

AN INTENSIVE MULTI-SITE PILOT STUDY INVESTIGATING ATMOSPHERIC MERCURY IN BROWARD COUNTY, FLORIDA

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Abstract. An intensive multi-site pilot study of atmospheric Hg was conducted in Broward County, Florida in August and September of 1993. Broward County, which contains the city of Fort Lauderdale, is located in southeastern Florida. The county borders the Florida Everglades on the west and the Atlantic Ocean on the east. A network of four sampling sites was set up for 20 days throughout Broward County to measure Hg in both the vapor phase and the particle phase as well as Hg in precipitation. The mean concentrations of total vapor phase Hg measured at two inland sites were found to be significantly higher (3.3 and 2.8 ng/m³) than that measured at a site located on the Atlantic shore (1.8 ng/m³). The mean concentrations of particle phase Hg collected at the two inland sites (51 and 49 pg/m³) were found to be 50% greater than that measured at the coastal site (34 pg/m³). In addition, event precipitation samples were collected at four sampling sites over the 20 day study period and were analyzed for both reactive and total Hg. The mean concentration of total Hg in the precipitation samples was found to be 44 ng/L, with a range of 14 to 130 ng/L. It was determined that further meteorological analysis and a more complete characterization of the aerosol and precipitation composition are needed to identify the probable source(s) contributing to the increased deposition of Hg.

1. Introduction

The importance of mercury (Hg) as an environmental contaminant stems from its ubiquitous nature due largely to the multitude of sources, its volatility, mobility and persistence in nature. While Hg was once thought to be a threat only in the locality of large industrial facilities, recent research has found that even remote and pristine waters have elevated levels of Hg compounds in fish. A statewide survey of Hg in sportfish was implemented in Florida after preliminary indications of Hg contamination in Florida freshwater fish (Hand and Friedemann, 1990). The study found concentrations of Hg in fish in the Savannas State Reserve and the Everglades that exceeded acceptable levels for human consumption. Hg concentrations sufficient to warrant limited consumption advisories were found in fish in numerous lakes, rivers, and wetlands. Other studies in Florida suggested that Hg is transported through the Everglades food web and that Hg bioaccumulation has diminished the viability of the endangered Florida panther (Roelke *et al.*, 1991). The risk of Hg biomagnification to other animal populations has not yet been quantified. However, the potential for perturbations of ecosystem structure and function seems apparent.

The studies described above provided an initial assessment of the magnitude of the Hg contamination in south Florida. However, they did not address issues regarding the origin, atmospheric transport and deposition, or availability of Hg in these habitats. The study reported here investigated the local impact of anthropogenic sources on the atmospheric Hg levels in Broward County, Florida, an area located immediately east of the Florida Everglades. This research was a collaborative effort between the Florida Department of Environmental Protection, the United States Environmental Protection Agency (AREAL and Region IV), the Broward County Department of Natural Resource Protection, and the University of Michigan Air Quality Laboratory (UMAQL). The

project served as a pilot investigation for more comprehensive sampling to be performed in urban areas in south Florida. The study included a limited investigation of the sampling and analytical methods for atmospheric mercury determinations which could be utilized in selected ecosystems in the Everglades or surrounding areas.

2. Experimental Methods

Ambient measurements of vapor phase and particle phase Hg, as well as Hg in precipitation were made at four sampling sites located in the Fort Lauderdale area (see Figure 1). Samples were collected at each of these sites from 19 August to 7 September, 1993. Since the prevailing winds are out of the east/southeast during the late summer and early fall, a site along the coast was chosen to provide a "local background". Three additional sites were chosen along a path leading inland or "downwind" from the coast. A brief description of each site and the reasons for choosing the site follows.

