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Estimated Variability of National Atmospheric Deposition Program/Mercury Deposition Network Measurements Using Collocated Samplers

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Abstract The National Atmospheric Deposition Program/Mercury Deposition Network (MDN) provides long-term, quality-assured records of mercury in wet deposition in the USA and Canada. Interpretation of spatial and temporal trends in the MDN data requires quantification of the variability of the MDN measurements. Variability is quantified for MDN data from collocated samplers at MDN sites in two states, one in Illinois and one in Washington. Median absolute differences in the collocated sampler data for total mercury concentration are approximately 11% of the median mercury concentration for all valid 1999–2004 MDN data. Median absolute differences are between 3.0% and 14% of the median MDN value for collector catch (sample volume) and between 6.0% and 15% of the median MDN value for mercury wet deposition. The overall measurement errors are sufficiently low to resolve between NADP/MDN measurements by ±2 $ng \cdot l^{-1}$ and ±2 $\mu g \cdot m^{-2} \cdot year^{-1}$, which are the contour intervals used to display the data on NADP isopleths maps for concentration and deposition, respectively.

Keywords Mercury · Wet deposition · NADP · MDN · Precipitation · Quality assurance · Variability

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1 Introduction

The National Atmospheric Deposition Program/Mercury Deposition Network (NADP/MDN, hereinafter MDN) is providing long-term, quality-assured records of the mercury (Hg) content of wet deposition in the United States. From its inception in 1996, the MDN has grown to include 88 monitoring sites (Fig. 1a) that collect regionally representative, weekly composite samples of Hg in wet deposition (Sweet and Prestbo 1999). Each MDN site is equipped with a modified Aerochem Metrics[1] (ACM) precipitation collector, and a Belfort[1] Model 5-780 (Belfort Instrument Company 1976) recording rain gage (Gordon et al. 2003). MDN methodologies are described by Vermette et al. (1995). The MDN data are used to assess the fate of Hg emissions to the atmosphere, and are useful for evaluation of the effects of environmental initiatives and regulations aimed at reducing Hg emissions to the atmosphere.

Interpretation of spatial and temporal trends in the MDN data requires knowledge of the variability in the data. The overall measurement variability comprises the combined variability from field equipment, sample handling, laboratory sample analysis, and natural variability. Quality assurance (QA) programs are in place to evaluate specific components of the overall measurement variability of the MDN data. For example, system blank and spike samples are collected at each MDN site to assess Hg contamination or loss due to sample handling and shipping. Variability and bias inherent in chemical analysis of MDN samples are evaluated through various interlaboratory comparison studies. Quantification of the variability and bias in the MDN data is useful for discerning between environmental signals and measurement variability. This paper assesses measurement variability in MDN data estimated from replicate samples obtained from collocated samplers.

2 Collocated Samplers and Replicate Samples

Collocated samplers (Fig. 1) were operated at MDN site IL11 during May 29, 2001, through March 13, 2002, and at MDN site WA18 during June 30, 1998, through December 21, 2002, to simultaneously collect replicate weekly composite samples at the same locations for quantification of overall variability of MDN measurements. The first two letters of the MDN site IDs designate the state where the site is located. For this study a collocated-sampler site consisted of a wet deposition collector and rain gage that were originally installed for MDN monitoring plus an additional collocated collector that replicates the original collector to the fullest extent possible, including the make and model of the collector and its orientation with respect to surrounding objects. The diagram in Fig. 2 illustrates the layouts of the collocated sites. The collection orifices of the original and collocated collectors were positioned at approximately the same elevation above the ground and were completely open to the sky within a 45° cone. In other words, the distance between surrounding objects and the collectors was at least as great as the object height. The collocated precipitation collectors were separated by a distance of between 10 to 15 m. The collocated equipment was field tested to ensure that it was in good working order before samples were collected.

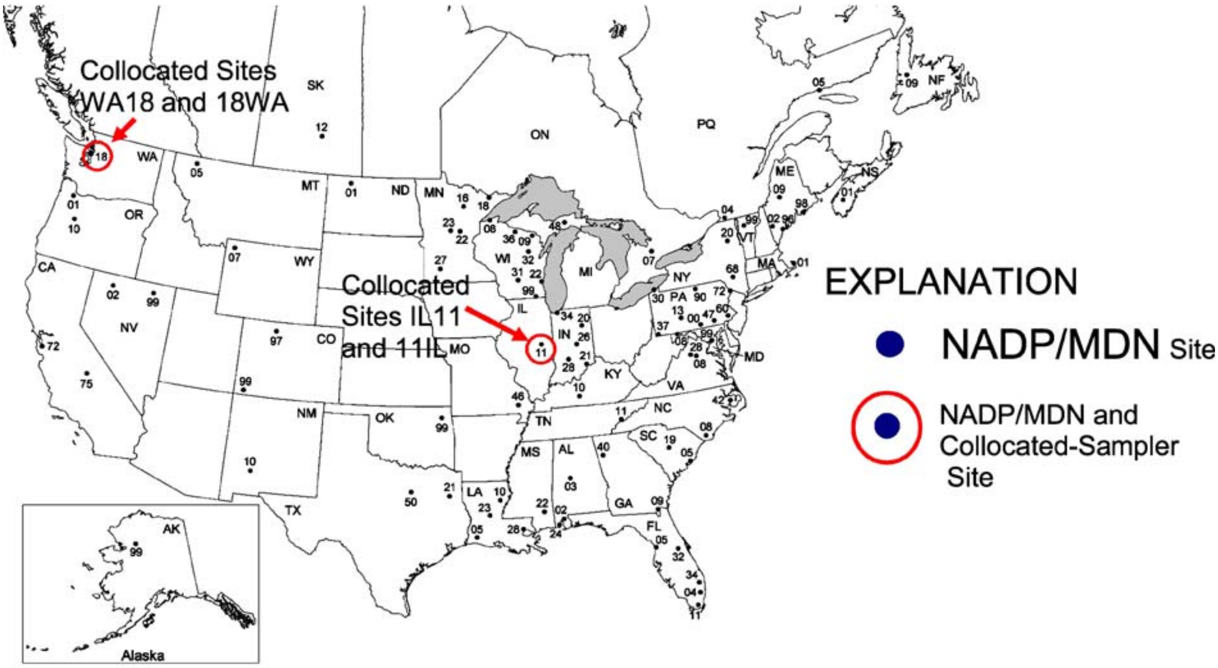
The bottoms of the collectors were enclosed to protect the sample and glass sampling train from the elements and contamination sources. The air temperature inside the collectors was thermostatically regulated to melt frozen precipitation in winter and to reduce evaporation during summer. Interior sampler temperatures are recorded with a maximum/minimum thermometer and regulated with thermostatically controlled heater and fan. Temperatures are kept below 38 °C and above 4.4 °C during all seasons (Frontier Geosciences, Inc. 2003).

The two collocated sites represent different ecoregions with different precipitation characteristics. The WA18 site is located in the Pacific Lowland Mixed Forest Province, which receives between 760 to 1,150 mm (millimeters) of precipitation annually (Bailey and Cushwa 1981). The WA18 site is dominated by low-intensity, semi-continuous rainfall, primarily during the fall, winter, and spring followed by dry summers. The IL11 site is in the Prairie Parkland (Temperate) Province, which receives between 510 to 1,020 mm of precipitation per year (Bailey & Cushwa). The IL11 rainfall tends to be higher-intensity rainfall events, separated by dry days, with summertime thunderstorms and substantially more wintertime snowfall than WA18.

The modified ACM precipitation collector accommodates a glass sampling train, which consists of a funnel that discharges into a thistle tube. The thistle tube directs the sample to a 2-l glass sample bottle that contains 20 ml (milliliters) of 1% (volume/volume) hydrochloric acid; a Hg preservative. At the laboratory, the sample bottles are weighed, and the preservative mass is subtracted to determine the sample volume. Under hot and dry weather conditions, some of

[1] Use of trade, firm, or product names in this paper does is for descriptive purposes only and does not imply endorsement by the US Government, the Illinois State Water Survey, or Frontier Geosciences, Inc.

a)



b)

Fig. 1 **a** Locations of National Atmospheric Deposition Program / Mercury Deposition Network sites and identification of collocated-sampler sites WA18/18WA and IL11/11IL (modified from R. Claybrooke, NADP Program Office, written communication), and **b** photograph of collocated sites WA18/18WA

the preservative can evaporate. For example, in extreme hot and dry conditions in New Mexico and Nevada, approximately 5 ml per week of preservative can be lost.

