July 2003. The equipment was deployed in a self-contained field trailer at the Experimental Field Station (EFS) four kilometers northeast of INTEC. The 2537A provides 5-min to 15-min continuous sampling and analysis of TGM at well below background levels (sub-ng/m^3). Monthly average concentrations were relatively steady, ranging from 1.42 ng/m^3 in November to 1.66 ng/m^3 in December. Maximum monthly concentrations ranged from 1.83 ng/m^3 in February to 5.53 ng/m^3 in October. In the northern hemisphere, background concentrations currently average about 1.5 to 2.0 ng/m^3,[3] although higher short-term peaks often occur due to emissions from local or regional sources and natural emissions from forest fires or volcanic activity. Based on this, Hg emissions from INTEC do not appear to have increased downwind Hg concentrations significantly above background during the monitoring period. These results were included in a poster presented at the International Conference on Air Quality IV, in Arlington, VA, September 23, 2003.

- Mercury surface-to-air flux measurements were made in October 2002 and from February through May 2003. Flux measurements were made to better understand the fate of the estimated 1500 kg of mercury emitted from 36 years of calciner operations at INTEC and to better understand the complex environmental cycling of deposited mercury in this region. Positive flux values indicate that mercury in the soil (both natural and deposited) is being released back to the atmosphere at rates that are higher than its deposition. Mercury flux at EFS during this time period typically showed diel cycling with daytime high values averaging 4.5 ng/m^2/hr and nighttime values dropping to zero or less (indicating net deposition). Maximum monthly fluxes reached 10 to 20 ng/m^2/hr. This cycling was positively correlated with solar radiation ($r = 0.65$), air temperature ($r = 0.64$), and wind speed ($r = 0.38$). The average flux over the entire measurement period was 0.8 ng/m^2/hr. These flux values are similar to or less than those measured by other researchers in Nevada (4-125 ng/m^2/hr), Michigan (1.4-7.6 ng/m^2/hr), and Germany (43 ng/m^2/hr). Based on this and previously measured soil concentrations around INTEC,[4] it appears that mercury emissions from INEEL soils immediately downwind from INTEC are not significantly different from other background areas and are not a major Hg source to the atmosphere.

- A new state-of-the-science Tekran Model 1130 mercury speciation unit was installed and operated at the EFS field trailer beginning in July. The 1130 allows the 2537A analyzer to sequentially measure two primary components of TGM—elemental gaseous mercury (EGM) and reactive gaseous mercury (RGM), the gaseous ionic (typically divalent) species that is emitted by certain types of thermal treatment processes. Since most of the background mercury in air is EGM and RGM does not travel far in the atmosphere, measurement of the RGM fraction provides a much clearer picture of the downwind impacts from local thermal treatment processes such as those currently operating at INTEC. RGM values at EFS during July typically ranged from 10 to 50 pg/m^3 and demonstrated a diel cycling with no unusually large peaks. These values are lower than those reported by Lindberg and Stratton[4] in 1998, which measured RGM values in Tennessee of 50-200 pg/m^3. Based on these results, potential RGM releases from ongoing thermal waste processing at INTEC were not distinguishable from background during July 2003.

- A student action team (SAT) of four high school students and one high school teacher was mentored from June 16–August 7, 2003. The team assisted in installation and operation of the Tekran 1130 and performed flux data analysis.

- A poster on these results was presented at the International Conference on Air Quality IV, in Arlington, VA, September 23, 2003.

METHODS

TGM Measurements

Continuous 5 to 15-min TGM concentrations were measured at EFS using the Tekran Model 2537A Hg vapor analyzer from October 2002 through July 2003 (Figure 1). Calibration of the unit was automatically performed every 25 hours using an internal certified Hg permeation source. In December 2002, a primary calibration using precision mercury vapor injections was made using the Tekran Model 2505 mercury calibration system.

A portable meteorological station (MetOne Instruments) was deployed next to the Tekran to collect 15-min measurements of wind direction, wind speed, air and soil temperature, relative humidity, and solar radiation (Figure 2). Measurement of these parameters contributes to better understanding of the conditions, which affect cycling of Hg in this region, and provides information on potential source directions during peaks in Hg air concentration.

Figure 1. Tekran deployment at EFS.

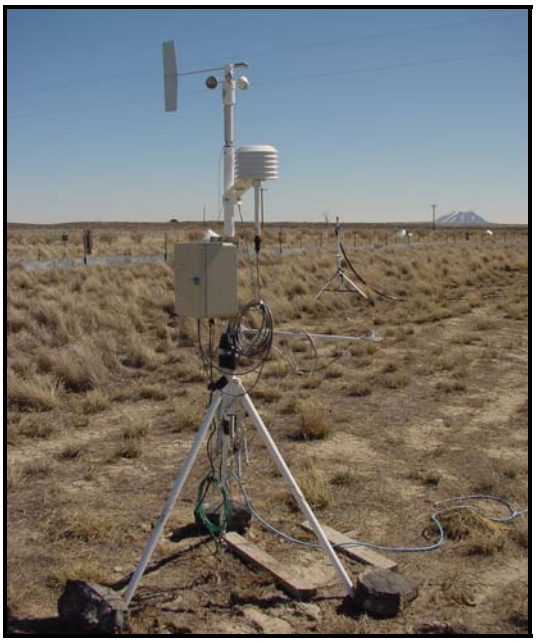

Figure 2. Micromet station (MetOne Instruments, Grants Pass, Oregon).