2.1. SAMPLING SITES

The John Lloyd State Park was chosen as the "local background" site (1). The site is also used by the Broward County Department of Natural Resource Protection as a background site for their air monitoring network. The site was located at the end of a service road in the park about 100 m west of the shore of the Atlantic Ocean and approximately 100 m east of the Intercoastal Waterway. Samples were collected daily at this site to measure vapor and particle phase Hg as well as Hg in precipitation. Since the site was close to the Atlantic Ocean and with winds predominately from the east/southeast, the levels of atmospheric mercury at this site were expected to represent "local background" levels. Because of land-sea breeze circulation, it was understood that this site may not provide a true marine background. However, this site did provide a "local background" for comparison with the three inland sites when winds were out of the east/southeast.

The central site (2) was located on the Broward Community College campus, approximately 13 km west of site 1. During periods with winds out of the east/southeast, this site location was expected to provide adequate distance for homogeneous mixing in the boundary layer to assess the impact of local sources. The central site was located on the roof of the campus gymnasium, which was approximately 10 m high. At site 2, vapor and particulate Hg samples as well as precipitation samples were collected daily. Another inland site (3) was located approximately 20 km west of site 1 in the backyard of a residential home. The residential area was moderately populated with several houses in the area adjacent to the sampling site. At this site vapor, particulate and precipitation samples were collected daily. This site was chosen because it was approximately 8 km east of a conservation area of the Everglades. An additional site (4) was located 10 km west of site 1 and also approximately 300 m southwest of a municipal waste incineration facility. Precipitation samples were collected daily at this site which was located on the property of one of the South Florida Water Management District pumping stations on the South New River Canal.

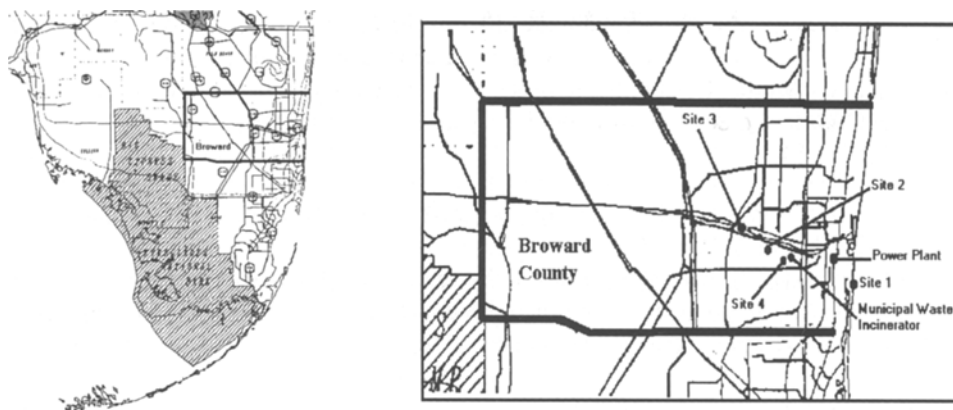


Fig. 1. Location of Sampling Sites in Broward County, FL

2.2. METHODS OF SAMPLE COLLECTION AND ANALYSIS

All equipment and supplies used in sampling were rigorously acid-cleaned in an 11-day cycle (Hoyer and Keeler, 1994). Sample bottles, gold sand traps and glass-fiber filter containers were Teflon-taped and triple-bagged. All of the samples collected were analyzed using ultra-clean techniques for trace metal analysis. The particulate and precipitation samples were processed and analyzed in a Class 100 ultra-clean laboratory at the UMAQL in order to minimize contamination. However, the vapor phase samples were analyzed on-site in Florida in a normal laboratory setting because the risk of contamination was minimal. Particle-free gloves were worn during all procedures of sample handling and analysis.

Vapor Phase Hg

Gold-coated sand traps were used at all of the sites because of their ability to quantitatively remove vapor species of Hg from an air stream. The quartz sand was gold-coated under vacuum in a gold plasma that uniformly deposited gold onto the sand. The collection efficiency of the sand traps for removal of gaseous Hg has been found to be >97% by the UMAQL and by Dumarey *et al.*, (1985). Two traps in series were used to characterize any amount of breakthrough during all measurements of vapor phase Hg. A pre-fired glass-fiber filter (Gelman type A/E) was used to remove particles from the air stream prior to reaching the gold-coated sand traps. Samples were collected at a flow rate of 300 cc/min. for durations varying from 3 to 24 hours. The gold-coated sand traps were analyzed by thermal desorption using a dual amalgamation technique and subsequent analysis by cold vapor atomic fluorescence spectroscopy (CVAFS) similar to the method described by Fitzgerald and Gill (1979). The instrument was calibrated daily by injecting Hg vapor standards.

