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Critical Evaluation of a Modified Automatic Wet-Only Precipitation Collector for Mercury and Trace Element Determinations

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In 1993, the University of Michigan Air Quality Laboratory (UMAQL) designed a new wet-only precipitation collection system that was utilized in the Lake Michigan Loading Study. The collection system was designed to collect discrete mercury (Hg) and trace element samples on either an event or weekly basis. Performance characteristics such as collector opening efficiency, collocated precision, spike recovery, field blanks, and bottle blanks were rigorously evaluated from October 1994 through October 1995 at a semirural site near Dexter, MI. Comparisons for Hg were made between HCl preserved versus unpreserved event collection, wet-only event versus manual event collection, and weekly volume-weighted wet-only event versus weekly bulk collection. Results of this investigation indicated that with proper preparation and ultra-clean collection techniques, wet-only precipitation collection utilizing the UMAQL modified MIC-B collector can provide virtually contamination-free Hg and trace element samples. On average, field blanks contributed <1% of the Hg and trace element sample mass. The absolute mean difference for collocated samples was 8.1% for Hg and from 3.6% to 14.1% for 21 other trace elements. Wet-only precipitation collection for Hg was found to be statistically equivalent ($\alpha = 0.05$) to manual event collection (absolute mean difference of 9.8%), demonstrating the suitability of the automatic wet-only technique.

Introduction

Mercury (Hg) is a pollutant of considerable concern in aquatic systems because of its strong tendency to bioaccumulate up the food chain and its demonstrated link to human health effects. The atmosphere plays an important role in the cycling of Hg in the environment (*1–5*). Research in the Great Lakes region has concluded that atmospheric wet deposition is the primary pathway for inputs of Hg to natural waters (*6–8*). As a result, the U.S. Environmental Protection Agency identified Hg as one of the compounds to be investigated as part of the Lake Michigan Loading Study (LMLS) from July 1994 to October 1995. The two main objectives of the Hg component of the LMLS were to quantify and identify the major sources of atmospheric wet deposition to the southern portion of Lake Michigan.

The investigation of source–receptor relationships for Hg required the precise quantification of Hg and a suite of other trace elements in each precipitation event. Wet-only col-

lectors have generally been used to sample precipitation for trace element determinations to minimize the contamination of samples from dry deposition (*9–14*). However, there was no general consensus on a precipitation collection methodology for Hg (*15*). While Hg deposition networks in Florida (*16*), Sweden (*2, 17, 18*), and Wisconsin (*19*) have used bulk precipitation collectors, sites in Michigan (*20*), Minnesota (*21*), Ontario (*5*), and Vermont (*22*) have used modified automatic wet-only collectors. A few investigators have compared bulk precipitation collection to a wet-only collection method with generally poor results (*19, 23*). The automatic wet-only precipitation collection method was chosen for the LMLS network to prevent contamination of samples from trace element dry deposition, particularly at the urban sampling location in Chicago, IL.

A new wet-only precipitation collection system (UM-B) was designed for the LMLS network and other Great Waters projects. The UM-B was designed to collect precipitation samples containing ultra-low Hg and trace element concentrations in a manner that (i) allowed ease of use, (ii) adapted to either event or weekly sample collection, (iii) provided for stabilization of Hg samples, and (iv) possessed a low potential for contamination. The UM-B collection system incorporated removable sampling trains for easy cleaning, a chemical preservative to stabilize the collected Hg sample, and a vapor lock to minimize vapor phase Hg exchange. This paper will outline the development and performance characteristics of the UM-B precipitation collection system for Hg and 21 other trace elements. In addition, (i) the need for the preservation of Hg samples during event collection and (ii) the suitability of a wet-only collection method for Hg will be evaluated.

Collector Design

The UM-B collector is a modified MIC-B (MIC, Thornhill, Ontario) automatic precipitation collector (Figure 1). The MIC-B collector was used because its precipitation detection circuitry was found to be more sensitive than the circuitry on the more commonly used Aerochem Metrics collector, especially with regard to light rain or snow (*24*). Orr *et al.* (*24*) found that the MIC-B precipitation sensing system resulted in greater sample volumes than the Aerochem sensing system for 93% of the summertime and 98% of the wintertime events. The MIC-B incorporated two separate sensor grids (40 cm² total area) that were heated to melt snow and evaporate accumulating precipitation. The MIC-B collector was expected to minimize the amount of precipitation missed at the onset of a precipitation event, which has been observed using the Aerochem Metrics sampler (*25*).