The Tekran uses two gold cartridge absorbers (A/B)—one that is absorbing Hg during the sampling period and one that is desorbing the Hg from the previous sampling cycle. The desorbed Hg is then measured by a cold vapor atomic fluorescence spectrometer (CVAFS) within the Tekran. This provides duplicate sequential measurements that help confirm reliable and stable instrument operations (Figure 3).

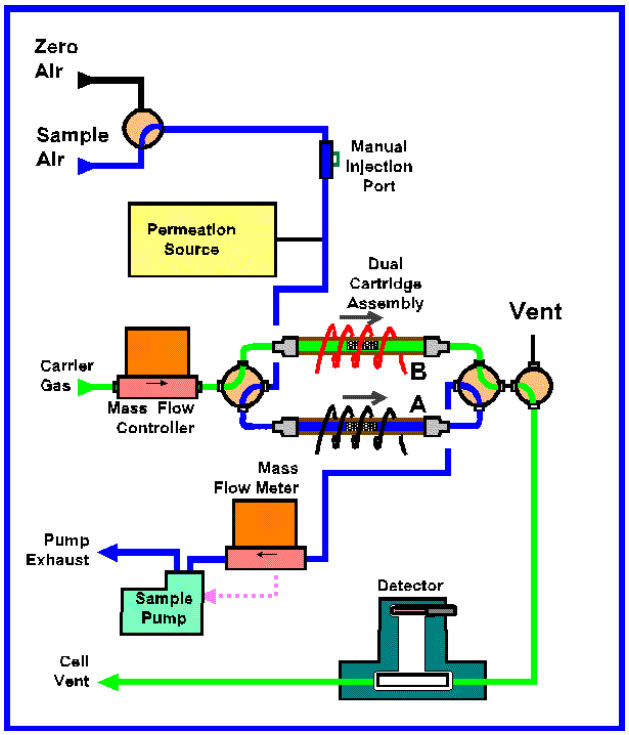

Figure 3. Tekran 2537A flow diagram.

Flux Measurements

A fraction of the atmospheric Hg that has been deposited from local sources or that exists naturally in the soil is subject to reduction processes (solar radiation, soil redox chemistry) and conversion to elemental Hg(0). The elemental Hg(0) is then re-emitted back to the atmosphere as elemental gaseous mercury (EGM), where it has an atmospheric half-time (before oxidation in the atmosphere) of approximately one year. This re-emitted EGM re-enters the global atmospheric Hg(0) pool and will not re-deposit locally. Measurement of Hg surface-to-air flux rates was done to better understand this cycling and to determine the site-specific fraction that is lost to re-emission in this region. This is important for future risk assessment work, which currently assumes that all of the Hg deposited remains in the local environment where it will contribute to the calculated human health and ecological risk.

Flux chamber runs were made in October 2002 and from February through May 2003. These flux measurements were made using a polycarbonate flux chamber, a large (30 L/min) chamber vacuum pump, a small (1.5 L/min) flow equalization pump, the Tekran Automated Dual Sampling System (TADS), the Tekran 2537A, and a controller (Figure 4). The TADS consists of two solenoid valve boxes synchronized to the Tekran sampling cycle, which provide automated alternate measurements of the chamber inlet (ambient) air concentration and chamber outlet air concentration (ambient + flux input).

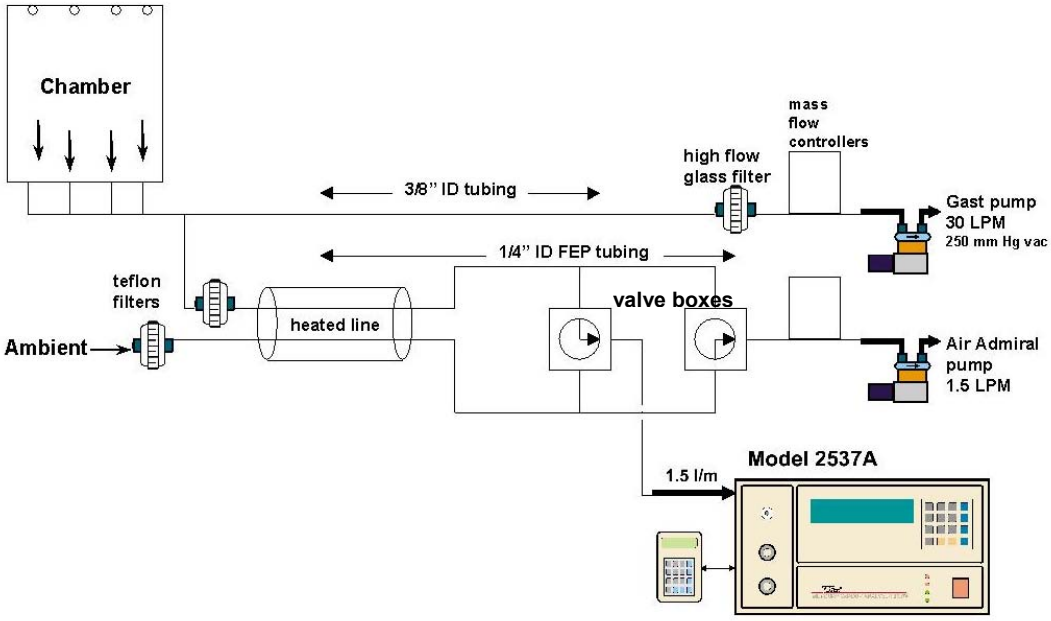

Figure 4. INEEL Hg flux measurement system.

