

Experiences with Mercury Emissions Monitoring Using Sorbent Traps in the U.S.

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ABSTRACT

Despite a 2008 court ruling that eliminated the U.S. Environmental Protection Agency's (EPA) federal Clean Air Mercury Rule (CAMR), many U.S. coal-fired power plants have been monitoring smokestack mercury (Hg) emissions for the last three years to meet individual state requirements. Anticipated federal standards for electric utilities and recently enacted regulations such as those for cement manufacturing facilities will continue to require U.S. industries to address Hg emissions monitoring. Hg can be monitored via continuous emissions monitoring systems (Hg CEMS) or a less complex sorbent-based monitoring approach. Both approaches have been used for compliance reporting purposes in the U.S. Although originally intended as either a back-up to or a way of independently validating Hg CEMS, sorbent-based monitoring systems have become more accepted as primary monitoring systems. As Hg concentrations are reduced by more stringent regulations, the sorbent trap approach, with its inherent ability to measure very low concentrations, becomes the preferred compliance monitoring approach.

INTRODUCTION

The use of sorbent traps for the measurement of Hg in flue gases from coal-fired power plants was originally conceived as an alternative to the more complex wet-chemical based measurement methods, such as the Ontario-Hydro method [1–3]. After successful validation testing [4], sorbent trap-based Hg measurement was adopted by the U.S. Environmental Protection Agency (EPA) as a reference method [5] and quickly embraced by the industry due to its ruggedness and ease-of-use while achieving high sensitivity.

The shift from a reference method to a monitoring approach for Hg emissions occurred when the U.S. power industry became concerned that conventional continuous emission monitoring systems would not be available in time to meet the rigors of compliance monitoring that the Clean Air Mercury Rule (CAMR) would eventually require [6]. Although this federal rule was vacated in 2008, and with it the regulatory driver to reduce and measure Hg emissions from coal-fired power plants nationwide, growing concern about those emissions compelled several state agencies to address the issue with individual state requirements.

In the absence of official protocols guiding the use of these sorbent trap monitoring systems, the resulting compliance monitoring installations have been operated

according to procedures that are either identical or similar to those established in the vacated CAMR. To provide a set of standardized procedures and performance benchmarks for any forthcoming federal regulations aimed at reducing Hg emissions from stationary sources, the U.S. EPA formalized the sorbent-trap monitoring approach in 2010 by issuing performance specifications for monitoring total vapor phase Hg emissions from stationary sources using a sorbent trap monitoring system (PS-12B) [7].

SORBENT TRAP MERCURY MONITORING

During sorbent trap monitoring, known volumes of flue gas are drawn concurrently through a pair of in-stack sorbent traps at flow rates that are in proportion to the stack gas flow rate. At the end of a monitoring run, which can last from a few hours up to several days, both traps are retrieved from the stack and analyzed in a laboratory to yield the mass of Hg captured on the traps during the monitoring period. Since the sorbent continuously captures Hg during a monitoring run and in turn pre-concentrates the analyte prior to analysis, this monitoring approach has an inherent ability to measure very low concentrations. The lowest level that can be measured using sorbent traps is essentially limited only by the time available to collect the sample.

Sorbent traps intended for continuous monitoring are required to consist of three identical sections of a sorbent that is able to selectively capture total gaseous mercury representing the sum of elemental Hg (Hg^0) and gaseous forms of oxidized Hg (i.e., Hg^{2+}). A commonly used sorbent material is activated carbon impregnated with iodine. Figure 1 shows a schematic introducing the principles of sorbent trap monitoring.