The standard MIC-B collection funnel is a permanently mounted 0.212 m² Teflon-coated stainless steel funnel with an internally threaded neck. This funnel was incorporated into a previous collector configuration (UM-A) used in a multisite Hg network (*20, 22*). The standard MIC-B funnel was not suited for the LMLS network since several trace elements were consistently elevated in UM-A collector funnel rinses (*26*), despite a routine funnel cleaning protocol (*20*). Subsequent collocated comparisons between the UM-A and UM-B collectors (*n* = 36) verified that samples collected with the standard MIC-B Teflon-coated stainless steel funnel were significantly enriched (*p* < 0.001) with Cr, Ni, Co, and Cd (Table 1). Equally significant losses (*p* < 0.001) of V, Zn, and Hg were also observed with samples collected using the UM-A collector configuration (Table 1).

Two major design modifications were incorporated into the UM-B collection system to prevent enrichment or adsorption of trace elements or Hg in precipitation samples. The first modification was to collect the precipitation directly

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FIGURE 1. Photograph of the UM-B modified MIC-B automatic wet-only precipitation collector.

TABLE 1. Absolute Percent Difference (APD) of UM-A and Collocated UM-B Collection Configuration

element	mean UM-A concn[a] ($n = 28$)	mean UM-B concn[a] ($n = 28$)	mean APD
V	0.220 ± 0.149	0.273 ± 0.183	21.5
Cr	0.645 ± 0.523	0.173 ± 0.141	115.4
Ni	3.228 ± 3.616	0.222 ± 0.197	174.3
Co	0.137 ± 0.133	0.059 ± 0.073	47.4
Zn	6.919 ± 7.207	9.655 ± 13.488	33.0
Cd	0.071 ± 0.118	0.052 ± 0.030	30.9
Hg	0.012 ± 0.007	0.016 ± 0.009	27.1

[a] Concentration in μg/L.

into separate sample bottles to minimize the absorptive behavior of trace elements and Hg to the walls of a collection vessel (27−29). Trace element samples were post acidified with HNO$_3$ to a pH < 1.5 (30−32), and Hg samples were oxidized with BrCl (33) to resolubilize any analytes lost to the walls of the sample bottle. Otherwise, these elements would have been quantitatively lost if aliquots were poured from a common collection vessel prior to sample preparation. The second design modification was to construct separate Hg and trace element collection funnels of materials determined to be suitable for each collection application (15, 32). The Hg sampling train consisted of a borosilicate glass funnel (181 cm² collection area), a Teflon adapter, a glass vapor lock, and a 1-L Teflon sample bottle (Figure 2a). The trace element sampling train consisted of a polypropylene funnel (167 cm² collection area), a polypropylene adapter, and a 1-L polypropylene sample bottle (Figure 2b). The funnels had high vertical sides to aid in efficient collection and to prevent loss due to "bounce off" during intense rain. In addition, the sampling trains were light, that allowed for ease in removing, disassembling, and acid-cleaning.

A custom acrylic insert was constructed to support the UM-B sampling trains in the MIC-B collector (Figure 3). The insert provided for the installation of two Hg and two trace element sampling trains. In the winter, a small ceramic space heater (750 W) was also installed inside the collector cabinet to maintain a temperature of approximately 10 °C to melt snow collected in the funnels and to prevent freezing.

Field Sampling

Precipitation samples were collected at a semi-rural research site located near Dexter, MI (42.25° N, 83.75° W). Sampling began in October 1994 and ran continuously through October 1995.

Initially, the UM-B collector was equipped with three sampling trains, two for Hg collection and one for trace elements. The two Hg sampling trains were used to compare event collection of acid-preserved and collocated unpreserved precipitation samples. Twenty milliliters of 0.08 M HCl was added to the sample bottle in the "standard Hg sampling train" to inhibit the reduction of Hg(II) to Hg(0) (34), which might be lost to volatilization. The second "modified Hg sampling train" did not have the vapor lock assembly or the HCl preservative. Inclusion of the modified Hg sampling train enabled determination of the necessity of including a preservative when collecting event precipitation samples. Sampling trains were replaced after each precipitation event in the UM-B collector. All components of the sampling trains were acid-cleaned and assembled in a Class 100 clean room prior to being taken to the sampling site. The sample bottle was threaded on immediately after installation of the funnel assembly to complete the sampling train.