The valve boxes switch after two 5-min Tekran sampling cycles, so that A/B cartridge bias is eliminated in the flux assessment. This gives two 5-min chamber measurements and two 5-min ambient measurements from which a 20-min average flux can be calculated. Surface flux (F, in ng/m^2/hr) is calculated as:

$$F = \frac{(C_o - C_i)}{A} \times Q$$

where

C_o = average of A/B cartridge Hg concentrations from flux chamber (ng/m^3)
C_i = average of A/B cartridge Hg concentrations from ambient air line (ng/m^3)
Q = flushing rate through flux chamber (30 L/min [1.8 m^3/hr])
A = bottom surface area of flux chamber (0.06 m^2)

Chamber blank measurements were made at intermittent intervals by placing the chamber over a clean Teflon sheet. These blank measurements evaluate whether the chamber is absorbing Hg from the sampled air or is internally contaminated and releasing additional Hg into the chamber sampling line. Good chamber blank performance is indicated by a near zero flux rate (chamber inlet concentration ≈ chamber outlet concentration). Typically, chamber blank measurements show a slight positive flux, which, depending upon the magnitude, may or may not be subtracted from subsequent flux measurements.

RGM Measurements

RGM measurements were made in July 2003, using a new Tekran ® Model 1130 Mercury Speciation Unit, which was mounted outside the Tekran instrument trailer on a permanently-installed extension ladder (Figure 5). This instrument gives the 2537A the ability to simultaneously monitor both EGM and RGM species in ambient air. A quartz annular denuder efficiently captures RGM while allowing elemental mercury to pass through. During the adsorption phase (80 min), EGM passes through the denuder and is measured by the 2537A. This is followed by the desorption phase, during which the denuder is flooded with Hg-free air and heated to 500°C. The heating converts the RGM to EGM, which is released from the denuder and detected by the 2537A (Figure 6).

Figure 5. Tekran 1130 denuder module being installed outside the EFS instrument trailer.

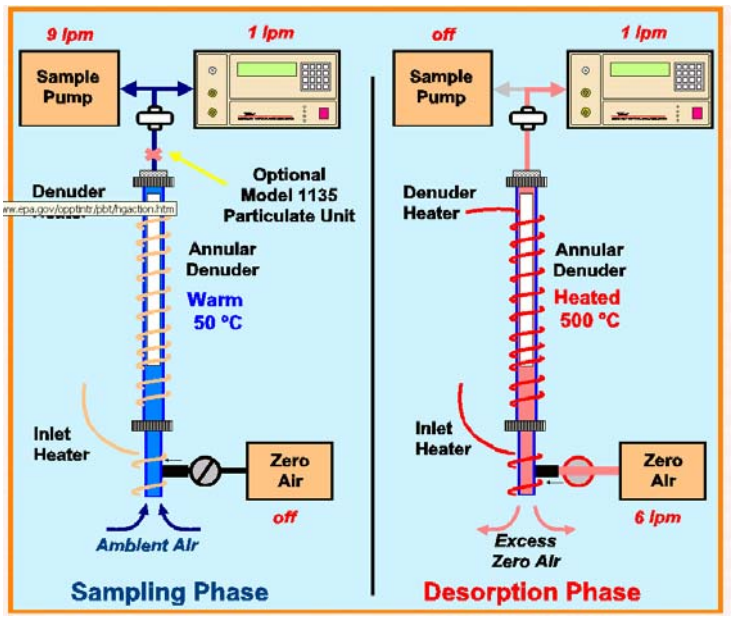

Figure 6. Tekran Model 1130 principals of operation.

A single RGM measurement cycle requires two hours and consists of:

- An 80-min adsorption cycle, during which RGM is absorbed by the denuder and EGM is measured (in ng/m^3) by the 2537A (sixteen 5-min 2537A measurements),
- A 15-min zero-air cycle, during which the denuder is flooded with Hg-free air and the 2537A reads residual Hg in pg/m^3 (three 5-min 2537A measurements),
- A 15-min denuder heating cycle, during which RGM is converted to EGM and measured (in pg/m^3) by the 2537A (three 5-min 2537A measurements),
- A 10-min zero-air cycle, during time the denuder is cooling (two 5-min 2537A measurements).

The RGM concentration averaged over the 80-min adsorption cycle is calculated by summing the concentrations from the three heat cycles and subtracting three times the last zero air concentration prior to desorption.[5]

The quartz denuder must be replaced on a bi-weekly basis with a reconditioned denuder that has been cleaned, coated with a saturated KCl solution, and blanked (Figure 7). Denuder reconditioning begins with rinsing with nano-pure (18.2 MΩ/cm) deionized water (DIW) and laboratory-grade methanol, and air drying with ultra high purity (UHP) argon. The denuder is then coated two times with the saturated KCl solution using a hand-operated vacuum pump and then dried with UHP argon. "Blanking" is then performed by heating the denuder in a tube furnace for one hour at 550°C while purging with UHP argon. This cures the KCl coating and removes any mercury in the coating.