Site operators processed samples from the collocated collectors using standard MDN procedures (NADP/MDN Site Operation Manual, http://nadp.sws.uiuc.edu/QA/, and Vermette et al. 1995). For this study, the collocated MDN site at IL11 was operated by Illinois State Water Survey personnel, and the collocated MDN site at WA18 was operated by Frontier Geosciences, Inc. personnel (Fig. 1a). Great

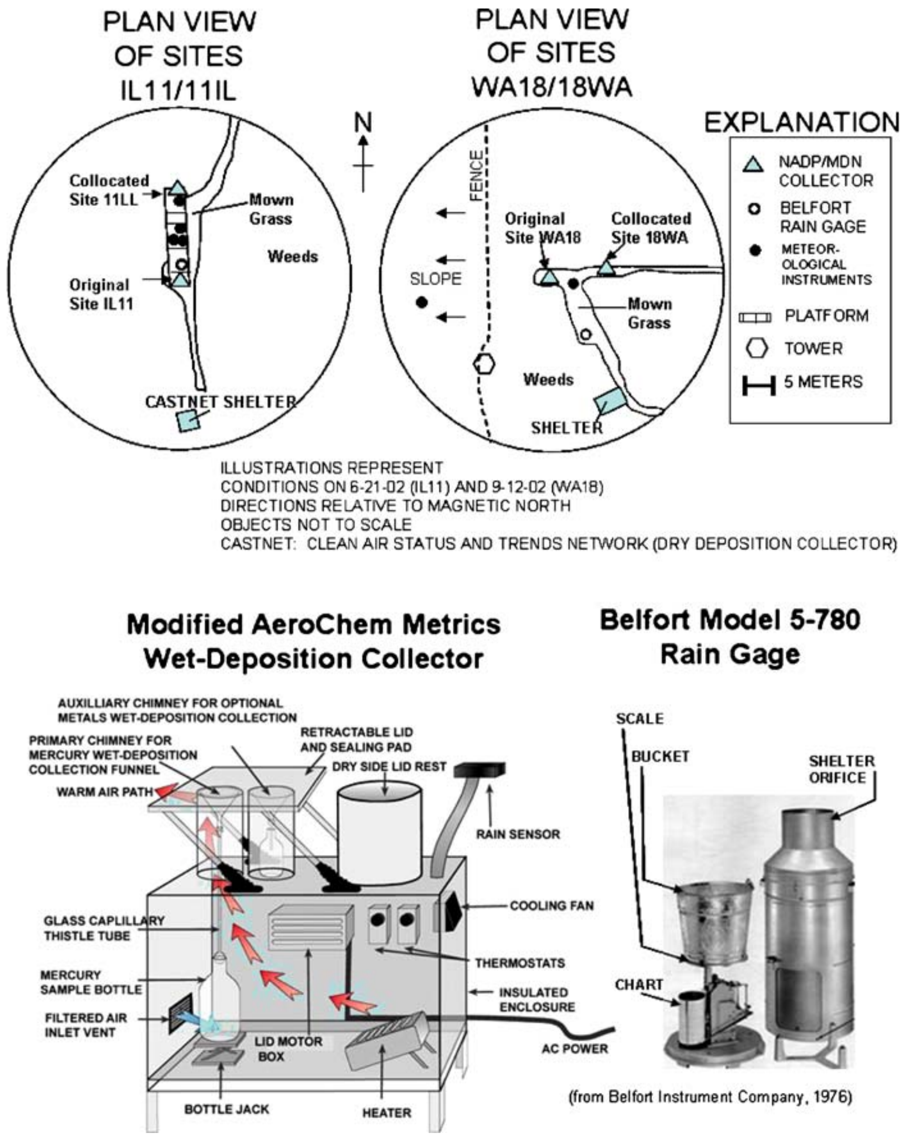


Fig. 2 Plan view diagrams of collocated sites IL11/11IL and WA18/18WA, and illustrations of a Mercury Deposition Network AeroChem Metrics precipitation collector modified for mercury wet-deposition collection and the Belfort Model 5-780 rain gage

care was taken to prevent sample contamination. Handling of the sample train and sample bottle was minimized. In addition, site operators wore class-100 vinyl ultra trace-metal-clean gloves when handling samples or the sampling trains. MDN wet-deposition samples were collected as seven-day composites of all rainfall incident on the collectors. At approximately 9:00 A.M. every Tuesday morning, the sample train was removed from the collector and mailed to the Hg analytical laboratory (HAL) at Frontier Geosciences, Inc. in Seattle, Washington, and a clean sample train was installed in the collector. The HAL analyzed the precipitation samples for total Hg using cold vapor atomic fluorescence (USEPA 2002). Total Hg is assumed to be the sum of dissolved Hg species, elemental Hg, and Hg associated with solid particles. The HAL analyzed each sample from the collocated samplers as routine, weekly MDN samples.

Only wet-deposition samples for weeks with measurable precipitation were used for this analysis. Data for three weeks for the Washington co-located sites and one week for the Illinois collocated sites were omitted because one collector obtained a sample, and the other did not. These data were censored so that estimates of variability would not be overestimated due to equipment failures. Only data qualified as 'valid' by the MDN protocol were selected for analysis (NADP Web site, http://nadp.sws.uiuc.edu/qa), and all data qualified as 'dry' or 'trace' per the database quality rating codes were removed because there were no samples collected for those weeks, which amounted to 1 week for the Washington collocated sites and eight weeks for the Illinois collocated sites. The MDN provides data for total Hg and methylmercury for selected sites, but methylmercury was not addressed in this collocated-sampler study.

The paired data for the week of February 18–25, 2002, for the IL11/11IL collocated-samplers were eliminated because of a large discrepancy in the collocated total Hg concentrations [3.2 nanograms per liter ($ng \cdot l^{-1}$) paired with 17.3 $ng \cdot l^{-1}$]. The data are qualified with a 'B' quality rating code, which identifies "valid data with minor problems". This pair of data also has a data note code of 'd' which means that debris is present in the sample, which suggests contamination of some type. The site operator's notes for this sample also indicate a potential mechanical problem with one of the collectors. The data qualifiers combined with low sampling efficiency justifies exclusion of the sample pair. In all, data for 41 samples (19 paired samples plus three samples without collocated replicates) were eliminated from the analysis because of 'dry' and 'trace' samples. The paired data retained for analysis had complete sets of measurements. In all, 37 paired samples from site IL11/11IL and 56 paired samples from site WA18/18WA were retained for analysis. The precipitation collectors at each pair of collocated sites operated acceptably approximately 99% of the time that precipitation occurred. Approximately 1% of the time, one collector obtained a sample when the other did not open or opened only long enough to obtain a trace amount of precipitation. The paired total Hg concentration data used for this analysis are plotted in Fig. 3.

The MDN precipitation chemistry data are published in terms of concentration and wet deposition (mass deposition). The weekly wet-deposition data are reported by the NADP in units of nanograms of Hg per square meter per week ($ng\ Hg \cdot m^{-2} \cdot week^{-1}$). Hg concentration and wet deposition are related per

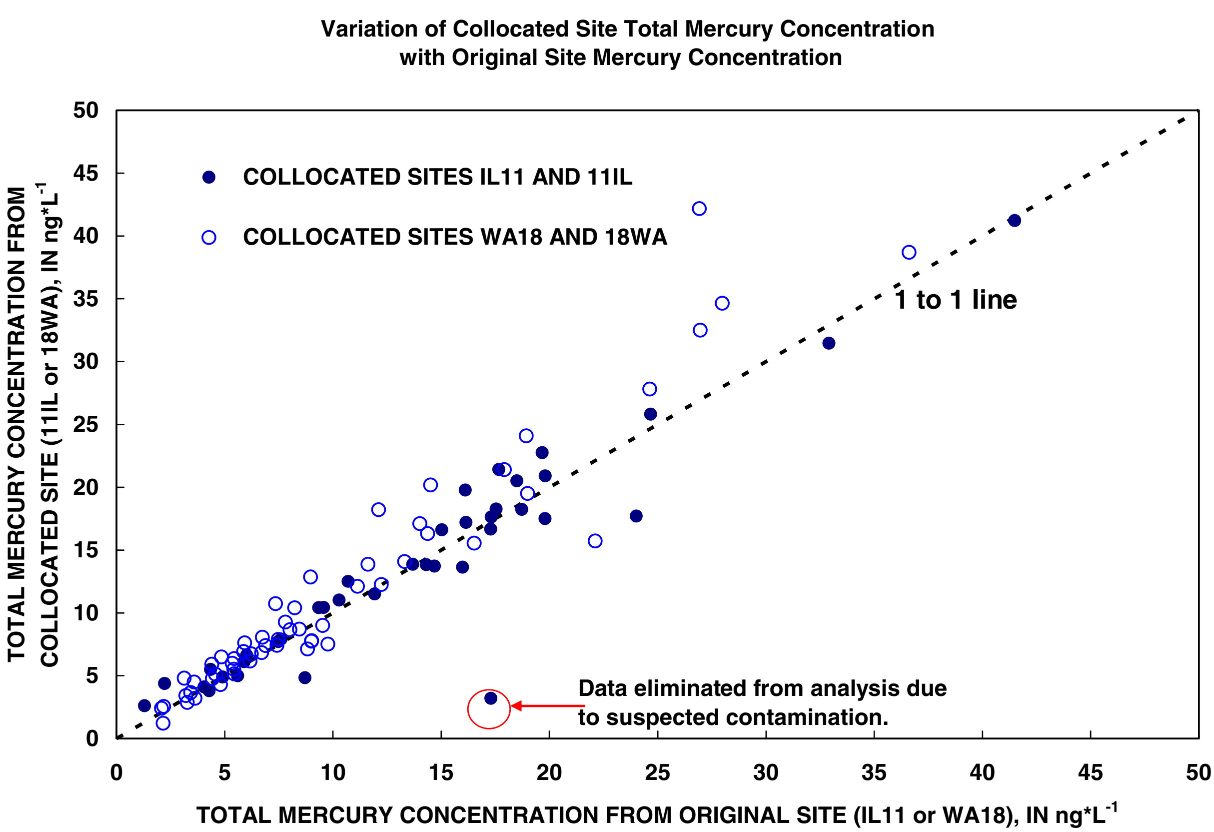


Fig. 3 Comparison of valid total mercury concentrations obtained from collocated Mercury Deposition Network precipitation collectors at sites IL11/11IL and WA18/18WA during 1998–2002. *Points* represent data pairs, not differences

Equation (1), where precipitation depth is measured by the rain gage. Note that a 1-mm depth of precipitation over 1 m^2 is 1 liter (l) of volume.

$$Hg\ wet\ deposition\ (ng{\bullet}m^{-2}{\bullet}week^{-1}) = Hg\ concentration(ng{\bullet}L^{-1}){\bullet}precipitation\ depth\ (mm{\bullet}week^{-1}). \quad (1)$$

In addition to the effects of collector performance, sample handling, and laboratory analysis, the variability in Hg wet deposition data is influenced by the physical precipitation depth measurements from NADP-standard rain gages. As mentioned, only one common rain gage was used to calculate the Hg wet deposition for both collocated collectors. Therefore, the variability associated with precipitation-depth measurements at IL11 and WA18 was assumed to be the same as variability estimated from collocated rain gages at NADP National Trends Network (NTN) sites during 1989–2003, which consistently has been less than or equal to 10% (Gordon et al. 2003, p. 68; Wetherbee et al. 2004, p. 53; Wetherbee et al. 2005, p. 54). Previous studies show that the variability estimated by collocated rain gages is greater for frozen precipitation than for rain (Nilles et al. 1992, p. 13).