Each of the three sections has a distinct purpose. The first section that the sample gas contacts is for primary capture of the total gaseous Hg. The second section is designated as a back-up section indicating whether any significant breakthrough (B) of total gaseous Hg has occurred during the sampling period. The performance specification requires that the mass of mercury collected on the second section (m_2) does not exceed 5 % of the mass of mercury collected on the first section (m_1) of the sorbent trap.

$$B = \frac{m_2}{m_1} \cdot 100 [\%] \quad (1)$$

The third section is spiked with a known amount of Hg^0 prior to sampling (m_s), which must be within $\pm 50\%$ of the Hg mass expected to be collected on the first section during the monitoring period. After retrieval from the stack, the third section is analyzed separately for its Hg content (m_3) and compared to m_s to determine the sample recovery efficiency and to assess any sample matrix interference. Spike recoveries (R) must range between 75 and 125 % for the sorbent trap results to be considered valid.

$$R = \frac{m_3}{m_s} \cdot 100 [\%] \quad (2)$$

In order to establish the concentration (C) of Hg in the flue gas during the monitoring period, the total mass of Hg recovered from the first and second trap section (m_1+m_2) is divided by the total volume of dry gas metered during the monitoring period (V). Note that all concentrations reported in this paper are based on dry gas volumes (unless noted otherwise) normalized to standard temperature and pressure defined as 20 °C and 760 mmHg, respectively.

$$C = \frac{m_1 + m_2}{V} \quad (3)$$

In contrast to the real-time results provided by conventional continuous emission monitoring systems (CEMS), sorbent trap results represent Hg concentrations integrated for the duration of the collection period (see Figure 2).

The method precision is evaluated through the paired trap agreement, which is expressed as relative deviation (RD)

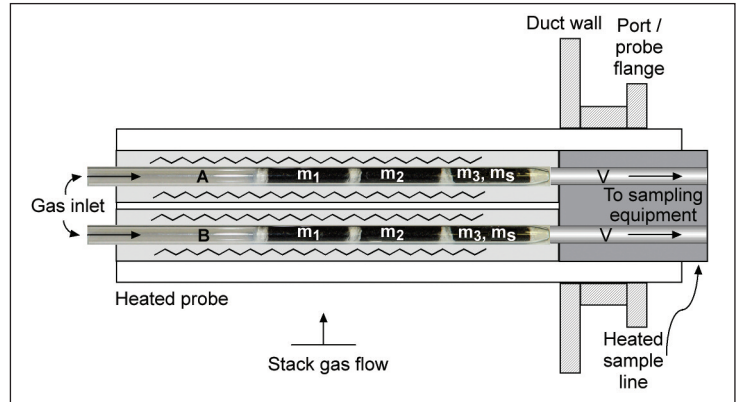


Figure 1:
Principles of sorbent trap monitoring.