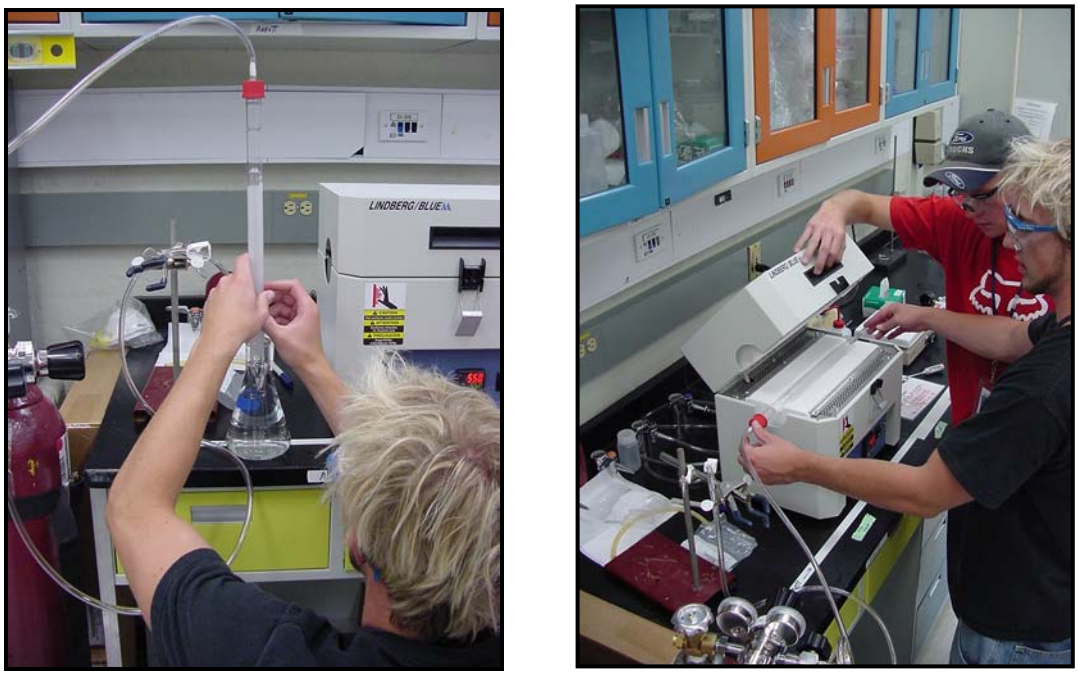

Figure 7. Denuder KCl recoating and thermal “blanking” process.

RESULTS AND DISCUSSION

TGM Measurements

TGM concentrations measured from October 2002 through May 2003 ranged from 0.45 to 5.53 ng/m^3, with an average value of 1.53 ng/m^3 (Table 1, Figures 8-15). Typical background concentrations for remote areas in the northern hemisphere with little industrial input range from 1.5 to 2 ng/m^3.[3] Isolated peaks can be attributed to local/regional industrial input and natural sources such as forest and range fires and volcanic activity. A relatively large spike (5.53 ng/m^3) occurred on October 10 from 12:20 pm to 4:20 pm. Because the wind was generally from the direction of INTEC during this time (southwest), a release from this facility cannot be ruled out, although no unusual waste treatment operations were occurring at the time. However, this spike is not considered to be a high ambient concentration – concentrations higher than this typically occur throughout the eastern U.S. and in metropolitan area throughout the U.S. In Nevada, TGM concentrations at typical regional sites ranged from 1.2 to 7.5 ng/m^3 while concentrations at anthropogenically contaminated areas (Carson River Superfund site) reached 13 to 866 ng/m^3.[6]

In summary, the ambient TGM concentrations measured at EFS indicate that the INEEL is in a area of low to average TGM background and that there is little if any environmental input from local INEEL sources. However, these measurements only reflect impacts from waste treatment operations that were on-going at the time of the measurements—continued sampling is recommend to monitor potential emissions from future operations.

Table 1. Monthly TGM concentrations at EFS from October 2002 through May 2003.

Ambient TGM Concentrations (ng/m^3)

	Maximum	Minimum	Monthly Average
October '02	5.53	0.45	1.44
November '02	2.04	0.68	1.42
December '02	2.79	0.82	1.66
January '03	2.07	0.97	1.54
February '03	1.83	0.73	1.46
March '03	3.29	0.93	1.55
April '03	2.58	0.85	1.63
May '03	2.47	0.86	1.54
Average max.	**Average min.**	**Average***	
5.53	0.45	1.53	

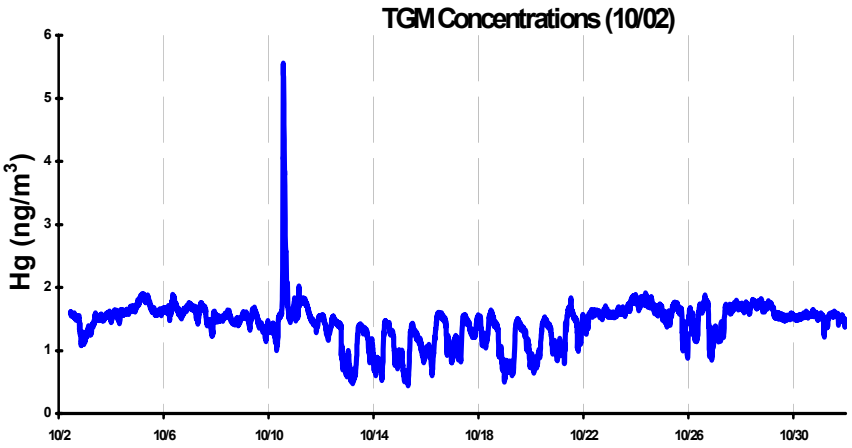

Figure 8. TGM concentrations measured at EFS during October 2002.