3 Statistical Methods and Approach

The collocated-sampler data were statistically evaluated in three different ways to produce three different products for MDN data users. First, the data were grouped by collocated-sampler site and summarized using non-parametric statistics to present the basic characteristics of the data. Next, the paired (replicate) collocated-sampler data were analyzed for measurement differences between the original sites and the collocated sites. The absolute differences between the collocated measurements are assumed to be directly proportional to data variability (i.e., error), and the arithmetic sign of the differences indicate the bias in the data. Absolute and percent differences were summarized to provide data users with traditional estimates of variability in MDN data for total Hg concentration, Hg wet deposition, and collector catch (sample volume). Finally, the paired collocated-sampler data were used to compute pooled estimates of relative standard deviation (RSD), and 95% confidence intervals (95% CIs) of RSD were used to estimate the smallest difference between two independent measurements that is resolved with 95% confidence, called the minimum resolvable difference (MRD).

3.1 Computation of summary statistics

In the analysis of collocated data, statistics were selected that were useful for describing overall sampling variability and bias, and were not overly sensitive to a few extreme values. The equations used to estimate variability from collocated-sampler data are:

$$Absolute\ Difference = |C_1 - C_2|; \quad (2)$$

$$Absolute\ percent\ difference = |[(C_1 - C_2)/((C_1 + C_2)/2)]|{\bullet}100\,;\ and \quad (3)$$

$$Median\ absolute\ percent\ difference = M\{|[(C_1 - C_2)/((C_1 + C_2))/2]|{\bullet}100\} \quad (4)$$

where

C_1 total Hg concentration ($ng{\bullet}l^{-1}{\bullet}week^{-1}$), or Hg wet deposition ($ng{\bullet}m^{-2}{\bullet}week^{-1}$, or collector catch ($ml{\bullet}week^{-1}$) from the original MDN collector;

C_2 same from the collocated MDN collector; and

M median.

Common statistical measures are used to describe the collocated-sampler results, with the exception of the *f*-pseudosigma, which is the interquartile range (75th percentile minus 25th percentile) divided by 1.349. The *f*-pseudosigma is a non-parametric analogue of the standard deviation (Hoaglin et al. 1983). Non-parametric statistics primarily are used to statistically summarize the data, which are not proven to be normally distributed. Parametric statistics are used for normally distributed data, but they are used herein to describe distributions of variances, which follow a chi-square distribution. Errors of measurement are assumed to be normally distributed. Therefore, properties of the normal (or *t*) distribution can be used to calculate confidence limits for the expected distributions of measurement errors.

3.2 Estimation of measurement variability for weekly MDN data

Statistical techniques described by Mueller (1998) and Martin (2001) were adapted to this study to estimate 95% CIs of the RSDs. Mueller's technique is obtained from Snedecor and Cochran (1980), who suggest that if the distributions of the standard deviations (SD) or the relative standard deviation (RSD, standard deviation divided by the mean concentration multiplied by 100), are generally uniform, then variability can be determined by a pooled estimate of SD or RSD. Formulas for the SD and RSD of a sample of a population are (Iman and Conover 1983):

$$SD_{pooled\ data} = \sqrt{\left(\frac{\sum_{i-1}^{n}\left(X_i - \bar{X}\right)}{n-1}\right)^2} \quad (5)$$

and

$$RSD_{pooled\ data} = \frac{SD}{\overline{X}} \bullet 100 \quad (6)$$

where:

- X_i a single measurement, in nanograms per liter, micrograms per square meter, or milliliters;
- $\overline{X}$ sample mean of the single measurements;
- n the number of measurements in the sample.

Martin's technique (2001) is similar to Mueller's, but Martin pools the replicate data by constant relative standard deviation and averages the variances first before taking the square root to compute the standard deviation of the replicates. Also, Mueller assumes the modeled variability is the true variability by calculating confidence limits using the Z-statistic, whereas Martin calculates confidence limits using the t-statistic from the t-distribution. Mueller's technique may give estimates of variability that are biased low by approximately 20% (Jeff Martin, US Geological Survey, written communication, 2005), and the bias is made more negative by using the Z-statistic instead of the t-statistic. But for large numbers (e.g., >50) of replicate data, the bias is smaller because the value of the t-statistic is nearly the same as the value of the Z-statistic.

The average RSD values were used to calculate upper and lower statistical confidence limits (UCL and LCL, respectively) and CI, which is the UCL minus the LCL for MDN collocated-sampler measurements. A CI about the mean of a single measurement is determined by the limits of random error associated with the measurement. On a per sample basis, the formula for the CI for a mean of a normally distributed population is:

$$\bar{X}_i - Z \bullet \frac{SD}{\sqrt{n}} < \mu < \bar{X}_i + Z \bullet \frac{SD}{\sqrt{n}}, \quad (7)$$

where

- $\overline{X}_i$ sample mean (in this case, the single weekly measurement, in nanograms per liter, micrograms per square meter, or milliliters);
- μ population mean (the mean of an infinite number of measurements of the water sample, in same units as $\overline{X}$,
- n sample pairs used to calculate the sample mean (in this case, n=1);
- SD standard deviation, in same units as $\overline{X}$,
- Z value of the normal distribution for $1-\alpha$ confidence (replaced by the t-value from the t-distribution with v degrees of freedom and $1-\alpha$ confidence for small sample sizes); and
- α the probability of a Type I error (the probability that the confidence interval does not include the population mean).

3.3 Preliminary data evaluation

Sources of variability in the MDN data include collector and rain-gage operational characteristics, sample handling and shipping, laboratory analysis, and natural variability of the wet deposition. Differences in the relative amounts of each precipitation event that each collector samples can strongly influence data variability. Catch efficiency, defined as the percentage of the total precipitation depth that the collector samples, is used to evaluate how the collectors influence data variability. However, a scatterplot of the between-collector Hg concentration differences and between-collector catch efficiency differences did not indicate any correlation between catch efficiency differences and Hg concentration variability. Therefore, variability estimated from the paired collocated-sampler data at WA18/18WA and IL11/11IL sites are not predominantly influenced by instrumentation effects.

The collocated-sampler RSD data were evaluated to determine whether all values from both collocated sites could be pooled to compute an average RSD. First, the mean, SD (i.e., $[(C_1-C_2)^2\ /\ (2)]^{1/2}$), and RSD for each pair of measurements were computed for all of the collocated-sampler data pairs. The distributions of SD and RSD values were evaluated for normality by the w/s test, for which the test statistic is the range divided by the standard deviation and comparing to critical values for given significance levels (Kanji, 1993, p.65). The distributions of the SD values for Hg, Hg deposition, and collector catch were not normally distributed at the $\alpha=0.05$ level, but the distributions of the RSD values were not significantly different from normal.

For many chemical constituents in water, SD values within a replicate set commonly are positively correlated with the mean concentrations of constituents in the replicates (heteroscedastic), in which case the variability over a large range of concentrations can be approximated by dividing this range into segments over which either the SD or the RSD are reasonably constant (Anderson 1987). The average SD and RSD of replicate samples are used to describe the variability in a single measurement.

Next, the RSD values were separated into two groups by collocated site (IL11/11IL and WA18/18WA) to test for equal variance using an F-test in SAS (SAS Institute, Inc. 1999). The F-test results indicated acceptance of the null hypothesis: "No difference in RSD between sites IL11/11IL and WA18/18WA" for total Hg concentration (P=0.2410) and Hg deposition (P=0.1390) at the $\alpha=0.10$ significance level, but the null hypothesis was rejected for collector catch (P=0.0240). Because the variances were not equal for collector catch at the $\alpha=0.10$ significance level, pooled estimates of variance may be biased high for some sites in the MDN network and biased low for others. Segregation of the MDN data by site, could not be justified. Therefore, data for both WA18 and IL11 collocated sites were pooled.

The replicate SD and RSD values were plotted relative to the mean values for total Hg concentration, Hg wet deposition, and collector catch in Figs. 4, 5, and 6. No definitive points for dividing the data into groups with constant variance were evident in these plots by simple inspection. Locally weighted scatterplot smoothing (LOESS) lines fit to the data using the LOESS procedure in SAS (SAS Institute, Inc. 1999) with smoothing factors of 0.5 and 0.9, did not provide enough evidence to warrant separation of the data into low- and high-range groups.

Finally, Kendall's Tau, a non-parametric measure of the correlation between two variables (Conover 1980), was used to test the RSD of replicates for homogeneity of variance at a significance level of 0.10 using the CORR procedure in SAS (SAS Institute, Inc. 1999). The Kendall Tau correlation coefficients and associated P values for the correlation of both SD and RSD values with mean values for each parameter are noted on Figs. 4, 5, and 6. The P value is the smallest level of significance that would allow the null hypothesis: "The data are homoscedastic (i.e., no trend)", to be rejected (Iman and Conover 1983). Per the Kendall's Tau results, the null hypothesis of homoscedasticity of the SD data was easily rejected. However the null hypothesis of homoscedasticity of the RSD data was not rejected at the $\alpha=0.10$ significance level. Therefore, the RSD data were pooled to compute the average RSD for each parameter.