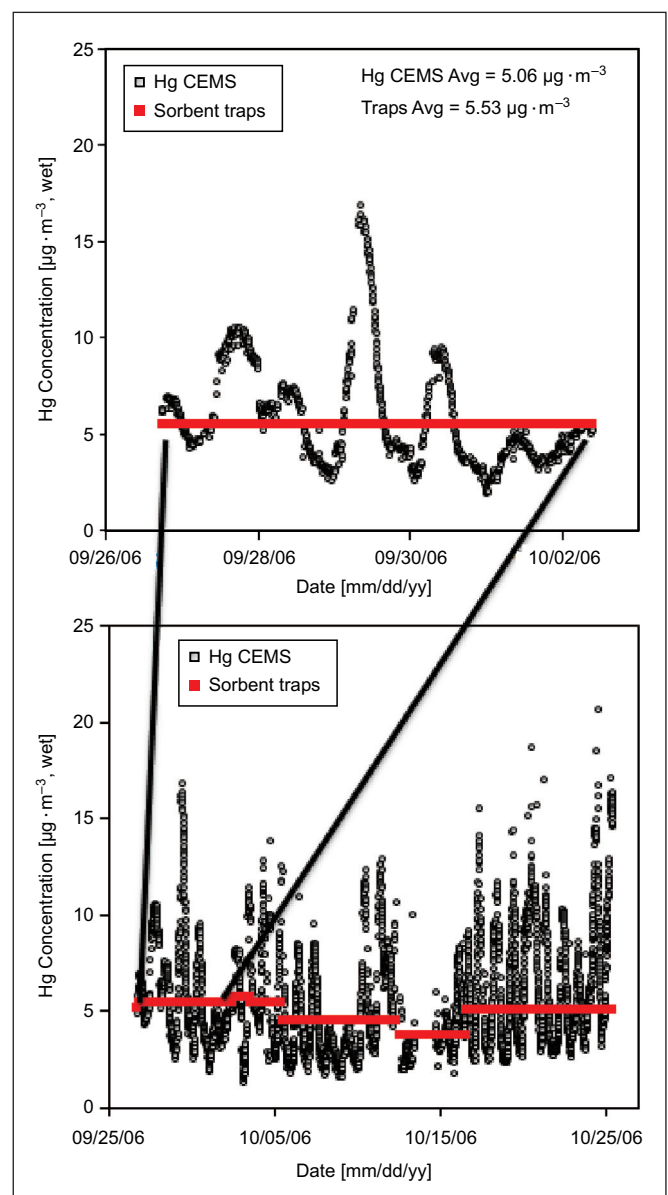


Figure 2:
Presentation of Hg data from CEMS compared with sorbent traps [8].

QA/QC Test or Specification	Acceptance Criteria
Sorbent trap section 2 breakthrough	$\leq 5\%$ of Hg mass collected on section 1
Spike recovery from section 3	75–125 % of spike amount
Paired trap agreement	<ul style="list-style-type: none"> – $\leq 10\%$ relative deviation if the average Hg concentration is $> 1.0 \mu\text{g} \cdot \text{m}^{-3}$; – $\leq 20\%$ relative deviation if the average Hg concentration is $\leq 1.0 \mu\text{g} \cdot \text{m}^{-3}$; – results are acceptable if absolute difference between concentrations from paired traps is $\leq 0.03 \mu\text{g} \cdot \text{m}^{-3}$
Relative accuracy	<ul style="list-style-type: none"> – relative accuracy $\leq 20\%$ of reference method mean value; – or if reference method mean value is $\leq 5.0 \mu\text{g} \cdot \text{m}^{-3}$, absolute difference between reference method and sorbent trap monitoring system mean values $< 1.0 \mu\text{g} \cdot \text{m}^{-3}$

Table 1:

Key QA/QC criteria for day-to-day sorbent trap monitoring system operation and system certification [7].

between the Hg concentrations from traps A (C_A) and B (C_B) and calculated via

$$RD = \frac{|C_A - C_B|}{C_A + C_B} \cdot 100\% \quad (4)$$

For the trap results to be considered valid, the RD should be not more than 10 % for Hg concentrations that are larger than $1.0 \mu\text{g} \cdot \text{m}^{-3}$ and not more than 20 % for flue gas Hg concentrations less than $1.0 \mu\text{g} \cdot \text{m}^{-3}$. Alternatively, results are also acceptable if the absolute difference between concentrations from paired traps is less than $0.03 \mu\text{g} \cdot \text{m}^{-3}$.

The accuracy of the sorbent trap monitoring system is evaluated periodically by comparing the Hg concentrations measured by the sorbent trap monitoring system to concurrent measurements made with a reference method (RM), typically EPA Method 30B – Determination of total vapor phase Hg emissions from coal-fired combustion sources using carbon sorbent traps [5]. The relative accuracy (RA) is established as the absolute mean difference between the Hg concentrations determined by the sorbent trap monitoring system and the values determined by the reference method plus the 2.5 % error confidence coefficient of a series of at least nine tests divided by the mean of the reference method tests. In order to pass a relative accuracy test audit (RATA), which is typically performed on an annual basis, each sorbent trap monitoring system must maintain a RA of 20 % or less. Alternatively, for sources with concentrations of less than $5.0 \mu\text{g} \cdot \text{m}^{-3}$, RA can be expressed as the absolute value difference between the mean sorbent trap monitoring system and reference method values [7]. This absolute value difference should not exceed $1.0 \mu\text{g} \cdot \text{m}^{-3}$. Some of the key quality assurance and control (QA/QC) criteria for the monitoring system certification as well as operation are summarized in [Table 1](#).