An additional trace element sampling train was later added to measure collection precision, and an additional standard Hg sampling train was added as a field blank. The Hg field blank sampling train was placed inside the collector cabinet to be shielded from precipitation. The Hg field blank sampling train was deployed and retrieved simultaneously with each of the event samples. These field blanks were used to evaluate passive contamination, including the potential contribution of vapor phase Hg absorption by the HCl preservative.

Manual event precipitation samples were collected to determine the UM-B collector's opening efficiency and to provide a quantitative comparison of the different collection methods. Manual event samples were collected with standard Hg sampling trains, identical to those used in the UM-B collector. A clean manual event sampling train was deployed only when precipitation was forecasted and was retrieved the morning following the event.

Weekly bulk collection was also undertaken to investigate the suitability of a weekly sampling interval in a semi-rural setting. Weekly bulk samples were collected using the standard Hg sampling trains, identical to those used in the UM-B collector. The weekly bulk sampling trains were deployed and collected every Tuesday morning. A clean sampling train was used for each weekly sampling period.

In the absence of precipitation for 7 days, funnel rinses were performed to quantify the level of contamination. A clean sample bottle was inserted into the bottom of each of the sampling trains, and 250 mL of Milli-Q (Millipore Corp., Bedford, MA) ultra-pure water (18.2 MΩ·cm) was poured through each funnel, rinsing the entire surface. Milli-Q water control samples for each corresponding funnel rinse were also collected.

Potential losses of Hg or trace elements to the glass and polypropylene collection funnels, respectively, were evaluated by performing a series of funnel spiking experiments. Unpreserved precipitation samples were brought into a Class 100 clean room, and 250-mL aliquots (average precipitation sample volume) were poured through each of the assembled sampling trains. An additional 250-mL aliquot was poured directly into a clean sample bottle as a control. A set of filtered precipitation samples was also used for funnel spiking experiments to determine if loss to the funnels was due to either chemical adsorption of dissolved species or physical adsorption of particles to the funnels. These samples were vacuum filtrated through 0.22 μm nitrocellulose filters (Millipore, Type GS) into acid-cleaned sample bottles.

Methods

Cleaning Procedure. All field and analytical supplies that came into contact with the precipitation samples were acid-cleaned in a procedure described by Rossmann and Barres (35). All supplies except sampling bottles were subsequently rinsed with Milli-Q water and allowed to dry in the Class 100 clean room. The Teflon sampling bottles were rinsed with Milli-Q water and filled with 0.05 M HCl and allowed to soak in the clean room until needed. Immediately prior to use, the Teflon bottles were rinsed with Milli-Q water, and 20 mL
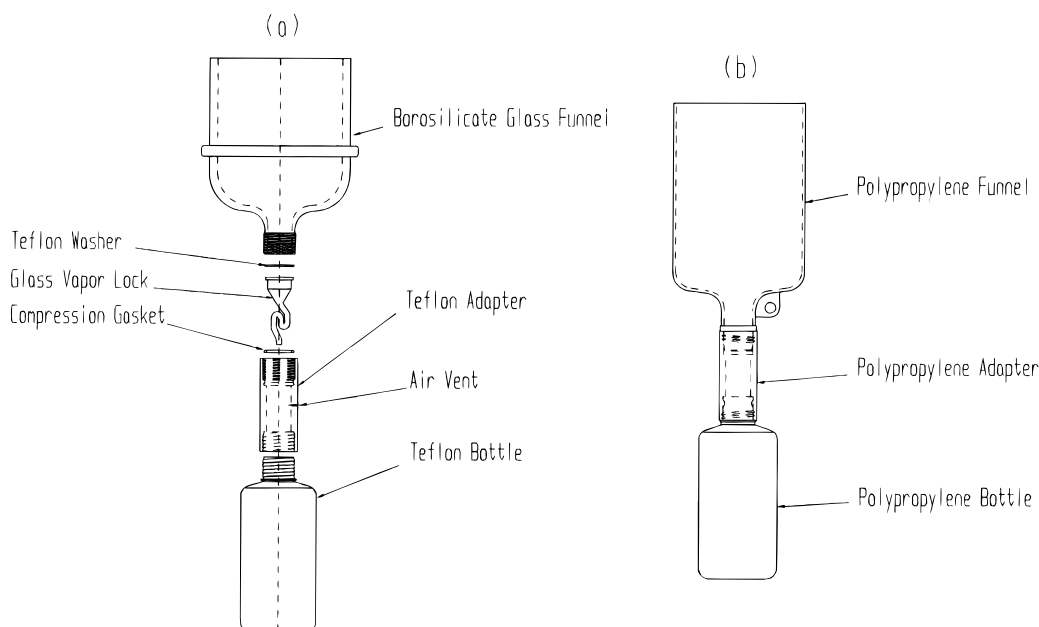
FIGURE 2. Diagram of the UM-B sampling trains for the collection of Hg (a) and trace elements (b).