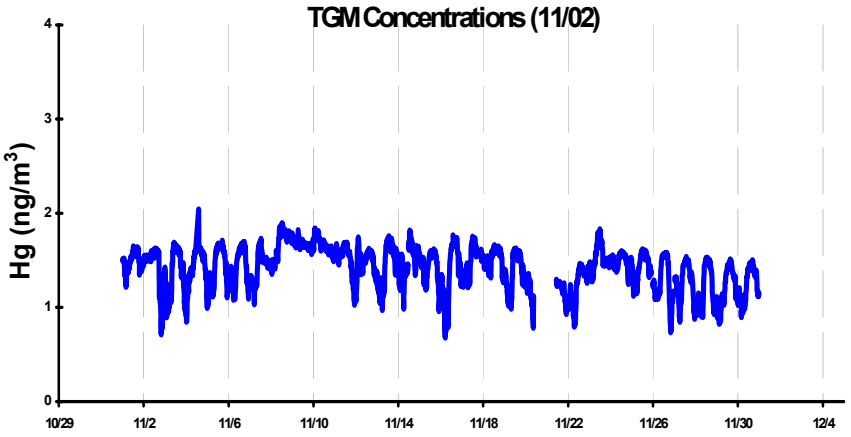

Figure 9. TGM concentrations measured at EFS during November 2002.

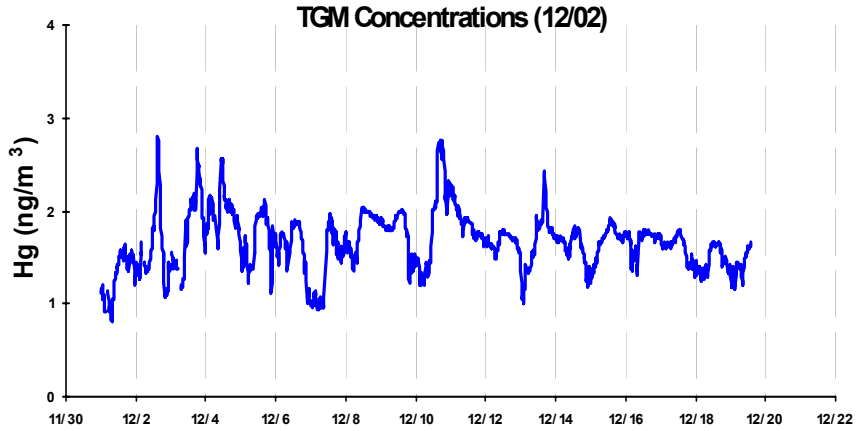

Figure 10. TGM concentrations measured at EFS during December 2002.

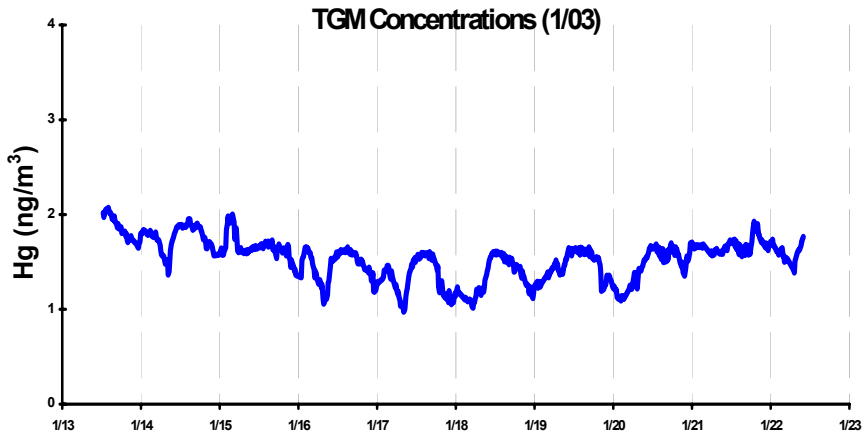

Figure 11. TGM concentrations measured at EFS during January 2003.

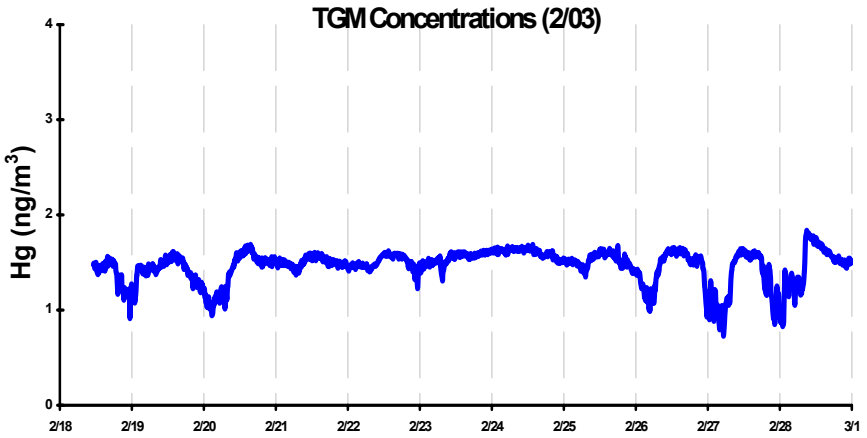

Figure 12. TGM concentrations measured at EFS during February 2003.

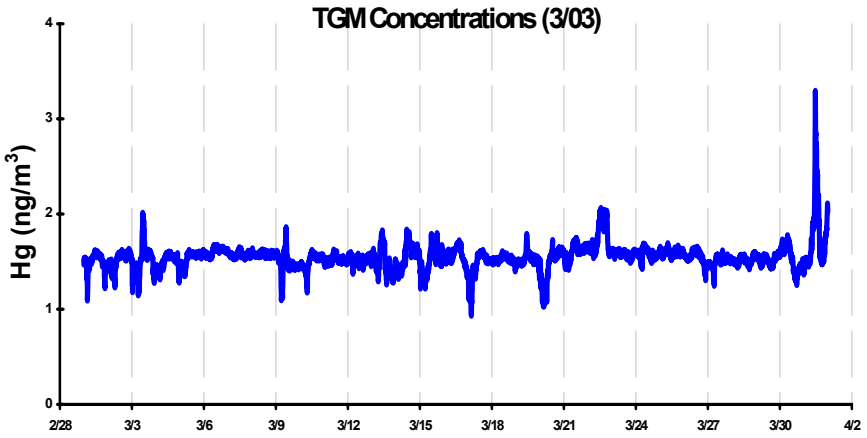

Figure 13. TGM concentrations measured at EFS during March 2003.