SALEM HARBOR POWER STATION

As a result of individual state requirements targeting the reduction of Hg emissions from coal-fired power plants, several facilities have been monitoring Hg emissions for compliance over the past years despite the lack of a federal regulation. Dominion's Salem Harbor Power Station is among them, being required to monitor Hg emissions for compliance with the Massachusetts emissions standards for power plants since January 1, 2008 [9].

Salem Harbor Power Station is located in Salem, Massachusetts, and began commercial operation in 1951. The power station consists of three coal-fired generating units and one oil-fired unit. The coal-fired Units 1, 2 and 3 produce 84 MW, 81 MW and 150 MW, respectively, while the oil-fired Unit 4 produces 440 MW. Design specifications for each unit are shown in [Table 2](#).

The coal burned at the power station is a bituminous coal from South America with a Hg content in the range of $0.02\text{--}0.12 \mu\text{g} \cdot \text{g}^{-1}$, a chlorine content of $20\text{--}170 \mu\text{g} \cdot \text{g}^{-1}$ and a sulfur content of 0.5–0.6 %. The resulting sulfur dioxide (SO_2) and nitrogen oxides (NO_x) emissions range from $200\text{--}270 \text{mL} \cdot \text{m}^{-3}$ and $20\text{--}150 \text{mL} \cdot \text{m}^{-3}$, respectively.

With pending state requirements setting stringent Hg emissions reduction goals, the plant operators decided to install three MET-80 sorbent trap monitoring systems from Clean Air Engineering (Palatine, IL, USA) in 2007. The systems were installed directly at the stack in order to monitor emissions from Units 1, 2 and 3. Systems 2 and 3 are shown in [Figure 3](#). Each system is fully integrated with the plant's data acquisition and handling system (DAHS) via Modbus TCP. Since the start of the compliance monitoring on January 1, 2008, the units have been in operation in excess of a combined 60 000 h, having sampled more than 1 200 sorbent traps, which were supplied by Ohio

Unit	Description of Emission Unit	Net Design Capacity [MW]	Pollution Control Devices
1	Babcock & Wilcox, Model No. RB103 Water Tube Boiler	84	<ul style="list-style-type: none"> - Low NO_x burners - Selective non-catalytic reduction - Electrostatic precipitator
2	Babcock & Wilcox, Model No. RB103 Water Tube Boiler	81	<ul style="list-style-type: none"> - Selective non-catalytic reduction - Electrostatic precipitator
3	Babcock & Wilcox, Model No. RB284 Water Tube Boiler	150	<ul style="list-style-type: none"> - Over-fire air - Low NO_x burners - Selective non-catalytic reduction - Electrostatic precipitator
4	Riley Stoker, Model No. 1SR Water Tube Boiler	440	<ul style="list-style-type: none"> - Low NO_x burners - Electrostatic precipitator

Table 2:
Unit configuration of Dominion's Salem Harbor Power Station.



Figure 3:
Salem Harbor MET-80 systems 2 and 3.

Lumex Company (Twinsburg, OH, USA). All subsequent operating data and performance benchmarks presented are based on this data set.

EVALUATION OF KEY QA/QC PARAMETERS

Breakthrough

One of the key QA/QC parameters of sorbent trap monitoring is the breakthrough of Hg into the second trap section. The results for all breakthrough analyses are presented in Figure 4. As can be seen, passing the breakthrough criteria of 5 % for each sorbent trap typically does not present a challenge. This is also evidenced by the low mean breakthrough of 0.38 % ± 0.07 % (2σ) for all traps

sampled and the fact that only 10 of all the approximate 1 200 traps analyzed exceeded the breakthrough limit.

If the breakthrough criterion is violated, it is usually the result of collecting an insufficient amount of Hg on the first section of the sorbent trap during the monitoring run. As shown in Figure 4b, almost all exceedances occurred when the section one Hg mass loadings were 40 ng or less. In these cases, no more than 2 ng of Hg can be found in section two in order for the breakthrough to be considered acceptable. At this level, low Hg blank levels per trap section and low analytical limits of detection (LOD) of the trap analysis become critical. Sorbent Hg blank levels of less than 0.69 ng per trap section and LODs of 0.49 ng (3σ) have been reported by the industry [10].