FIGURE 3. Photograph of the UM-B custom acrylic insert used to support the Hg and trace element sampling trains.

of 0.08 M HCl was added. The polypropylene sampling bottles were rinsed with Milli-Q water and capped. All supplies were then sealed into three successive polyethylene bags prior to being removed from the clean room. To quantify the blank associated with the sample bottles, one sample bottle from each batch was filled with 250 mL of Milli-Q water, prepared as a sample, and analyzed (bottle blank).

Sample Preparation. Precipitation samples typically contain very low concentrations of trace elements. Therefore, samples were processed in a Class 100 clean room to avoid contamination. Samples were typically prepared within 24 h of collection. The volume of each precipitation sample was determined gravimetrically. Mercury samples were oxidized with concentrated BrCl to a 1% solution (v/v) and were stored in a dark cold room for a least 12 h before being analyzed. The trace element samples were acidified with concentrated HNO_3 to a 0.2% solution (v/v) and were stored for a minimum of 2 weeks in a dark cold room to allow desorption of trace elements off particles and the walls of the collection bottle.

Sample Analysis. All analytical procedures for the determination of Hg and trace elements were carried out in a Class 100 clean room. Mercury in precipitation was purged from solution in a Hg-free nitrogen stream after reduction of BrCl with NH_2OH and reduction of divalent Hg by $SnCl_2$ to

Hg(0) and concentrated onto a gold-coated bead trap. Total Hg was then quantified using a dual amalgamation technique followed by cold-vapor atomic fluorescence spectrometry (CVAFS) (36). All Hg samples were analyzed in duplicate; reported concentrations are based upon the mean of the replicate analyses. The method detection limit (MDL) for Hg (0.1 ng/L) was calculated as 3σ of the total reagent blank.

Trace element determinations were made using a Perkin Elmer 5000A inductively coupled plasma mass spectrometer (ICP-MS) equipped with a thin film electron multiplier detector. The samples were introduced into the ICP-MS by pneumatic nebulization. All trace element samples were analyzed in triplicate, and reported concentrations are based upon the mean of the replicate analyses. A MDL was generated for each of the 21 trace elements. The MDLs listed in Table 2 were calculated using a modification of EPA Method 200.8 (37), in which a precipitation sample was substituted for the fortified reagent water to simulate the actual sample matrix. The MDL is the product of the standard deviation of seven replicate analyses of the precipitation sample and the Student's t value at a 99% confidence interval. Trace element measurements below the calculated MDL were not used in any of the comparisons.

Results and Discussion

Performance Characteristics. The volume collected by the UM-B collector exceeded 98% of that collected by the adjacent manual event collector. No significant contamination was found in any of the wet-only funnels after 7 days in the UM-B collector. The mean funnel rinse values ($n = 9$) were less than the MDL for Hg and all other trace elements (Table 2). The 95% confidence interval for the Teflon bottle checks ($n = 53$) was 0.01−0.02 ng/bottle. The mean polypropylene bottle check ($n = 21$) values were under the MDL for each of the trace elements in Table 2. The mean Hg field blank ($n = 43$) was 0.04 ng/bottle, and the average precipitation sample Hg mass was 4.28 ng/bottle. The reported Hg and trace element concentrations were not blank corrected since the average mass contributed by the field blanks was <1%.

Collection funnel spike recovery for unfiltered samples was 96% for Hg and >99% for the other trace elements ($n = 10$), suggesting minor adsorption of Hg to the clean funnel surface. The Hg funnel spike recovery was equivalent to that reported by Vermette *et al.* (38) for a borosilicate glass funnel.