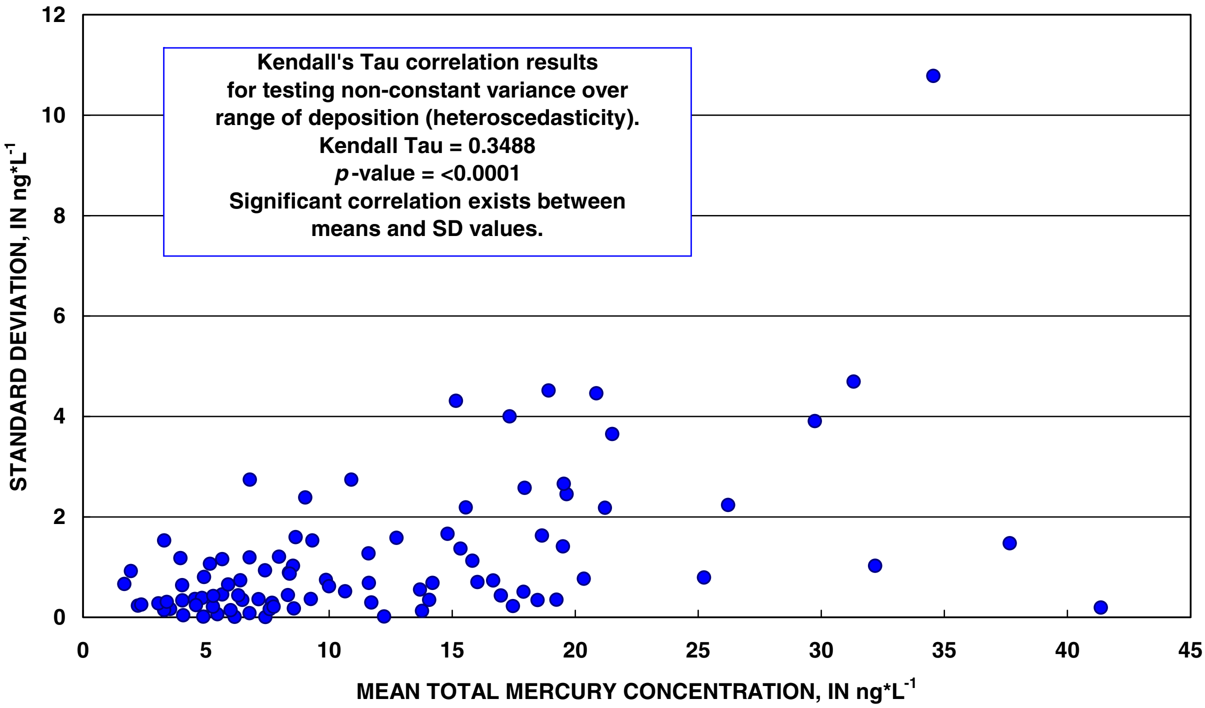
3.4 Estimation of weekly MDN data resolution

It would be useful to know how different two MDN measurements need to be in order to be considered different with statistical confidence, which was defined earlier as the minimum resolvable difference (MRD). The MRD indicates the sensitivity of MDN measurements. Two measurements are considered significantly different if their confidence intervals do not overlap. The 95% CIs are estimated by multiplying the Z-value for 95% confidence (1.96) by the mean, pooled RSD (Mueller 1998, p.8).

$$CI_{\alpha=0.05} = C \cdot 1.96 \cdot RSD_{average} \quad (8)$$

where

$CI_{\alpha=0.05}$	95% confidence interval;
C	total mercury concentration of sample or collector catch; and
$RSD_{average}$	average relative standard deviation calculated for the paired collocated measurements.



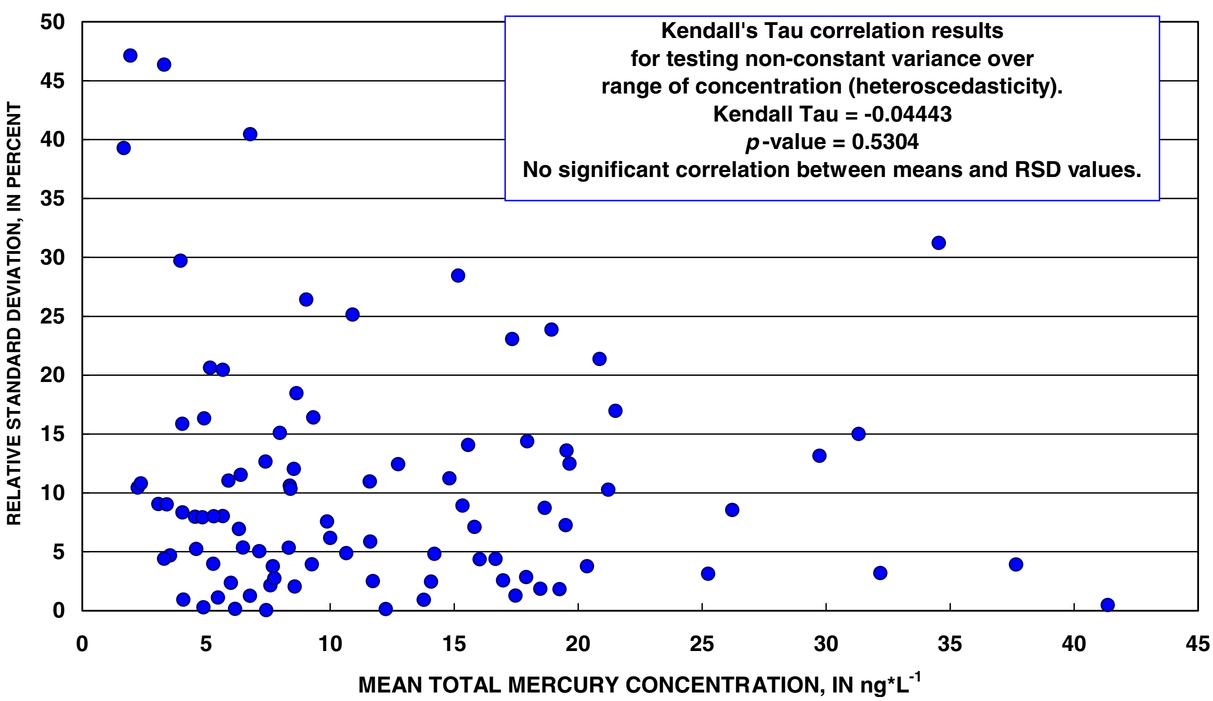


Fig. 4 Variation of standard deviations and relative standard deviations with mean values for paired total mercury concentrations data from collocated wet-deposition collectors at Mercury Deposition Network sites IL11 and WA18

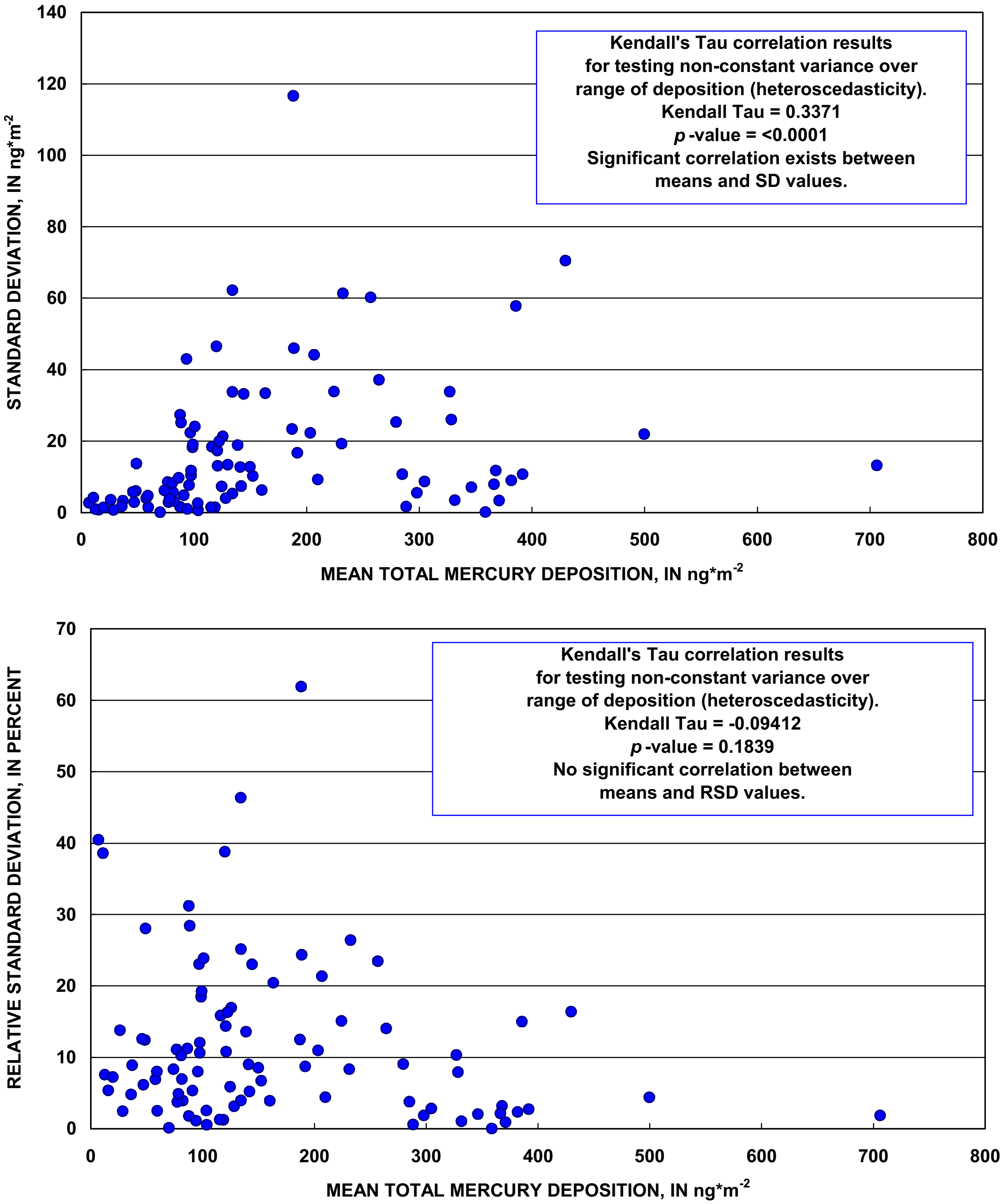


Fig. 5 Variation of the standard deviations and relative standard deviations with mean values for mercury wet deposition for paired data from collocated wet-deposition collectors at Mercury Deposition Network sites IL11 and WA18