Particle Phase Hg

Particle phase Hg samples were collected using pre-fired glass-fiber filters (Gelman type A/E). These filters have been proven to efficiently collect particulate Hg and have

now been used for three years to measure particulate Hg levels in the Great Lakes region (Keeler *et al.*, 1995). The filters efficiently capture coarse and fine particles. The filters were run at a nominal flow rate of 30 L/min. for a duration of 24 hours. After sampling, filters were removed from the filter pack using Teflon coated forceps, placed in an acid-cleaned petri dish, Teflon taped and shipped to UMAQL to be stored at -40°C until analysis. The analysis method employed was similar to that previously described (Lamborg *et al.*, 1994). The filters were extracted by sonication for 30 minutes in a 10% acid solution (7% HNO_3 : 3% H_2SO_4) in Teflon vials. After sonication, the solution was oxidized with BrCl followed by reduction with NH_2OH and SnCl_2 . The reduced sample was purged onto a gold-coated sand trap and analyzed using the dual amalgamation technique and subsequent analysis by CVAFS.

Hg in Precipitation

Daily event precipitation samples were collected manually at each site. The collectors consisted of an acid-cleaned 1 L borosilicate glass sample bottle and a 28 cm (diameter) polyethylene funnel supported in a polyethylene housing system. The collectors were elevated 2 m above the ground in order to avoid possible contamination from ground splashing during precipitation. The bottle and funnel were deployed at 8 AM for 24 hours and replaced each morning regardless of a precipitation event. In the event of precipitation occurring at 8 AM, the sample was not collected until the completion of the precipitation event. The precipitation samples were shipped to UMAQL by overnight mail for processing and analysis. The analysis method was similar to the one described by Hoyer and Keeler (1994). An aliquot of the sample was poured off for analysis of major ions and samples of sufficient volume were analyzed for the operationally-defined reactive Hg species by acidifying an aliquot of sample to a 1% HCl solution before reduction with SnCl_2 . In addition, a subset of samples with sufficient volume were poured off into 125 ml polyethylene bottles and acidified to a 0.2% HNO_3 solution for analysis by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS). The analysis method employed was a modification of the procedure described by Long and Martin (1992), using an ultrasonic nebulizer instead of chelation for pre-concentration. The remaining sample volume was oxidized to a 1% BrCl solution and refrigerated overnight prior to analysis for total Hg. The oxidized Hg was reduced and purged onto a gold-coated sand trap and analyzed using the dual amalgamation technique and subsequent analysis by CVAFS.

Additional Trace Constituents

Measurements of gaseous SO_2 were made continuously at site 2 from 28 August to 7 September. These measurements were made using a Differential Optical Absorption Spectrometer (DOAS) as described by Stevens *et al.*, (1993). In addition, aerosol trace metals were also collected at site 2 from 28 August to 7 September using 2- μm pore Teflon (PTFE) membrane filters (Gelman) in an all Teflon filter pack. Analysis of these filters was performed at USEPA-AREAL using X-Ray Fluorescence (XRF) similar to the method described by Dzubay *et al.*, (1982).

2.3. QUALITY CONTROL AND QUALITY ASSURANCE

For event precipitation, measurements of the sampling blank were obtained by rinsing the collection funnel with ultra-pure water and analyzing the rinse for Hg. The average concentration of Hg in 12 precipitation collector blanks was 0.26 ± 0.2 ng/L. The method of collection used for the present study was slightly different than the automated wet-only sample collection method used in the UMAQL Great Lakes data (Hoyer and Keeler, 1994). With the manual method, the collection bottle was exposed to dry deposition for the entire period that the funnel-bottle was deployed. Since the maximum amount of time that the funnel-bottles were deployed was 24 hours, the amount of Hg added by dry deposition was negligible relative to the magnitude of Hg present in the precipitation. The contribution of dry deposition was determined by performing collector rinses on funnels that had been deployed for 24 hours without collecting any precipitation. From the funnel rinses, dry deposition of Hg to the funnels was found to be insignificant. Furthermore, the manual method used in this study had been previously determined at UMAQL to compare very well to the automated method based on co-located sampling (Hoyer and Keeler, 1994).