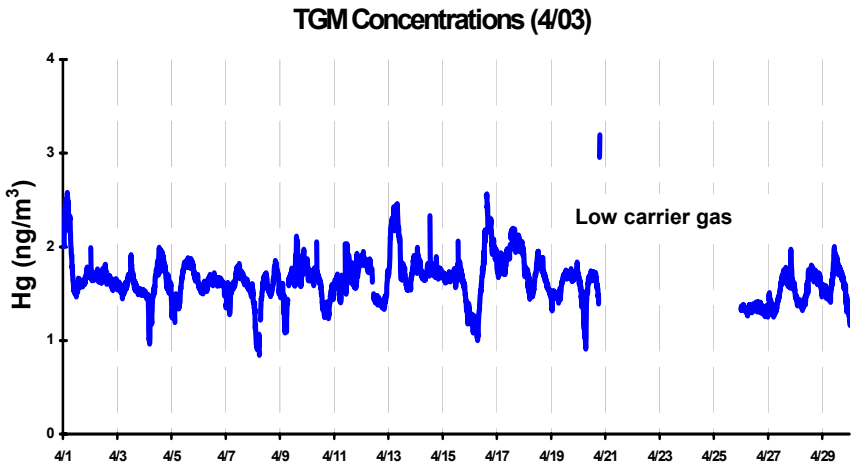

Figure 14. TGM concentrations measured at EFS during April 2003.

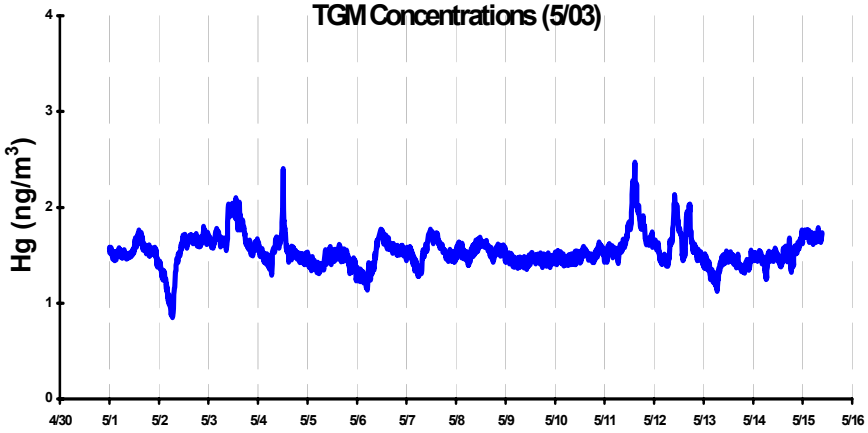

Figure 15. TGM concentrations measured at EFS during May 2003.

Flux Measurements

Hg surface-to-air flux exhibited a strong diel variation, with mid-day peaks and nighttime lows (Figure 16). The average 24-hour maximum over the observation period was 4.5 ng/m^2/hr, while nighttime lows typically dropped below zero. Maximum monthly flux values ranged from 10 to 20 ng/m^2/hr with minimums of −8 to −12 ng/m^2/hr (Table 2). When averaged over all the data, the flux was 0.81 ng/m^2/hr. The average of the chamber blanks was 0.28 ± 1.4 ng/m^2/hr (n = 990), which is good performance (no significant adsorption or release of Hg from the flux system) compared that measured in other flux studies.

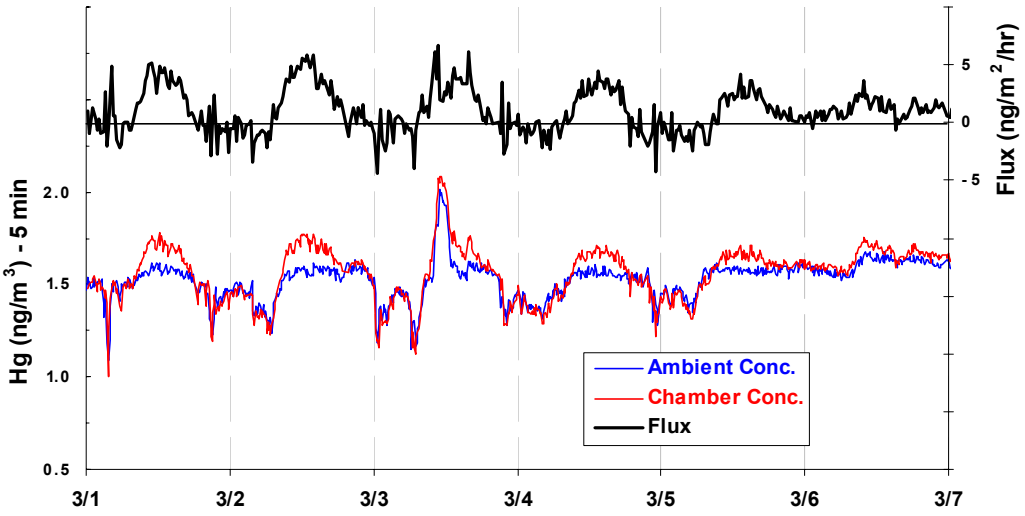

Figure 16. Typical diel variation of Hg flux measured at EFS (March 1 – 7, 2003).