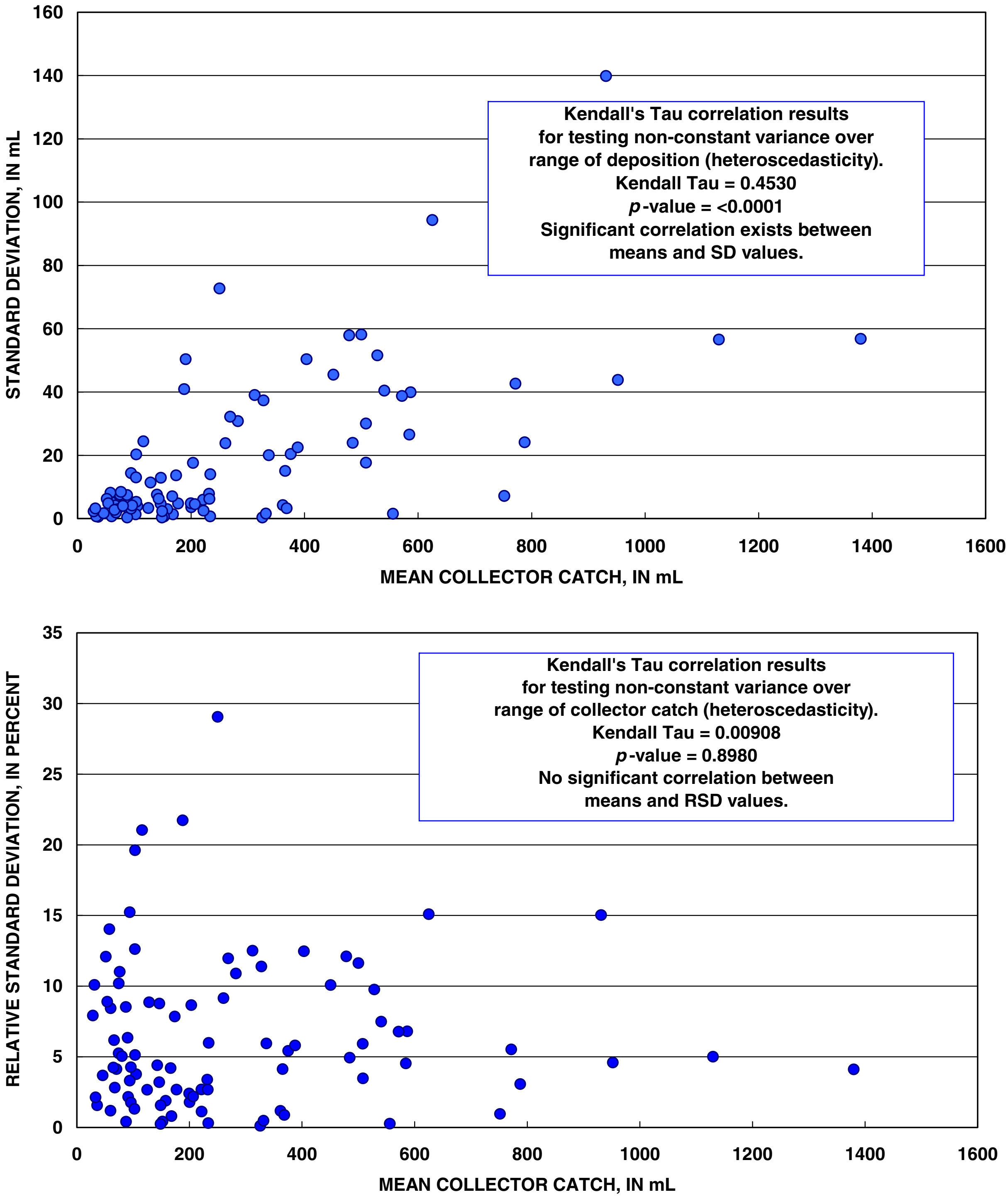


Fig. 6 Variation of the standard deviations and relative standard deviations with mean values for collector catch for paired data from collocated wet-deposition collectors at Mercury Deposition Network sites IL11 and WA18

Equation (8) uses the RSD instead of the SD because the RSD values exhibited more constant variance over the range of mean concentrations than the SD values, and it is more convenient to calculate the MRD using percentages instead of concentration units. After the 95% CIs are estimated, the MRD can be calculated for any measurement and estimate of RSD_{average}. Consider two measured concentration values: C_1 and C_2, where $C_1 < C_2$. If C_1 and C_2 are to be considered different with 95% confidence, then their 95% confidence intervals cannot overlap. Because the CIs are calculated from RSD_{average}, they are expressed as percentages, and the following must be true:

$$C_1 \bullet (1 + CI_{\alpha=0.05}) < C_2 \bullet (1 - CI_{\alpha=0.05}), \tag{9}$$

Solving Equation (9) for C_2, yields:

$$C_2 > \left(\frac{C_1 \bullet (1 + CI_{\alpha=0.05})}{(1 - CI_{\alpha=0.05})} \right) \tag{10}$$

Therefore, C_1 and C_2 are related by the ratio $(1+CI_{\alpha=0.05})$ / $(1-CI_{\alpha=0.05})$, which is called the MRD estimator (m_{d}). The m_{d} can be calculated directly from RSD_{average} for any significance level directly as

$$m_d = \left(\frac{(1 + Z \bullet RSD_{average})}{(1 - Z \bullet RSD_{average})} \right). \tag{11}$$

Multiplying or dividing any measured value by m_{d} gives the upper or lower MRD, respectively, for the measured value. For example, the m_{d} for total Hg concentration measurements is 1.52. To obtain the MRDs for a weekly total Hg concentration measurement of 2.0 ng•l^{-1}, the measured value of 2 ng•l^{-1} is multiplied by 1.52 to obtain 3.05 ng•l^{-1} (upper MRD) or divided by 1.52 to obtain 1.32 ng•l^{-1} (lower MRD). The 95% CIs of ±20.6% do not overlap for measurements of 1.32 ng•l^{-1} or less and 2 ng•l^{-1}, nor for 2 ng•l^{-1} and 3.05 ng•l^{-1} or greater. In other words, the MDN data-collection process can resolve between measurements of 1.32 and 2.00 and also between 2.00 and 3.05 ng•l^{-1} with 95% confidence.

3.5 Estimating measurement variability for annual average MDN data

The weekly MDN data are used to calculate annual precipitation-weighted mean concentrations and annual total Hg wet deposition for presentation on isopleth maps in the NADP annual summary reports, which illustrate the spatial variability of Hg wet deposition across approximately the eastern half of the lower 48 states of the USA (NADP 2004). No contours are available for the western states because only seven MDN sites are located in the western portion of the country (Fig. 7). Annual precipitation-weighted mean Hg concentrations (Hg_{pwm}) are calculated by taking the sum of the products of each week's total Hg concentration times the corresponding precipitation depth and dividing by the total precipitation depth for the entire year. The annual Hg wet-deposition values (Hg_{dep}) for each site are computed as the sum of the weekly precipitation-depth measurements for an entire year multiplied by the annual precipitation-weighted, mean Hg concentration (Hg_{pwm}). These calculations are expressed in Equations (12) and (13):

$$Hg_{pwm} = \frac{\sum_{i=1}^{j \le 52} (ppt_i \bullet [Hg_i])}{\sum_{i=1}^{j \le 52} ppt_i}, \tag{12}$$

$$Hg_{dep} = Hg_{pwm} \bullet \sum_{k=1}^{l=52} (ppt_k), \tag{13}$$

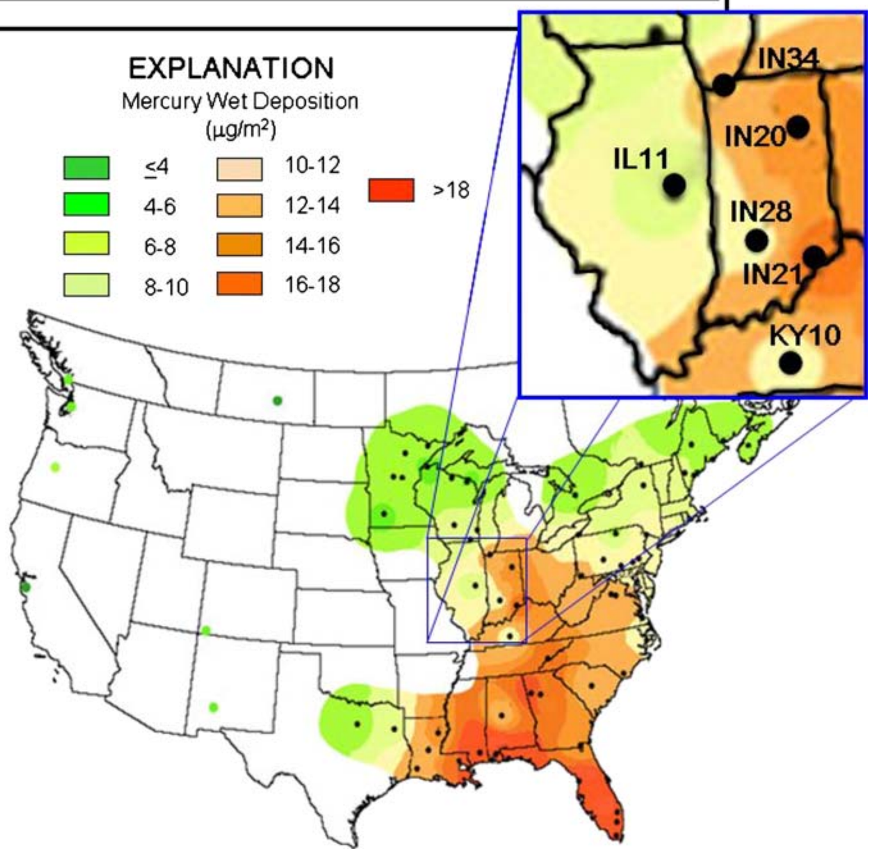
where

- ppt_i weekly precipitation depth in millimeters for weeks when samples were collected;
- $[Hg_i]$ total mercury concentration in weekly MDN samples, in nanograms per liter;
- i week w/ valid samples;
- j number of weeks for which samples were collected;
- ppt_k all weekly precipitation depths in millimeters regardless of whether samples were collected or not; and
- l 52 weeks in a year.