Field blanks were collected regularly for vapor phase and particulate Hg samples. For both types of samples, field blanks were performed by assembling the sampling equipment and placing it in the sampling box without drawing air through the system. Field blanks for vapor phase Hg averaged 0.015 ng Hg on the trap, which corresponds to 0.03 ng/m³ for a 24-hour sample or 1.3% of the average vapor phase Hg concentration. Particulate Hg field blanks averaged 17 pg Hg on the filter, which corresponds to 0.4 pg/m³ for a 24-hour sample or less than 1% of the particulate Hg typically collected.

For precipitation and particulate samples, a reagent blank was analyzed on each day of analysis. The appropriate amounts of reagents were analyzed to determine the contribution of the reagents to the concentration of Hg obtained for the sample. All samples were blank corrected using the corresponding reagent blank analyzed that day. The current detection limit for Hg in precipitation (calculated as three times the standard deviation of the reagent blanks) is 0.15 ng/L.

All particulate samples and 50% of precipitation samples were analyzed in duplicate. Analytical precision calculated from these results was better than 10% for analysis of Hg in both precipitation and particulate samples.

3. Results and Discussion

3.1. VAPOR PHASE Hg

Vapor phase Hg levels in Broward County were slightly elevated, on average, above typical background levels reported elsewhere. As seen in Figure 2, concurrent 24-hour averaged vapor phase Hg concentrations at sites 2 (central) and 3 (house) were found to be significantly different and higher than those at site 1 (beach) as determined from t-tests (paired two-sample comparison of means, $p < 0.01$). The elevated Hg levels at sites 2 and 3 relative to the beach site were most evident for the period 30 August to 7 September. Vapor phase Hg values observed during the two-week period were elevated

when compared to typical vapor phase measurements ($\sim 2.0 \text{ ng/m}^3$) made using the same techniques in the Great Lakes Basin (Keeler *et al.*, 1994).

At site 2 (central) where day and night samples were collected, a strong diurnal relationship was observed in the vapor phase Hg levels. The average night time vapor phase concentration (4.5 ng/m^3) was nearly twice the concentration found during the day time (2.4 ng/m^3) at this site. The strong diurnal variation seen in the vapor phase Hg measurements can be explained by the diurnal changes observed during the study in the structure of the boundary layer in south Florida. During the day time, intense heating resulted in considerable vertical mixing of the ambient pollutants. However, calm winds ($< 1.0 \text{ m/s}$), little vertical mixing, and lower mixing heights during the night resulted in higher concentrations.

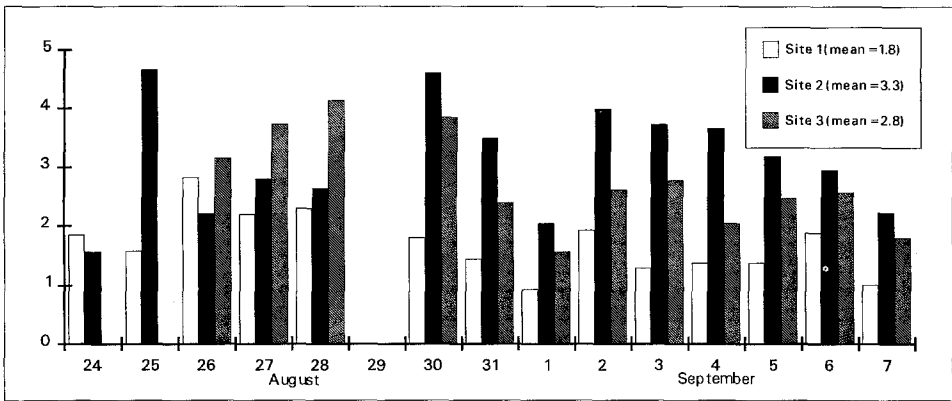


Fig. 2. 24-Hour Averaged Vapor Phase Hg Concentrations in ng/m^3 Measured in Broward County, FL