Table 2. Maximum, minimum and average monthly Hg fluxes measured at EFS.

	Hg Flux (ng/m^2/hr)		
	Maximum	**Minimum**	**Monthly Average**
October '02	12.71	-10.34 (-70.31)[1]	0.13
February '03	10.57	-7.84	1.21
March '03	10.16	-9.75	0.53
April '03	23.53	-12.79	1.19
May '03	20.58	-8.62	1.81
	Average max.	**Average min.**	**Average[2]**
	15.51	-9.868	0.81

1. The -70 value occurred after a relatively large transient air concentration spike and likely has significant sampling error due to the sequential sampling design inherent in the TADS.
2. Average of all the data. Not a monthly average.

The flux values observed at EFS are in the range of those observed for other low background sites and significantly less than those observed in naturally Hg-enriched areas or in areas that have been subject to moderate development (Table 3). These relatively low flux rates are likely influenced by the low soil concentrations found at the INEEL[4] and the fact that the NWCF has been shut down for three years.

Table 3. Comparison of EFS Hg fluxes to those measured in other locations.

Researcher	Ave. Flux (ng/m^2/hr)	Location
Abbott	0.81	Idaho (INEEL) - Average 24-hr
	4.45	Idaho (INEEL) - Average Daily Max
Engle	17.1	Nevada (Naturally Enriched Substrate)
Gustin	5-125 (± 50%)	Nevada (Naturally and Anthropogenicly Enriched Substrate)
Wallschlager	43 ± 5	Germany (Floodplains)
Zehner	4.2 ± 1.4	State of Nevada
Zhang	1.4 ± 1.4	Michigan (Forested)
	7.6 ± 1.7	Michigan (Open Field)

Flux Model

Some effort was made to statistically evaluate the effects of meteorology on flux in order to build a predictive model and to better understand the parameters that affect Hg cycling at the INEEL. Flux was found to be primarily correlated with solar radiation (r = 0.65), air temperature (r = 0.64), and wind speed (r = 0.38). Using these parameters, a multi-variate general linear model (GLM) was created which produced reasonably accurate predictions of flux during the March time period (Figure 17). However, it was found that the March model did not perform as well for other months, indicating that seasonal models may be required for accurate prediction of flux throughout the year.

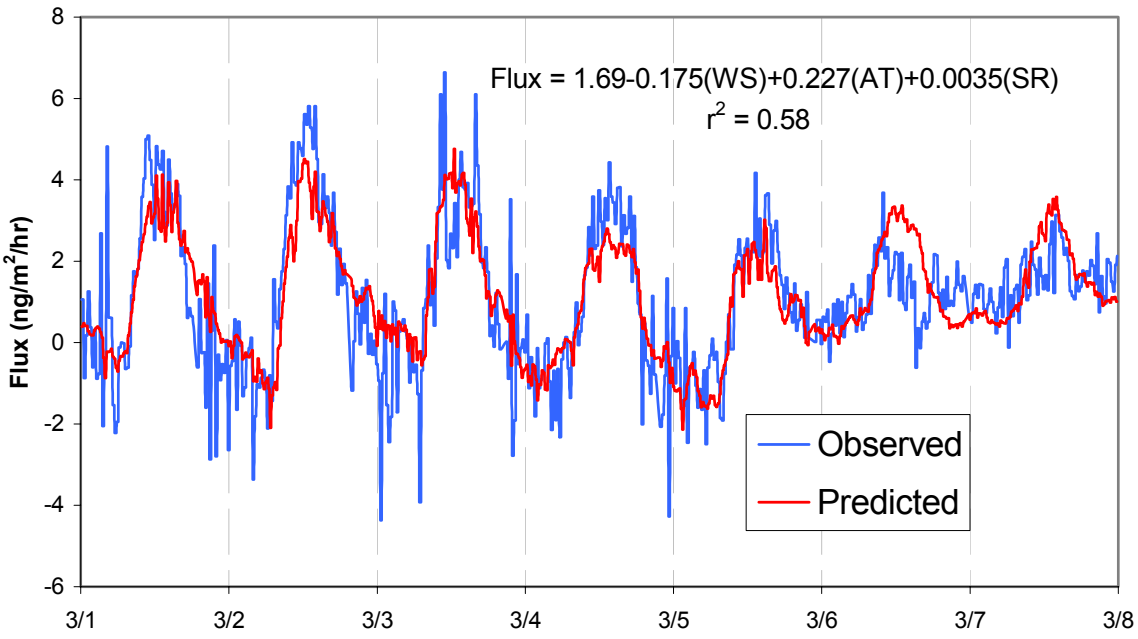

Figure 17. Comparison of the predicted-to-observed Hg flux during the first week in March 2003, using a general linear model with wind speed (WS), air temperature (AT), and solar radiation (SR) parameters.

RGM Measurements

RGM measurements with the Tekran 1130 speciation unit were started in late June 2003, and reliable data were obtained during most of July 2003 (Figures 18-20). As with TGM, RGM values show a diel pattern with daily maximums of 10 to 50 pg/m^3 and daily lows of 3 to 13 pg/m^3. The RGM fraction of TGM ranged from approximately 0.2 to 4%. These values are significantly lower than the 50 to 200 pg/m^3 range measured in Tennessee by Lindberg and Stratton (1998).[7] Based on this, and the lack of large peaks observed, potential RGM releases from INTEC or other local INEEL sources are not distinguishable from background during the period of observation.