Figure 7 highlights a portion of the 2003 Hg wet-deposition isopleth map in the Midwestern USA. There are several different concentration and deposition contours at a contour interval of 2 µg•m^{-2} within the boundaries of Illinois and Indiana. It is important to know whether this detailed illustration of spatial variability is reliable after accounting for measurement variability. For example, one might want to

Fig. 7 Annual mercury wet deposition for 2003 (modified from NADP 2004)

MDN Site	Precipitation-weighted annual mean Hg concentration (ng•L^{-1})	Precipitation-weighted annual mean Hg concentration variability based on collocated data (ng•L^{-1})	Total Annual Hg deposition (µg•m^{-2})	Total Annual Hg deposition variability based on collocated data (µg•m^{-2})
IL11	11.3	0.996	9.68	0.943
IN20	11.1	.696	15.4	1.15
IN21	13.2	.748	17.3	1.15
IN28	9.69	.582	11.4	.807
IN34	14.7	.839	12.2	.818
KY10	8.62	.414	10.8	.617



know the statistical confidence associated with an 11 µg•m^{-2}•year^{-1} value being different from a 13 µg•m^{-2}•year^{-1} value.

The resolution of the contoured isopleths for Hg_{pwm} and Hg_{dep} was evaluated by assigning a variability (error) term equal to one half the 95% confidence interval to each weekly Hg concentration and deposition value for the six MDN sites located in Illinois, Indiana, and Kentucky (Fig. 7). The variability for precipitation depth measurements was obtained from 41 collocated rain gages operated between 1986 and 2001 (Wetherbee et al. 2005, table 8). Standard propagation of error protocols were used to compute the variability associated with each calculated Hg_{pwm} and Hg_{dep} estimate for each of the six sites highlighted in Fig. 7 (http://teacher.nsrl.rochester.edu/phy_labs/AppendixB/ AppendixB.html).

3.6 Methods for evaluation of catch efficiency differences

Catch efficiencies of the collocated collectors were compared to evaluate the influence of collector operation on overall data variability. For this study, the catch efficiencies of both collectors are based on the one, common rain gage at each collocated-sampler site. Collector catch is measured by weighing the sample bottles and subtracting the tare weight of the sample bottle and hydrochloric acid preservative. Catch efficiency is calculated as

$$Catch\ Efficiency = \left(\frac{equivalent\ precipitation\ depth\ based\ on\ collector\ catch}{precipitation\ depth\ measured\ by\ the\ rain\ gage}\right). \tag{14}$$

Catch efficiencies were calculated for each collector for each valid sample, and were evaluated for statistically significant differences using the Wilcoxon Signed Ranks test (Iman and Conover 1983) at the α =0.10 significance level. A significant difference in catch efficiency between the two precipitation collectors at a collocated site could indicate an influence of the collectors on the estimated concentration and deposition variability.

4 Results

4.1 Summary statistics

Table 1 provides a comparison of selected summary statistics for weekly total Hg concentration, Hg wet deposition, collector catch, and catch efficiencies for the collocated-sampler sites, and for all valid MDN data collected during 2001. The median weekly total Hg concentration at IL11/11IL is nearly double that of the WA18/18WA site, but the median weekly collector catch at the WA18/18WA site is nearly double that of the IL11/11IL site. The data in Fig. 3 indicate little bias for the IL11/11IL total Hg concentration data. However, the total Hg concentrations obtained for collocated site 18WA are slightly higher than for the original WA18 site, especially for concentrations greater than 10 ng•l^{-1}.

Figure 8 shows that the collector catch data for the 18WA site typically was slightly higher than the col-

Table 1 Percentiles and *f*-pseudosigma for total mercury concentration, mercury wet deposition, collector catch, and catch efficiency for data obtained at Mercury Deposition Network collocated-sampler sites IL11/11IL and WA18/18WA during 1998–2002 and for all valid MDN data collected during 2001

MDN parameter	Percentiles				
	N	25th	Median	75th	*f*-Pseudosigma[e]
Collocated sites IL11/11IL					
Total mercury concentration (ng•l^{-1})[a]		6.36	13.8	18.0	8.63
Mercury wet deposition (ng•m^{-2}•week^{-1})[b]	37	57.2	107.	241.	136.
Collector catch (ml)[c]		69.8	115.	226.	116.
Catch efficiency (%)[d]		103.	112.	139.	26.7
Collocated sites WA18/18WA					
Total mercury concentration (ng•l^{-1})[a]		5.37	7.77	14.1	6.47
Mercury wet deposition (ng•m^{-2}•week^{-1})[b]	56	86.7	127.	214.	94.4
Collector catch (ml)[c]		93.9	203.	404.	230.
Catch efficiency (%)[d]		105.	119.	136.	23.0
All valid MDN data collected during 2001[f]					
Total mercury concentration (ng•l^{-1})[a]		5.85	9.74	15.4	7.08
Mercury wet deposition (ng•m^{-2}•week^{-1})[b]	2,295	54.3	129.	283.	170.
Collector catch (ml)[c]		61.4	164.	337.	204.
Catch efficiency (%)[d]		87.4	99.4	104.	16.6

[a] Wet deposition total mercury concentration in nanograms per liter (ng•l^{-1})

[b] Mercury wet deposition, in nanograms per square meter per week (ng•m^{-2}•week^{-1})

[c] Wet deposition collector catch (sample volume) in milliliters (ml)

[d] Wet deposition catch efficiency (ratio of precipitation depth from collector : precipitation depth from rain gage), in percent

[e] *f*-Pseudosigma=interquartile range / 1.349, a non-parametric analogue of the standard deviation (Hoaglin et al. 1983)

[f] Data obtained from NADP database by Bob Larson, NADP Program Office, Illinois State Water Survey, 2004

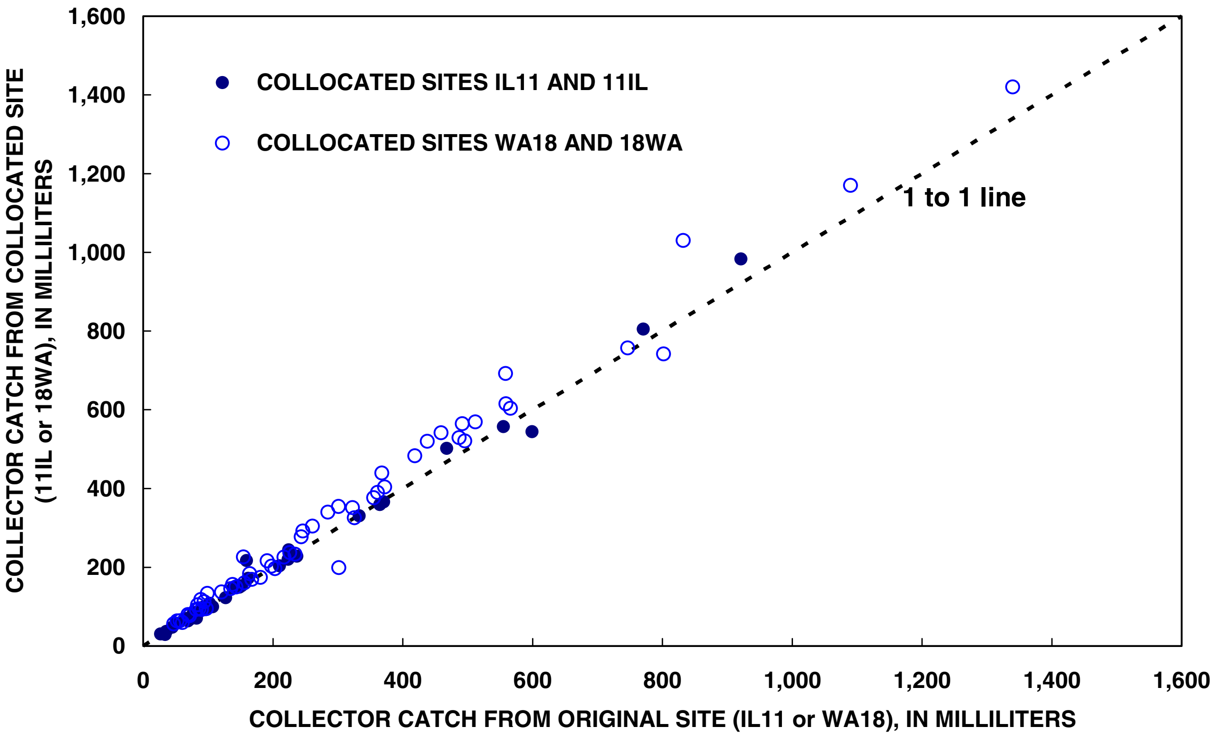


Fig. 8 Comparison of collector catch (sample volume) obtained from collocated wet-deposition collectors at Mercury Deposition Network at sites IL11/11IL and WA18/18WA during 1998–2002. *Points* represent data pairs, not differences

lector catch for WA18, especially when the collector catch was greater than 200 ml. This could be caused by several different factors; the most plausible being differences in the length of time that the collectors stayed open during precipitation periods due to sensor differences. For example, the 18WA collector might have been open longer than the WA18 collector during precipitation events due to sensitivity differences in the collector sensors. Graham and Obal (1989) measured catch efficiencies for six collocated ACM collectors to differ by as much as 14% along an approximate 75-m transect, but collection efficiencies for two of the ACM collectors that were linked to a common sensor differed by less than 1%. By comparison, the median absolute percent difference in catch efficiency obtained for the WA18/18WA samples was 6.5%, and 90% of the catch efficiency values differed by less than 15%. WA18/18WA samples with high concentrations and relatively high variability tended to be for smaller weekly precipitation depths. Hence, the high-concentration data with high variability have a small effect on computation of annual precipitation-weighted mean concentrations and annual wet-deposition.