Spike Recovery

Sample recovery efficiencies and sample matrix interference are determined by measuring the Hg mass loading of the third section after the monitoring period and comparing it to its pre-spiked amount. The box plot of spike recoveries per MET-80 system and year in Figure 5 reveals that almost all of the recovery non-conformances occurred in 2008. These traps were all part of the same batch of sorbent traps with spike levels of 1 600 ng. In addition, high (but acceptable) spike recoveries for MET-80 systems 1 and 2 during 2009 are all linked to traps that were used exclusively during relative accuracy (RA) testing during that year, and consequently were spiked at relatively low levels (50 ng). Since then, spiking approaches and procedures have improved, allowing reliable spike delivery of Hg levels from 5 ng up to 200 000 ng [11]. As a result, the mean spike recovery for all traps is 98.8 % ± 0.5 % (2σ).

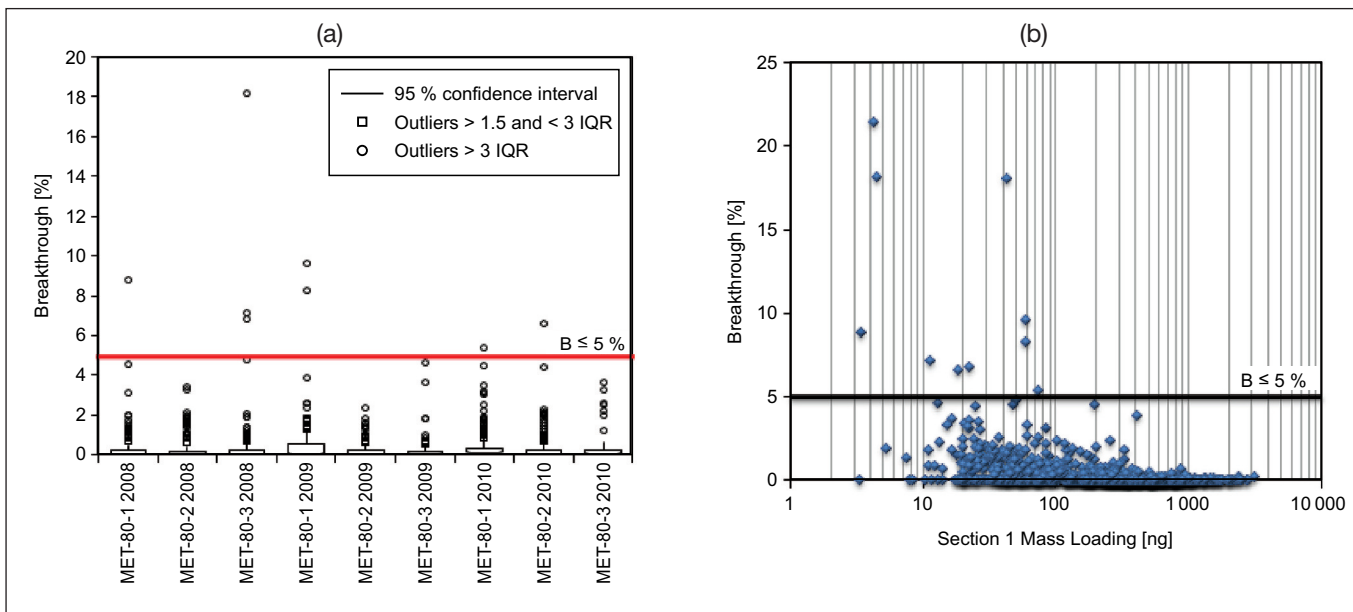


Figure 4: Sorbent trap breakthrough (B) presented as (a) a box-and-whiskers plot for each MET-80 system per year, and (b) a log plot over the section 1 mass loading for each trap. The horizontal lines show the applicable QA/QC limit on breakthrough. IQR interquartile range