3.2. PARTICLE PHASE Hg

Particulate Hg samples were taken concurrently at sites 1, 2, and 3 during the period 25 August to 7 September. Figure 3 reveals that the concentrations of particulate Hg measured at site 2 (central) were significantly ($p < 0.01$) elevated with respect to those measured at site 1 (beach), a result also observed with the vapor phase Hg. The average concentrations at site 2 (51 pg/m^3) and site 3 (49 pg/m^3) were 50% greater than the average at site 1 (34 pg/m^3). As with the vapor phase Hg, this observation was most evident during the period 30 August to 7 September. For measurements made on the days before 30 August, the site to site differences were not as evident due to highly variable meteorological flow patterns that changed notably every several hours during the day. Since 24-hour ambient Hg measurements were performed at all sites except site 2, most of the time-averaged Hg measurements made during this study were not of short enough duration to observe site to site differences over short periods of time (less than 12 hours). However, for the period 30 August to 7 September when flow was much more consistent from the east/southeast, the trend of higher vapor phase and particle phase Hg at sites 2 and 3 compared to site 1 was strongly evident. Consistent air mass transport from the southeast was observed for the period 30 August to 7 September as a result of the semi-permanent Bermuda high.

Particle phase Hg comprised less than 5% of the total atmospheric Hg (vapor and particulate) for the days with both measurements. This was consistent with other values reported (Burke *et al.*, 1995). The levels of particulate Hg found during this study were generally higher than those typically measured (about 10-30 pg/m^3) at rural sites in the Great Lakes Basin (Keeler *et al.*, 1995). In addition, the two-week average of particulate Hg measured at all sites during this study was 5 to 10 times higher than other measurements made in south Florida (Guentzel *et al.*, 1994). The levels measured in Broward County were not as high as other measurements made in large urban/industrial source areas such as Detroit, where short-term average particulate Hg concentrations were found to be near 100 pg/m^3 (Keeler *et al.*, 1994; 1995). The elevated levels of particulate Hg observed in Broward County during this study, however, do suggest a local source influence.

A significant relationship was observed between measurements of aerosol vanadium (V) and gaseous SO_2 made at site 2 as seen in Figure 4. Both V and SO_2 are emitted during oil combustion. A relationship was also observed between particle and vapor phase Hg, and V and SO_2 , also seen in Figure 4. These relationships were strongest

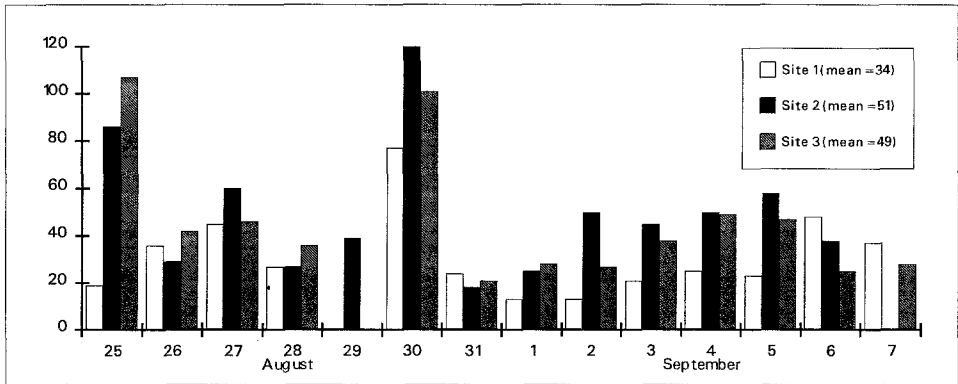


Fig. 3. Particle Phase Hg Concentrations in pg/m^3 Measured in Broward County, FL