The precipitation sensors are also less sensitive to light rain events, which are typical of the climate at WA18/18WA. Sometimes during a light rain or snow event, not enough precipitation will build up on the sensor to trigger a collector opening (Graham et al. 1988, p. 146). Work by Graham et al. (1987, pp. 18–29) shows that collocated ACM collectors spaced approximately 15 m apart performed similarly, but collectors separated by approximately twice that distance produced significantly different (α=0.05) results; this suggests that heterogeneity of potential precipitation catch within relatively close distances cannot be completely discounted as a source of variability in measured precipitation characteristics.

If one assumes that the IL and WA collocated median absolute differences are representative of the network, then the collocated results can be used to assess the potential range of measurement variability across the network. The median absolute differences and median absolute percent differences for weekly collocated-sampler measurements are summarized for each parameter in Table 2. The median absolute difference for weekly total Hg concentration for each collocated site is 1 ng•l^{-1}, which equates to site-specific median absolute percent differences between 5% and 10%. The median absolute differences for weekly total Hg wet deposition are between approximately 8 and 19 ng•m^{-2}, which equates to median absolute percent differences between 6% and 11%. Median collector catch absolute differences range between 5 and 23 ml (4% to 7%). These variability estimates for the MDN are comparable to those obtained for nitrate and sulfate concentrations and collector catch for NTN collocated sites (Nilles et al. 1994, pp. 9–15; Wetherbee et al. 2004, pp. 53–55). The comparison of the MDN variability estimates with those obtained for the NTN is reassuring, considering that Hg concentrations are three orders of magnitude smaller than nitrate and sulfate concentrations, and the area of the MDN collector funnel is approximately 80% smaller than the area of the NTN sample-bucket orifice.

Weekly median absolute differences for the collocated samplers expressed as a percentage of the median values for all valid weekly data obtained at

Table 2 Comparison of absolute and percent differences for weekly total mercury concentrations, mercury wet-deposition values, and collector catch (total sample volume) determined with collocated Mercury Deposition Network precipitation collectors at collocated sites IL11/11IL during May 29, 2001, through March 13, 2002, and at collocated sites WA18/18WA during June 30, 1998, through December 21, 2002

		Collocated site median absolute difference[a]	Collocated site median absolute percent difference[b]	Collocated site median absolute difference as a percentage of median values for original sites, 1999–2004[c]	Collocated site median absolute difference as a percentage of median of all valid 1999–2004 MDN data[d]
Parameter (units)	Number of sample pairs	(units)	(%)	(%)	(%)
	Collocated sites IL11/11IL				
Total mercury concentration (ng•l^{-1})		1	5	8.6	11
Mercury wet deposition (ng•m^{-2}•week^{-1})	37	7.8	6	5.7	6.3
Collector catch [sample volume (ml•week^{-1})]		5	4	3.5	3
	Collocated sites WA18/18WA				
Total mercury concentration (ng•l^{-1})		1	10	13	11
Mercury wet deposition (ng•m^{-2}•week^{-1})	56	19	11	17	15
Collector catch [sample volume (ml•week^{-1})]		23	7	15	14

ng•l^{-1} Nanograms per liter, *ng•m^{-2}•week^{-1}* nanograms per square meter per week

[a] Equation (1)

[b] Equation (2)

[c] Median of valid 1999–2004 IL11 and WA18 data computed from data obtained from MDN database available at http://nadp.sws.uiuc.edu/nadpdata/mdnsites.asp

[d] Median of valid 2001 MDN data computed from data obtained from MDN database available at http://nadp.sws.uiuc.edu/nadpdata/mdnsites.asp

each original site (IL11 and WA18) during the period 1999–2004 are similar to the absolute differences expressed as a percentage of the median values for all MDN data obtained during 1999–2004 (Table 2). Therefore it is reasonable to assume that variability estimates obtained from the IL11/11IL and WA18/18WA collocated data are representative of the entire MDN. For IL11/11IL and WA18/18WA, the differences for total Hg concentration are 11% of the median total Hg concentration value for all valid 1999–2004 data. Differences for Hg wet deposition and collector catch data obtained from IL11/11IL are 6.3% and 3.0%, respectively, while differences for Hg wet deposition and collector catch at WA18/18WA are 15% and 14% of the median 1999–2004 data.

4.2 Measurement variability of weekly MDN data

CIs applied to each weekly MDN measurement provide statistical confidence that individual measurements are indeed different and thus the credibility of seasonal patterns or spatial differences can be established. For example, data collected during 2002–2003 at MDN site CO97 (Buffalo Pass) show a seasonal pattern with higher concentrations in the summer and lower concentrations in the winter (Mast et al. 2003) (Fig. 9). The 95% CIs applied to the data in Fig. 9 are derived from the collocated-sampler data and supply the needed confidence to conclude that the seasonal pattern is real and not due to measurement variability because many of the confidence intervals for summer time measurements do not overlap with those for winter.

The average RSDs, 95% CIs, and m_ds for individual MDN measurements of total Hg concentration, Hg wet deposition, and collector catch are shown in Table 3. Weekly MDN Hg concentration measurements are bounded by an estimated 95% CI of ±20.6%, while Hg wet-deposition measurements are bounded by at least ±22.7% (Table 3). The variability in precipitation-depth measurements is not incorporated into the estimated 95% CI and MRD for Hg wet deposition, in Table 3, because the collocated-sampler wet-deposition data were computed using one common rain gage. Weekly MDN collector catch data are bounded by an estimated 95% CI of +12.3%.

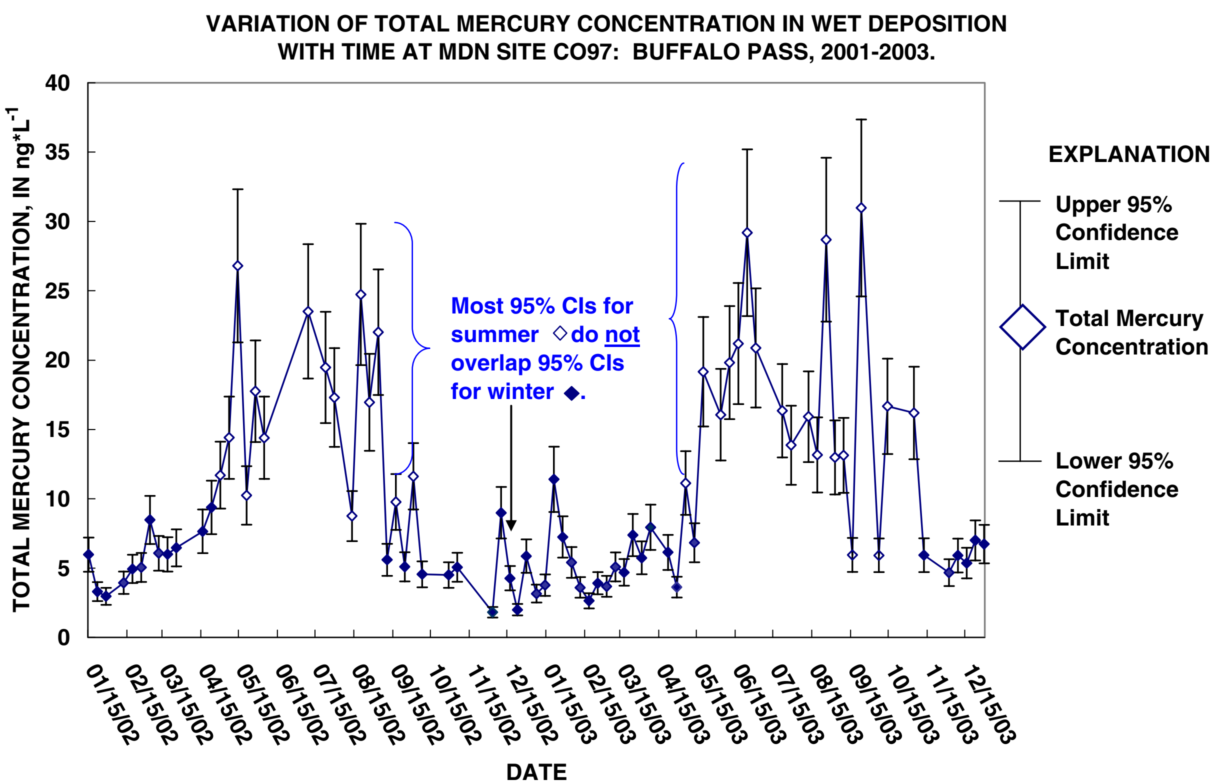


Fig. 9 Variation of total mercury concentration in wet deposition with time at Mercury Deposition Network site CO97 (Buffalo Pass, Colorado) during 2002–2003 and 95% confidence intervals based on collocated-sampler data

Table 3 Estimated 95% confidence intervals and factors for estimating the minimum resolvable differences for weekly Mercury Deposition Network measurements as determined by collocated-sampler data

Parameter monitored weekly	Average relative standard deviation[a] (%)	n	Estimated 95% confidence interval[b] (%)	Minimum resolvable difference estimator[c] (m_d)
Total mercury concentration ($ng{\bullet}l^{-1}{\bullet}week^{-1}$)	10.5	93	20.6	1.52
Mercury wet deposition ($ng{\bullet}m^{-2}{\bullet}week^{-1}$)	11.6	92	22.7	1.59
Collector catch ($ml{\bullet}week^{-1}$)	6.3	92	12.3	1.28

$ng{\bullet}l^{-1}{\bullet}week^{-1}$ Nanograms per liter per week, $ng{\bullet}m^{-2}{\bullet}week^{-1}$ nanograms per square meter per week, $ml{\bullet}week^{-1}$ milliliters per week

[a] Mean of relative standard deviations for all data pairs.