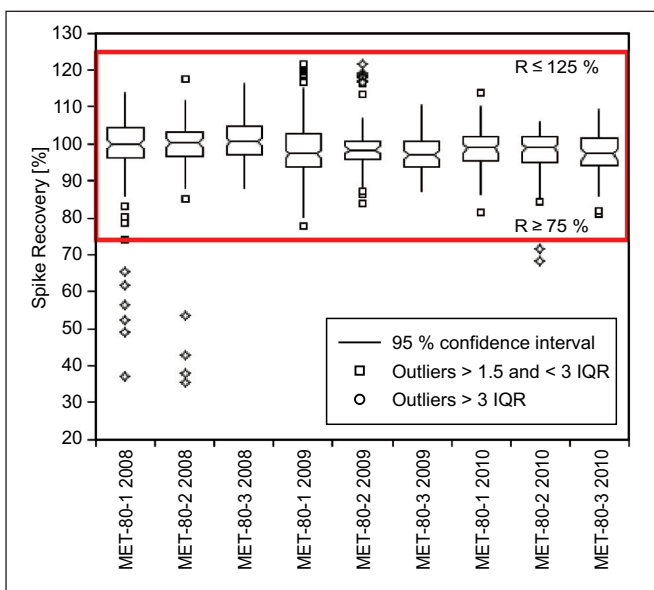


Figure 5: Box-and-whiskers plot for spike recoveries (R) per MET-80 system and year. The horizontal lines show the applicable QA/QC limit on spike recoveries.

Paired Trap Agreement

The paired trap agreement is expressed as relative deviation defined in Eq. (4). From an operational standpoint, paired trap agreement is the most useful QA/QC param-

eter for assessing the ongoing performance of a sorbent trap monitoring system. As a measure of method precision, it serves as an indicator for any sorbent inconsistencies, sampling process upsets, monitoring equipment malfunctions or analytical procedure complications. Figure 6a illustrates the RD results for each sorbent trap pair used with the installed MET-80s. With a mean RD of 4.9 % ± 0.9 % (2σ) and median of 2.2 %, almost all trap pairs passed the corresponding RD criterion of either 10 % for Hg concentrations larger than 1.0 μg · m⁻³ or 20 % for Hg concentrations less than 1.0 μg · m⁻³. In addition, Figure 6b shows that an acceptable RD can be maintained at Hg concentrations as low as 0.02 μg · m⁻³. As sorbent trap monitoring systems do not provide immediate feedback on their monitoring performance, the paired trap agreement serves as an indicator for overall system performance. It was found that scheduling preventive maintenance when RD values exceed 5 % prevents sudden data loss and in turn increases system data availability.

External Audit Results

The accuracy of a sorbent trap monitoring system is evaluated annually by auditing it against a standard reference method during a RATA. The reference method of choice for low-level Hg measurement is sorbent-based US EPA Method 30B, sharing the identical analytical procedure