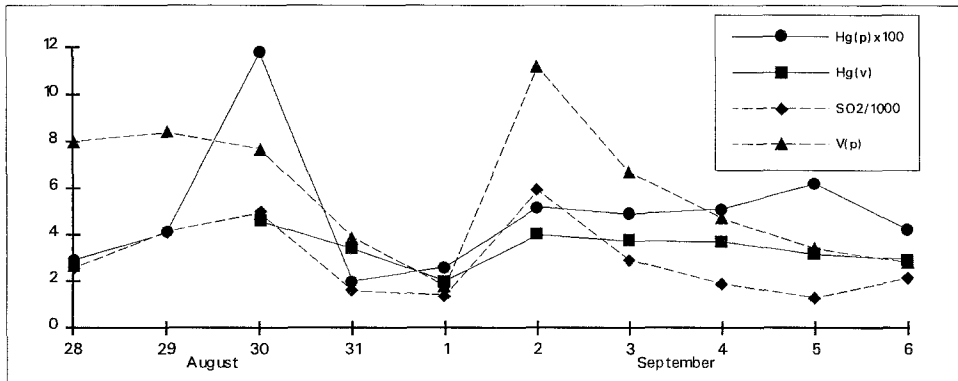


Fig. 4. Particle and Vapor Phase Hg, Particulate V, and Gaseous SO_2 in ng/m^3 Measured at Site 2

during the period 30 August to 2 September. As previously stated, a sea breeze circulation was observed with winds out of the east/southeast during the day, and calm conditions during the night. On 30 August, a sea breeze was present with winds out of the east/southeast corridor during the day. However, Hurricane Emily disrupted the pattern on 31 August and 1 September as it approached the Carolinas and rode up the eastern seaboard. The strong gradient flow caused by the hurricane prevented the typical sea breeze pattern during this 48-hour period. Sustained winds out of the south/southeast during the entire 2-day period resulted in the cleanest 2 days of the study, as seen in Figure 4. However, on 2 September the hurricane had moved far enough north allowing the Bermuda high to re-establish itself as the dominant feature. The sea breeze circulation was then again present, and as seen in Figure 4, the concentrations of all 4 components were again elevated.

3.3. Hg in EVENT PRECIPITATION

The levels of Hg measured in precipitation collected at the four sites are summarized in Table I. Average total Hg concentrations measured at sites 2 (central), 3 (house), and 4 (near incinerator) were elevated relative to concentrations measured at site 1 (beach). All samples collected were analyzed for total Hg and samples of sufficient volume were analyzed for reactive Hg. Table I suggests that the same pattern seen for total Hg was also present for reactive Hg since the average concentrations of reactive Hg were also elevated at sites 2, 3, and 4 relative to site 1. However, this trend was not as distinct for Hg in precipitation as it was for vapor phase and particle phase Hg.

It should be noted that most precipitation events during this study were the result of isolated convective systems rather than associated with frontal activity. With the convective storms, a strong spatial gradient would not be expected in 20-day averaged Hg concentrations measured at sites separated by relatively short distances (<10 km). However, spatial gradients may be seen in precipitation collected daily (individual events) at these sites, depending upon the source and transport of the feed air for each individual convective storm.

During this study, site-to-site differences in precipitation Hg concentrations were observed on several days. On 25 August air mass transport was from the east/southeast. Precipitation samples were collected at all four sites on this day, one of only two days during the entire study on which this occurred. Concentrations of Hg measured at the inland sites were all elevated when compared with site 1 located at the beach as seen in Figure 5. It is also clear from Figure 5 that a relationship existed between the measured concentrations of Hg, V, and Ni in the precipitation collected at sites 1, 2, and 4 (insufficient volume for ICP-MS analysis of the sample collected at site 3). Vanadium and nickel are both trace elements emitted during oil combustion (Gordon, 1988).