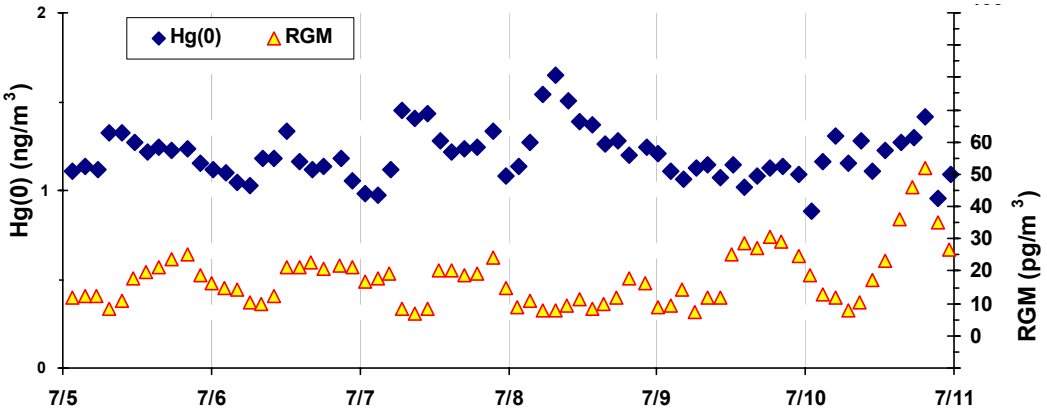

Figure 18. RGM values measured at EFS from July 5 to July 11, 2003.

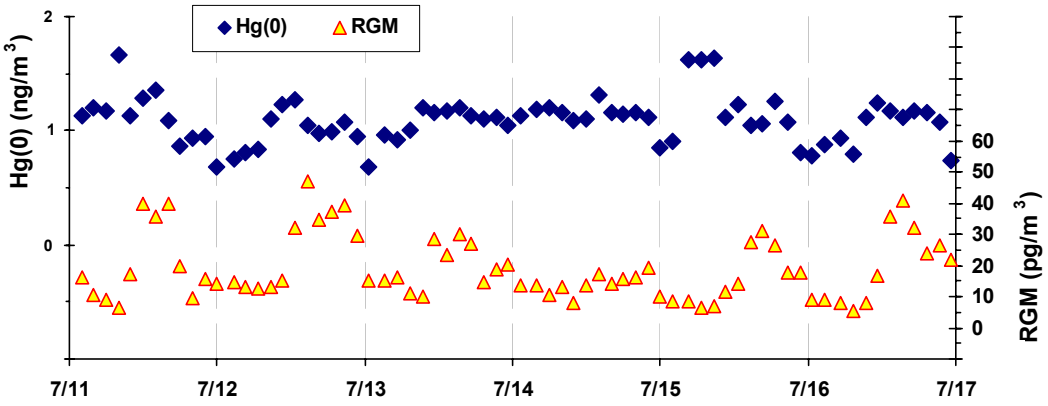

Figure 19. RGM values measured at EFS from July 11 to July 17, 2003.

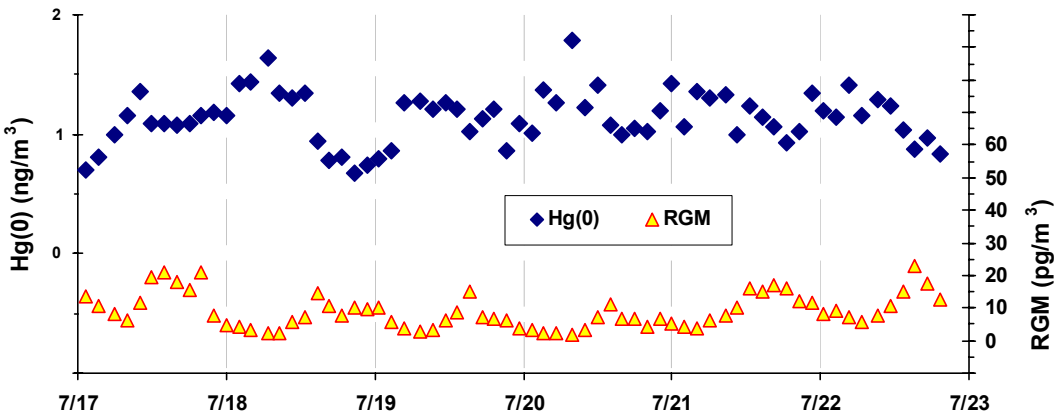

Figure 20. RGM values measured at EFS from July 17 to July 23, 2003.

FY-04 WORK

Environmental sampling work will continue in FY-04 with the following activities:

1. Operations of the Tekran 2537A and 1130 at different locations around INTEC to monitor on-going waste treatment operations at INTEC (LET&D, PEWE, NWCF ETS, filter leach). These locations will be determined by local weather patterns and waste treatment operations schedules.

2. Re-emission flux measurements at the maximum fallout location downwind from INTEC (1 km northeast of the fence line) to better understand the fraction of deposited Hg that is retained locally and might contribute to risk.

3. Snow sampling around the INTEC grid to assess the trace element and common ion fallout that may occur as a result of liquid waste treatment operations. This will help establish an INTEC pollutant input baseline, which will enhance future permitting activities by providing data for model validation and parameter calibration. Also, efforts will be made to identify a unique INTEC chemical signature that can be source apportioned at downwind sampling locations where there is a mixture of source inputs.[8]

4. Development of a sampling strategy and initial procedures for downwind measurements of metal and organic toxic air pollutants (TAPs) regulated by the State of Idaho to support RCRA Part B permitting of waste treatment facilities. This will provide valuable measured data to support modeling efforts required for the permitting process.

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