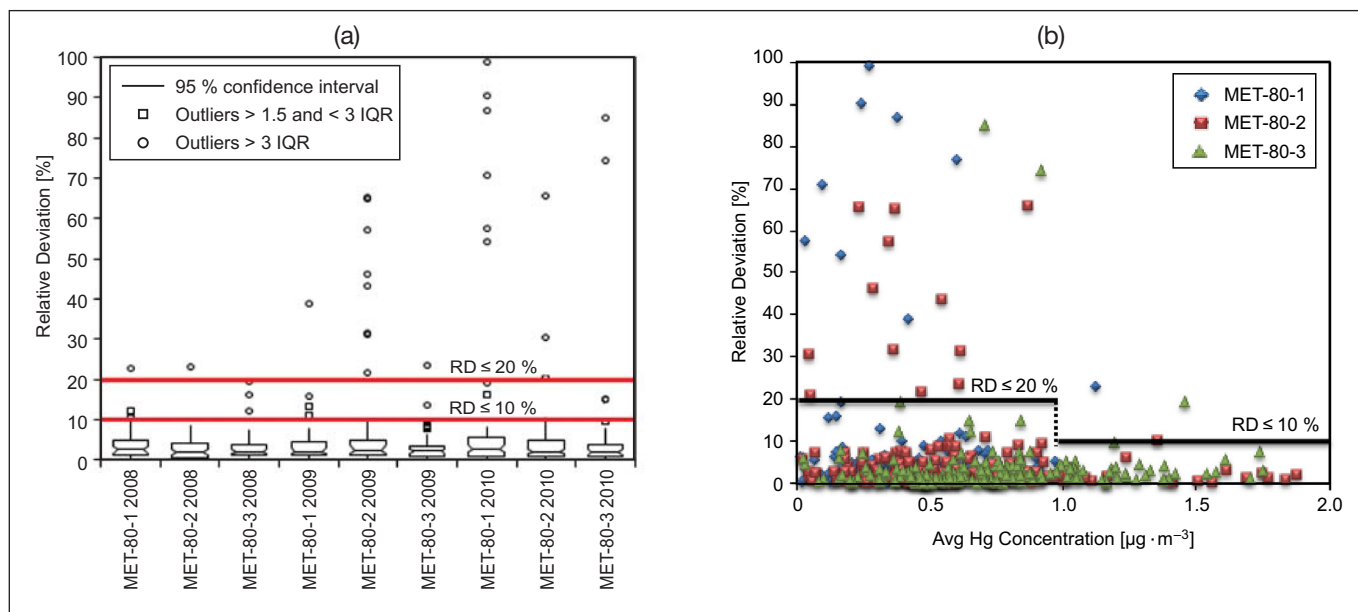


Figure 6:

Relative deviation (RD) results presented as

(a) a box-and-whiskers plot per MET-80 system and year, and (b) plotted over the Hg concentrations averaged over the paired traps. The horizontal lines show the applicable QA/QC limit for the relative deviation.

and similar methodology with the sorbent-trap monitoring approach. All RATA results per MET-80 system and year are presented in Table 3. Each MET-80 system has passed every annual RATA either on the 20 % RA or alternate $1.0 \mu\text{g} \cdot \text{m}^{-3}$ absolute mean difference criterion. Typically, the differences between the mean RM and MET-80 results are negligible down to individual RATA run concentrations as low as $0.27 \mu\text{g} \cdot \text{m}^{-3}$.

Monitor Data Availability

High monitor data availability is the basis for any meaningful emissions monitoring program. As a result, many environmental regulations give strong incentives to maintain high monitor data availability by requiring data substitution for missing data periods. Data substitution procedures are usually designed to provide conservatively high substitute data values ensuring that emissions are not underestimated. In addition, they typically take into account both

Year	Unit	# of Runs	Average RM [$\mu\text{g} \cdot \text{m}^{-3}$]	Average MET-80 [$\mu\text{g} \cdot \text{m}^{-3}$]	Difference [$\mu\text{g} \cdot \text{m}^{-3}$]	RA [% of RM]
2008	MET-80-1	11	0.363	0.365	-0.002	10.8
	MET-80-2	9	0.443	0.446	-0.003	4.9
	MET-80-3	9	0.677	0.677	0.000	3.4
2009	MET-80-1	9	0.411	0.518	-0.107	37.9*
	MET-80-2	9	0.646	0.692	-0.046	13.2
	MET-80-3	9	0.513	0.515	-0.003	2.1
2010	MET-80-1	9	0.436	0.474	-0.038	10.9
	MET-80-2	9	1.216	1.331	-0.115	12.6
	MET-80-3	9	0.887	0.918	-0.031	5.2

Table 3:

Annual relative accuracy test audit (RATA) results for each MET-80 system and year.

* Inconsistencies in reference method (RM) results yielded higher relative accuracy (RA). Annual RATA passes on the alternate $1.0 \mu\text{g} \cdot \text{m}^{-3}$ absolute mean difference criterion for low concentration sources.

the monitor data availability and the length of the missing data period, where substitute data values become increasingly conservative to ensure that emissions are not underreported.