The levels of total Hg measured in event precipitation in this study were elevated 3 to 5 times over those made by the UMAQL in Vermont (Burke *et al.*, 1995) or the Great Lakes Basin (Hoyer *et al.*, 1995). However, it is difficult to make any definitive conclusions as to the source(s) responsible for the elevated levels of Hg in precipitation with the limited number of events collected during this study.

TABLE I
Summary of Hg in Precipitation in ng/L at Sites in Broward County, FL

	Site 1	Site 4	Site 2	Site 3
Total Hg Mean	35	57	40	46
Std. Dev.	16	15	19	28
Range	15 - 56	43 - 81	15 - 73	14 - 130
N	6	5	8	13
Reactive Hg Mean	1.0	2.5	1.9	2.0
Std. Dev.	0.4	1.0	1.1	1.1
Range	0.5 - 1.4	1.7 - 3.7	0.8 - 3.3	1.0 - 3.2
N	4	4	5	4

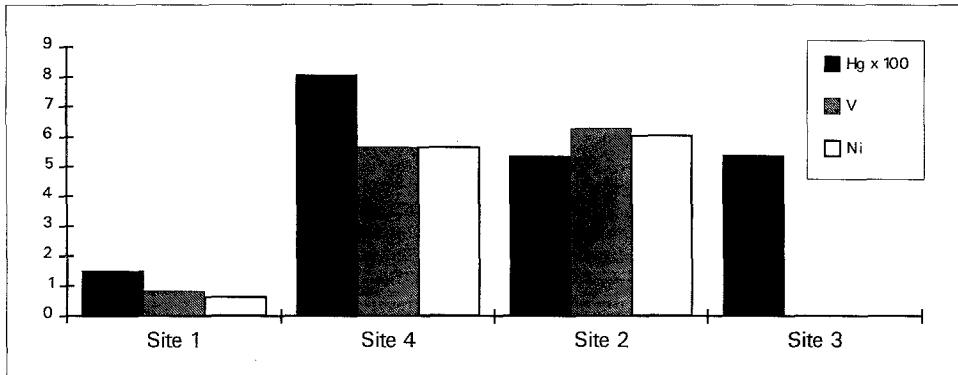


Fig. 5. Hg, V, and Ni in $\mu\text{g/L}$ Measured in Precipitation Collected in Broward County on 25 August, 1993

4. Summary and Conclusions

The data obtained from this pilot study indicate that levels of vapor and particle phase Hg measured at sites 2 (central) and 3 (house) were elevated above levels measured concurrently at site 1 (beach). One explanation for this is that a source, or sources, located near or between site 1 (beach) and site 2 (central) was impacting the portion of Broward County which lies west of site 2. While the association of ambient Hg with V and SO_2 , combined with elevated Hg in precipitation being found with elevated V and Ni suggest an oil combustion source, the present study was not designed for source apportionment of the Hg. Therefore, making any definitive conclusions as to the specific source(s) responsible for these elevated levels of Hg will require further meteorological analysis and a more complete characterization of the aerosol and precipitation composition.

Levels of total Hg in precipitation observed in daily event collections at several sites in Broward County during this study were significantly higher than those previously reported for more remote sites in southern Florida (Guentzel *et al.*, 1994). The

relatively large variation in Hg concentration measured simultaneously at multiple sites separated by relatively short distances (<10 km) suggests that more research is needed to adequately characterize atmospheric deposition to south Florida caused by sources in the two urbanized counties (Broward and Dade). The enhanced deposition in these areas may be quite important to the overall Hg loading to the sensitive ecosystems in south Florida due to the combination of the high amount of annual rainfall and high precipitation Hg concentrations.

Since wet deposition is the major removal process of atmospheric mercury, future studies in south Florida should include more comprehensive precipitation collection at a grid of sites in the two counties. Also, vapor and particulate measurements at selected sites would provide a better understanding of the processes leading to Hg in precipitation. In addition, a more detailed elemental analysis of both precipitation and particulate samples is needed to characterize the probable source(s) contributing to the increased deposition of mercury. The additional information obtained from the increased sampling and analysis would allow for a proper evaluation of the impact of local and regional source(s) to the Hg deposition to the region.

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