Mercury Monitoring at Coal-Fired Power and Cement Producing Plants in the U.S.

The majority of coal-fired power and cement producing plants in the U.S. have to demonstrate compliance with regulations set forth in the Mercury and Air Toxics Standards and the National Emission Standards for Hazardous Air Pollutants from the Portland Cement Manufacturing Industry beginning in 2015. In the aggregate, these rules aim to significantly reduce mercury emissions from affected facilities over the upcoming years. This article provides a brief overview of the respective regulations and introduces sorbent trap mercury monitoring (STMM), which has the ability to accurately and reliably measure a wide range of mercury concentrations including the very low levels resulting from these regulations.

"Measurement reliability is another area in which sorbent trap systems typically excel over other mercury monitoring approaches. Reliability can be assessed with "data availability", which is a measure of the number of hours in an operating period that the monitoring system provided reliable, quality-assured data."

Introduction

Mercury emissions from industrial sources have received continued attention from regulators in the U.S. over the past decade. As a result, on February 12, 2013, the U.S. Environmental Protection Agency (US EPA) promulgated the final amendments to the National Emissions Standard for Hazardous Air Pollutants from Portland Cement Manufacturing Industry, also known as the PC MACT [1], requiring cement plants in the US to continuously monitor for mercury emissions starting September 9, 2015. In addition, on March 28, 2013, the US EPA submitted for publication the final amendments of the Mercury and Air Toxics Standards (MATS), establishing national emissions limitations and work practice standards for mercury and certain other hazardous air pollutants (HAP) emitted from coal-fired and oil-fired electric utility generating units (EGU) [2] with a compliance date of April 16, 2015. Although many units were able to secure a limited extension to the compliance with the rule, the majority of electric utilities has been continuously monitoring for mercury emissions since the initial compliance date.

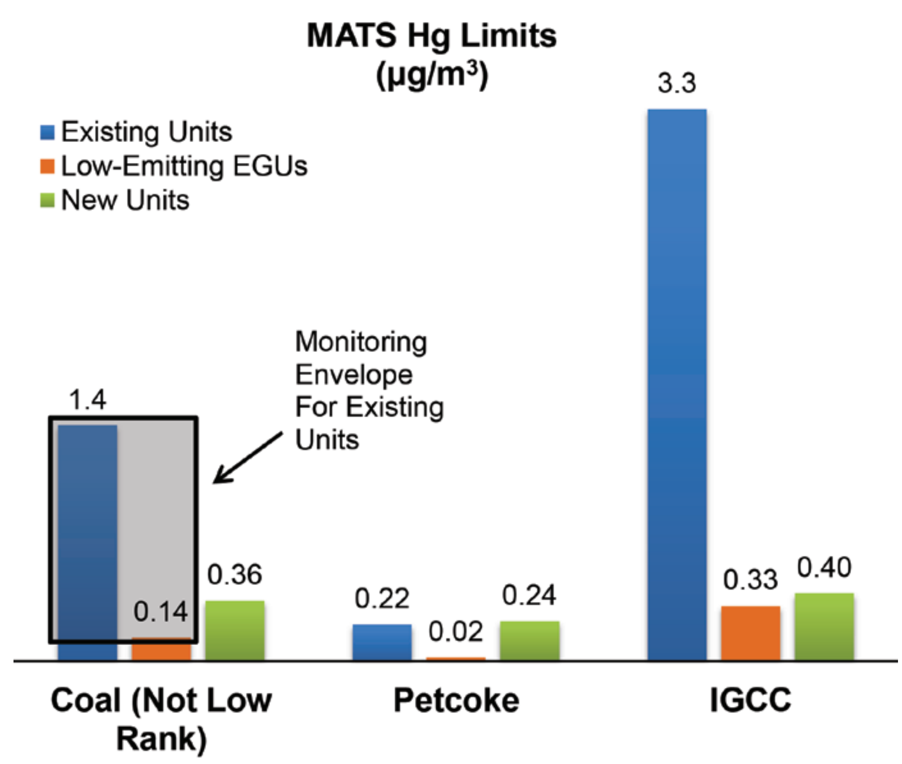

Figure 1. MATS mercury limits for various fuel types, illustrating monitoring envelope for existing coal-fired electric utilities in the U.S.

The mercury emission standards in the PC MACT apply to all new and existing cement kilns and are based on the production rates of clinker, the manufactured product from the kiln. They correspond to equivalent average flue gas concentrations of approximately 5 µg/m³ for new kilns and 12 µg/m³ for existing kilns. These limits apply to normal operation and are assessed on a 30-operating-day rolling average. Approximately 100 cement kilns are affected by the PC MACT.

The EGU MATS impacts over 500 fossil-fired utility boilers in the U.S. The mercury emission limits for these units are based on the date on which a facility is constructed or substantially modified and the type of fuel burned to produce electricity. These limits are applicable based on four source categories: coal-fired units designed to burn coal with a gross calorific value (GCV) ≥ 8,300 Btu/lb, coal-fired units designed to burn low-rank virgin coal (GCV < 8,300 Btu/lb), Integrated Gasification Combined Cycle (IGCC) units and solid oil-derived fuel (i.e., petroleum coke)-fired units.