TABLE 2. Method Detection Limit (MDL), Funnel Rinse (FR), Bottle Blanks (BB), and Absolute Percent Difference (APD) for Trace Elements in Collocated Samples of Precipitation

element	MDL[a]	mean FR concn[a,b] (n = 7)	mean BB concn[a,b] (n = 21)	mean sample concn[a] (n = 20)	mean APD (n = 20)	median APD (n = 20)
Mg	1.686	1.515 ± 2.604	0.350 ± 0.442	132.114 ± 115.968	5.5	6.1
Al	0.451	0.258 ± 0.365	0.290 ± 0.327	56.849 ± 41.877	7.0	5.0
V	0.006	0.003 ± 0.004	0.000 ± 0.000	0.285 ± 0.171	6.4	4.1
Cr	0.025	0.003 ± 0.003	0.003 ± 0.008	0.183 ± 0.129	14.1	12.7
Mn	0.035	0.035 ± 0.074	0.001 ± 0.001	6.597 ± 7.361	3.6	3.3
Ni	0.012	0.009 ± 0.008	0.002 ± 0.006	0.233 ± 0.193	11.9	8.0
Co	0.003	0.000 ± 0.000	0.000 ± 0.000	0.066 ± 0.055	13.5	7.7
Cu	0.024	0.004 ± 0.005	0.002 ± 0.003	0.862 ± 0.488	9.5	5.9
Zn	0.237	0.078 ± 0.055	0.011 ± 0.015	7.719 ± 7.554	11.2	6.2
As	0.018	0.001 ± 0.001	0.001 ± 0.002	0.183 ± 0.093	4.5	3.4
Rb	0.015	0.001 ± 0.002	0.001 ± 0.001	0.168 ± 0.155	10.7	8.8
Sr	0.026	0.013 ± 0.024	0.000 ± 0.000	2.308 ± 1.352	6.3	4.0
Cd	0.009	0.000 ± 0.000	0.000 ± 0.000	0.059 ± 0.036	10.5	5.6
Sb	0.030	0.000 ± 0.000	0.000 ± 0.007	0.101 ± 0.058	9.0	7.2
Ba	0.050	0.008 ± 0.016	0.001 ± 0.002	2.097 ± 1.546	6.5	4.4
La	0.002	0.000 ± 0.000	0.001 ± 0.002	0.098 ± 0.086	7.6	5.1
Ce	0.001	0.001 ± 0.001	0.001 ± 0.001	0.205 ± 0.181	7.1	6.0
Nd	0.002	0.000 ± 0.001	0.000 ± 0.001	0.097 ± 0.085	8.0	5.3
Sm	0.002	0.000 ± 0.000	0.002 ± 0.002	0.023 ± 0.018	11.8	5.0
Tl	0.001	0.000 ± 0.000	0.000 ± 0.000	0.005 ± 0.004	5.3	2.9
Pb	0.037	0.007 ± 0.007	0.001 ± 0.001	1.384 ± 0.974	13.2	9.3

[a] Concentration in μg/L. [b] Note: All values are below MDL.

Filtered spike recovery was 98% for Hg and >99% for the other trace elements (n = 6). Filtered funnel spike experiments revealed that a portion of the Hg loss was likely due to particulate adhesion to the glass funnel and some Hg loss was likely due to chemical absorption of dissolved species onto the clean funnel surface. Trace element determinations revealed no detectable losses to the polypropylene collection funnel from filtered or unfiltered samples.

Collocated Precision. Collocated Hg samples were collected at Bondville, IL (40.03° N, 88,22° W); Kenosha, WI (42.50° N, 87.81° W); and Sleeping Bear Dunes, MI (44.76° N, 86.06° W) from June through October 1995 as part of the LMLS. The absolute mean difference between the collocated samples (n = 33) was 8.1%. Analytical precision of laboratory replicates during this period (n = 181) was 95.5 ± 2.8%. The concentrations of trace elements in collocated samples collected at Dexter, MI, also indicated good agreement. The absolute mean difference was generally <10% but reached as high as 14% (Table 2). Lower precision for some anthropogenic trace elements (Cr and Ni) were most likely due to higher relative standard deviations for replicate analyses.

HCl Preservation Comparison. Data from the HCl preserved and collocated unpreserved comparison are presented in Figure 4a. Mercury concentrations ranged from 2.0 to 96.3 ng/L. The volume-weighted mean concentrations for the HCl preserved and unpreserved samples were 15.5 and 15.6 ng/L, respectively. The mean absolute difference between the HCl preserved and collocated unpreserved samples was 7.3% (0.3 ± 1.6 ng/L), indicating extremely good agreement. A paired T-test ($\alpha = 0.05$) for this comparison did not indicate a significant difference between the preserved and unpreserved Hg samples.