[b] Using Z=1.96 times the mean of the relative standard deviations for replicate data pairs.

[c] Factor used to estimate the minimum resolvable difference between two measurements (i.e., the smallest difference between two independent measurements that is resolved with 95% confidence).

These values may be used given the assumption that the average RSD is representative of all locations in all seasons. As mentioned earlier, catch efficiency is lower for frozen precipitation than for rain. Therefore, variability is expected to be greater in winter months at snow-dominated locations. Likewise, sample evaporation and Hg volatilization might increase variability in warm, dry regions.

The MRD estimators in Table 3 are used to determine whether weekly measurements at separate sites are different, given the resolution of MDN measurements. Figure 10 illustrates an example of how the MRD can be used to evaluate differences in the weekly measured Hg wet deposition for MDN sites CO97 and CO99. The discrete weekly measurements at these two sites do exceed the MRD for six out of nine weeks during the period of July 23 through October 8, 2002, despite the fact that the overall pattern of deposition is very similar. Therefore, the weekly measurements for CO97 and CO99 are significantly different (α=0.05) for those six weeks. MDN data users can use the MRDs to guard against over interpretation of differences between weekly values that are within the variability inherent in the data-collection processes.

4.3 Measurement variability of annual average MDN data

Using one-half the 95% confidence interval as an error term for weekly measurements of Hg concentration and Hg wet-deposition (Table 3) and standard propagation of error protocols, the variability in Hg_{pwm} and Hg_{dep} [Equations (12) and (13)] was computed for six sites during 2003 (Fig. 7). The calculated variability was less than ±1.0 $ng{\bullet}l^{-1}{\bullet}year^{-1}$ for Hg_{pwm} and less than ±1.2 $\mu g{\bullet}m^{-2}{\bullet}year^{-1}$ for Hg_{dep} for the six MDN sites IL11, IN20, IN21, IN28, IN34, and KY10 during 2003. The contour intervals for the isopleths published by the NADP are 2 $ng{\bullet}l^{-1}{\bullet}year^{-1}$ and 2 $\mu g{\bullet}m^{-2}{\bullet}year^{-1}$ for Hg_{pwm} and Hg_{dep}, respectively (NADP 2004), which are approximately two times the calculated variability in Hg_{pwm} and Hg_{dep}. Therefore, given the assumption that the average RSD for the collocated measurements is representative of all seasons and all locations, the NADP contour intervals are reasonable and meaningful.

5 Conclusions

The median absolute total Hg concentration differences obtained for collocated MDN samplers is approximately 11% of the median total Hg concentration obtained for all valid 1998–2004 MDN data. The median absolute percent differences obtained were between 6% and 15% for Hg wet deposition and between 3% and 14% for collector-catch measurements. Median values for Hg concentration, Hg deposition, and collector catch at IL11/11IL and WA18/18WA are similar to the median values obtained for the entire MDN. Therefore, the variability estimated by the collocated-sampler data is considered to be representative of the entire MDN.

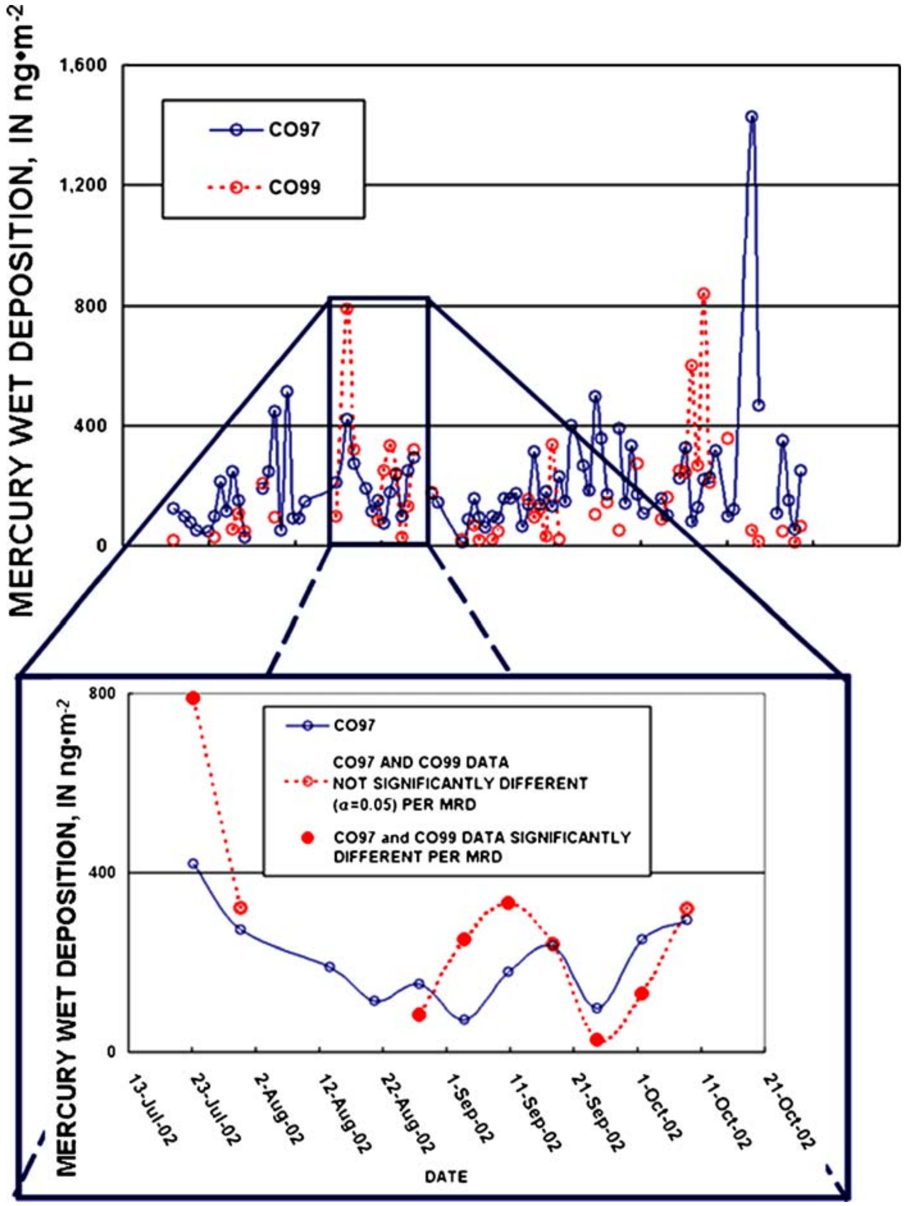


Fig. 10 Comparison of weekly mercury wet deposition for MDN sites CO97: Buffalo Pass and CO99: Mesa Verde National Park with significantly different (α=0.05) measurements identified using the minimum resolvable difference as computed from collocated-sampler data

Data obtained from collocated MDN wet-deposition collectors indicate that the overall measurement variability in MDN total Hg concentration measurements, as estimated by the average relative standard deviation of the replicate sample data, is 11%. Average relative standard deviations for overall measurement variability for MDN total Hg deposition and collector catch are 11% and 8.5%, respectively.

The 95% CIs for weekly MDN measurements of total Hg concentration, Hg wet deposition, and collector catch are estimated as 20.6%, 22.7%, and 12.3%, respectively. The 95% CIs and MRDs for weekly MDN measurements are useful for comparing weekly measurements from a single site over a period of time and for comparison of weekly measurements from geographically distinct sites. The 95% CIs were used to calculate factors (m_d) for estimating MRDs; the smallest difference between two measurements that is resolved with 95% confidence.

NADP publishes annual precipitation-weighted mean Hg concentration- and wet-deposition-isopleth maps in annual reports (NADP 2004). The variability in weekly MDN measurements was propagated to estimate the variability in annual Hg_{pwm} and Hg_{dep}. The results indicated that the contour interval isopleths of 2 ng•l^{-1} and 2 μg•m^{-2}, are within the resolution of the MDN data. Therefore, the NADP maps provide a reasonable representation of the spatial distribution of Hg wet deposition.

Differences in catch efficiencies for the collocated samplers did not correlate with Hg concentration variability. Conversely, variability estimates are predominantly influenced by natural variability, not instrumentation effects. An ongoing collocated-sampler program is needed to provide ongoing monitoring of sources of overall measurement variability in MDN data. Additional investigation of the factors affecting catch efficiency and the relation between catch efficiency and MDN data variability could lead to improved instrumentation and data-collection protocols.

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