In its simplest form, the monitor data availability can be defined as the ratio of the number of hours with quality-assured data to the number of unit operating hours in a specified look-back period. Figure 7 shows the data availability on a 12-month rolling basis (8 760 unit operating hours). It turns out that, after an initial learning curve, power plant environmental staff were able to maintain monitor data availability above 90 %.

Data availabilities in excess of 90 % are typical for a sorbent trap monitoring system. The key is the existence of a proper QA/QC plan addressing all aspects of system operation and maintenance, the proper handling of system alarms, the use of quality sorbent traps with precise spike levels, and a quality laboratory performing the trap analysis. However, the single most important factor is the use of data and status indicators generated by the monitoring system to schedule preventive maintenance, thus avoiding excessive periods of missing data.

CONCLUSION

Although originally intended as a back-up to Hg CEMS or stop-gap until all concerns about continuous emissions monitoring for Hg would have been addressed, sorbent-based monitoring systems are becoming the preferred choice for continuously monitoring Hg emissions at coal-fired power plants. This is partially due to the inherent ability of sorbent traps to measure very low concentrations coupled with anticipation of increasingly stringent mercury standards imposed by future regulations.

Dominion's Salem Harbor Power Station has operated three CleanAir MET-80 monitoring systems since 2007. Salem Harbor has used these systems to monitor for compliance with the Massachusetts mercury requirements since January 1, 2008. They have measured Hg concentrations as low as $0.02 \mu\text{g} \cdot \text{m}^{-3}$, while maintaining all required QA/QC parameters within acceptable levels. Salem Harbor's three sorbent trap monitoring systems have sampled over 1 200 sorbent traps. Evaluation of the applicable QA/QC criteria such as breakthrough, spike recovery and paired trap agreement shows that this monitoring approach is extremely sensitive and robust down to very low Hg concentrations. The accuracy of the monitoring systems has been verified via annual external audits. The results indicate that this monitoring approach is able to maintain its accuracy consistently, as all three MET-80 systems have passed every relative accuracy test to date.

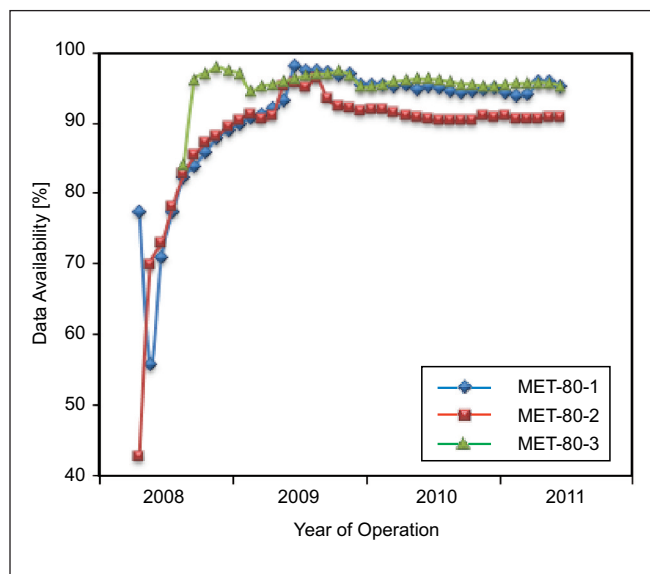


Figure 7: Monitor data availability of all three MET-80 systems. Data availability is reported on a 12-month rolling basis.

Combining these results with reported data availabilities for the three sorbent trap monitoring systems of 90 % and higher makes this monitoring approach a strong choice as a primary compliance monitor.

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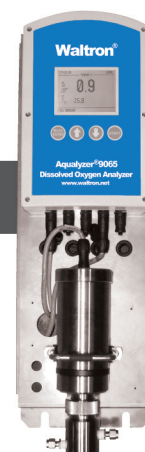
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