Figure 4b shows the volume-weighted seasonal concentrations for the HCl preserved and unpreserved data pairs from October 1994 to October 1995. Loss of Hg(0) from the unpreserved samples was expected to be highest in the summer, when the temperature inside the collector cabinet can exceed 45 °C; however, no seasonal difference was observed. The results of this comparison indicate that field preservation of event precipitation samples for Hg was not required when samples were oxidized within 24 h.

UM-B Wet-Only and Manual Event Comparison. The results from the UM-B automatic wet-only precipitation collection and collocated manual event collection for Hg are shown in Figure 5. The volume-weighted mean concentrations of the events collected from May to October 1995 were 15.8 ng/L for the UM-B collector and 15.9 ng/L for the manual event collector. The absolute mean difference for this comparison was 9.8% (0.5 ± 2.0 ng/L). A Shapiro−Wilk test (39) found that the distribution of differences in concentration to be significantly different from normal ($p < 0.001$). A nonparametric Wilcoxon sign rank test (40) determined that there was no significant difference ($\alpha = 0.05$) between the UM-B and the event manual collector. In fact, the deposition calculated from UM-B and the manual event methods are identical, 7.78 μg/m².

This comparison indicated that the UM-B automatic wet-only collection system was capable of correctly characterizing precipitation for Hg in terms of both concentration and deposition. This was in stark contrast to what has previously been reported for a wet-only collector and a collocated manual collector (23).

UM-B Wet-Only and Weekly Bulk Comparison. The weekly volume-weighted mean wet-only event collection and weekly bulk collection data pairs are compared in Figure 6. The absolute mean difference between the collection methods was 11.7% (1.2 ± 4.1 ng/L). A Shapiro−Wilk test found that the distribution of differences in concentration was significantly different from normal ($p < 0.001$). The Wilcoxon sign rank test did not indicate a significant difference ($\alpha = 0.05$) between the sampling methods. The three weekly bulk samples with the highest mean difference (outlined on Figure 6) involved weekly precipitation totals of 0.4, 0.2, and 0.2 cm, respectively, which were quite small in comparison to the 2.5 cm average. Higher Hg concentrations in the weekly bulk samples may have been due to pollen (clearly visible in one sample) or minor Hg enrichment from dry deposition to the bulk collection funnel.

The volume-weighted averages for the weekly bulk and the wet-only event samples, from May through October 1995, were 17.7 and 17.5 ng/L, respectively. The deposition for the 6-month period calculated using the collected volumes, however, was 8.45 μg/m² for the weekly bulk and 8.58 μg/m² for volume-weighted wet-only collection. The weekly bulk deposition was marginally underestimated because the total volume collected was 2.5% less than the total volume collected by the wet-only collector. Since the manual event collector typically collected slightly more volume than the wet-only
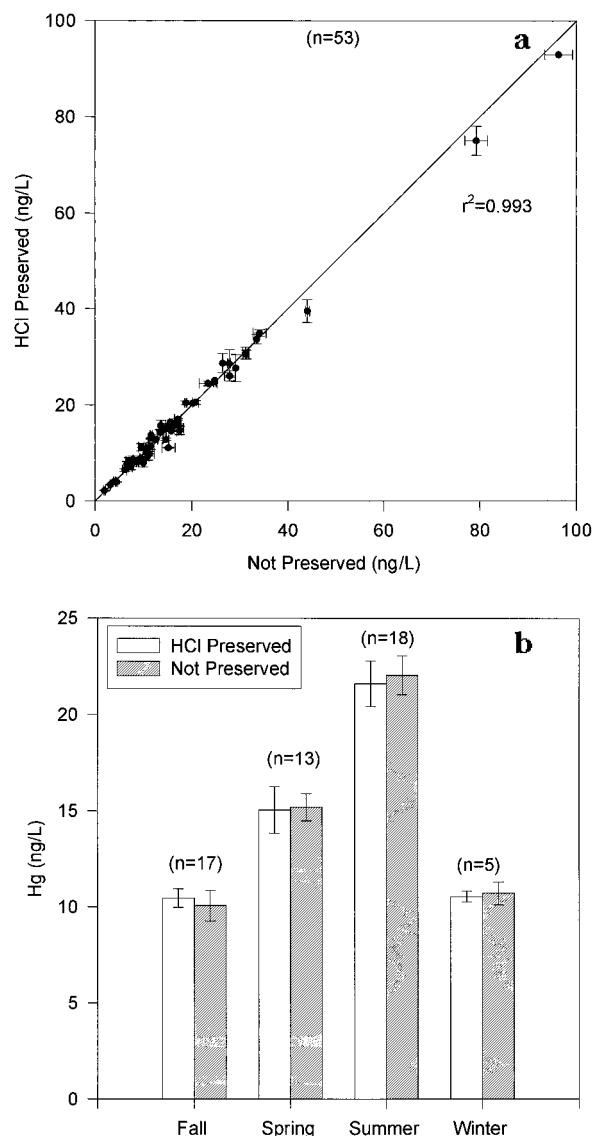
FIGURE 4. (a) Hg determinations for HCl preserved and collocated unpreserved precipitation samples (October 1994—October 1995). (b) Seasonal variation of volume-weighted Hg concentrations near Dexter, MI.

FIGURE 5. Hg determinations for wet-only and collocated manual event collection (March—October 1995).

FIGURE 6. Hg determinations for volume weighted wet-only and collocated weekly bulk collection (May—October 1995).

collector, it appears that, despite the vapor lock, some of the weekly bulk precipitation sample was lost due to evaporation.

The results of this comparison indicate that the HCl-preserved bulk Hg sample remained stable during the week it was deployed. In addition, the UM-B Hg sampling train appears to be relatively inefficient at incorporating dry deposition into the collected sample. This weekly bulk methodology may be acceptable for sampling Hg in semi-rural locations such as our sampling site near Dexter, MI. We would, however, discourage this collection technique in any location substantially impacted by anthropogenic sources of Hg or in urban/industrial areas with elevated levels of total suspended particulate.

Summary

The UM-B automatic wet-only collection system was determined to be an appropriate method for quantifying Hg and trace element wet deposition. The evaluations conducted during this investigation indicate that UM-B gave an accurate and precise representation of Hg and trace elements in precipitation while minimizing the potential contamination from d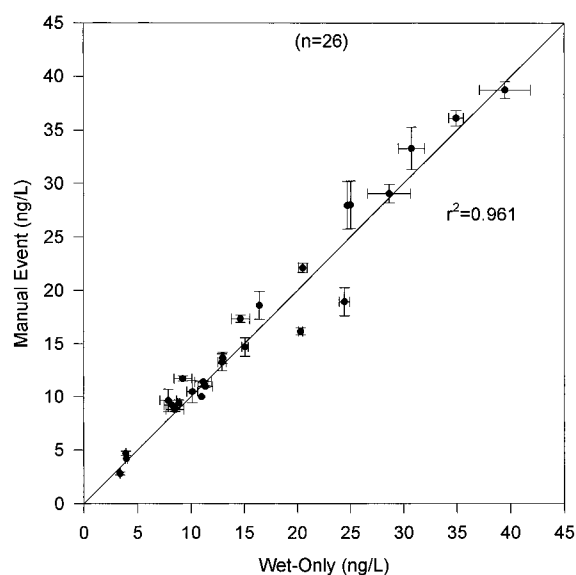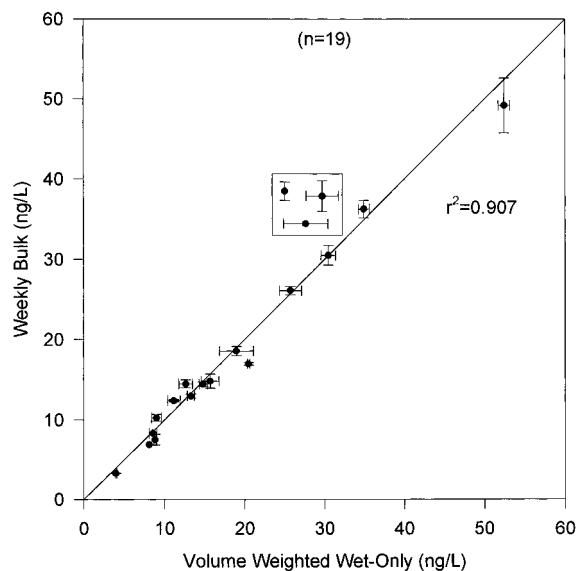ry deposition. Field blanks, funnel rinses, and funnel spikes revealed that Hg and other trace elements were quantified without artifacts and without significant losses to the collection funnels.

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