Certain units can comply with the rule by qualifying as "Low-Emitting EGUs" (LEEs). For mercury, a LEE is an existing unit that emits at less than 10% of the applicable emissions limit, or has the potential to emit no more than 29.0 lb of mercury per year. This option may not be used for new units or existing units with configurations that allow them to bypass their wet flue gas desulphurisation scrubbers. Units that do not qualify as a LEE must continuously monitor mercury (excluding oil-fired units) and report their emissions on a 30-operating-day rolling average. Figure 1 illustrates the MATS limits for three fuel source categories. The limits are converted to the approximate equivalent unit of µg/m³ for easier comparison to readings normally obtained from mercury monitoring systems. Comparison of the LEE limits

James Wright & Dr Volker Schmid, Clean Air Engineering
Email: jwright@cleanair.com
Email: vschmid@cleanair.com

with the existing non-LEE limits provides an operating envelope for monitoring systems at existing units. For example, existing units firing coal with a GCV ≥ 8,300 Btu are anticipated to generate emissions bounded on the low end by the LEE limit of 0.14 µg/m³ and on the upper end by the existing non-LEE limit of 1.4 µg/m³.

Sorbent Trap Mercury Monitoring

Meeting the mercury monitoring requirements of these new rules has been a challenge. Continuous monitoring using on-line analyser-based technology to provide real-time mercury concentration data is available. However, U.S. utility mercury monitoring experience indicates that this approach is difficult and costly to implement as a continuous compliance reporting tool [3].

A sorbent trap mercury monitoring system (STMMS) following U.S. EPA Performance Specification 12B (PS12B) [4] is an alternative to the continuous analyser approach and has gained wide-spread recognition as the preferred method for continuous compliance reporting. A STMMS provides an average mercury concentration that is integrated over a period of time that could be hours, days, or even weeks. Flue gas is sampled through a pair of traps filled with a sorbent that captures mercury. The rate at which the sample passes through the sorbent is varied in proportion to the flue gas flow rate in the stack to provide so-called proportional sampling. After a period of time (up to 14 days), the sorbent traps are removed and replaced. The retrieved sorbent traps are analysed for total mercury using spectroscopic analytical techniques, and the mass of mercury trapped divided by the volume of gas sampled is then used to determine the average mercury concentration over the sample period. Since the sorbent continuously captures mercury 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. Mercury concentrations as low as 0.001 µg/m³ are not uncommon for one week sampling runs.

Sorbent traps intended for continuous compliance reporting of mercury emissions are required to consist of three equal sections of a sorbent that is able to selectively capture total gaseous mercury. A schematic of a sorbent trap sampling probe is shown in Figure 2. The first two sections of sorbent are used to collect total gaseous mercury and ensure that there is no breakthrough. PS12B requires that no more than 5% of the total collected sample be present in the second section for average flue gas mercury concentrations that are in excess of 0.5 µg/m³, or 10% for concentrations below that threshold. In addition, PS12B calls for duplicate samples to be taken and the results for these traps need to agree within ± 10% relative deviation (RD) for average mercury concentrations of more than 1.0 µg/m³, or 20% for lower concentrations. Alternatively, results are also acceptable if the absolute difference between concentrations from paired traps is less than or equal to 0.03 µg/m³. The third sorbent section is spiked and contains a known quantity of elemental mercury ranging from 50% to 150% of the anticipated mercury mass loading captured in the first section during a sampling run. Laboratory recoveries of the spike amount must range between 75 to 125%. Recoveries outside this range will lead to an invalidated trap pair.

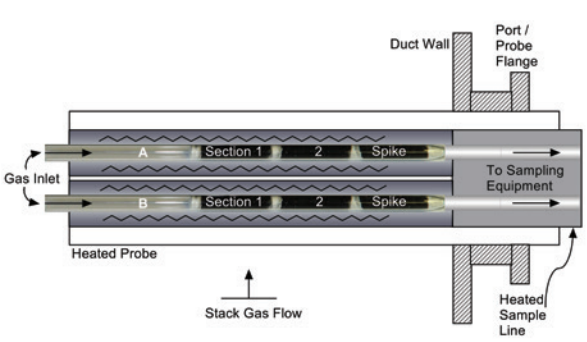

Figure 2. Principles of sorbent trap monitoring.

The accuracy of sorbent trap data hinge on accurate measurement of two key quantities – the mass of mercury captured on the sorbent, and the volume of gas sampled through the traps. Traceability to NIST standards is incorporated into each of these measurements. The elemental mercury solutions used for trap spiking and the oxidized mercury solutions used for instrument calibration in the laboratory analyses are traceable to NIST references. Flow sensors used in the gas sample volumetric measurements are all compared against NIST-traceable references on a quarterly basis. This approach ensures that the accuracy of each sorbent trap measurement can be traced back to verifiable NIST standards.

Typical Sorbent Trap Monitoring Results

The following figures illustrate the actual implementation of some of the quality assurance and control (QA/QC) criteria for day-to-day sorbent trap monitoring system at concentrations prevalent under MATS as described earlier. The data displayed are from actual installations of sorbent trap monitoring systems used for site-specific compliance reporting prior to implementation of the MATS requirements. Figure 3 shows spike recoveries from more than 500 sorbent traps collected over a three-year period at a power station burning a bituminous coal from South America with a mercury content in the range of 0.02 - 0.12 ppm, a chlorine content of 20 - 170 ppm and a sulphur content of 0.5 - 0.6%. More than 97% of all the traps sampled during this period met the applicable spike recovery criteria, which are also indicated in Figure 3. The average concentration of mercury emissions during this time was less than 1 µg/m3.

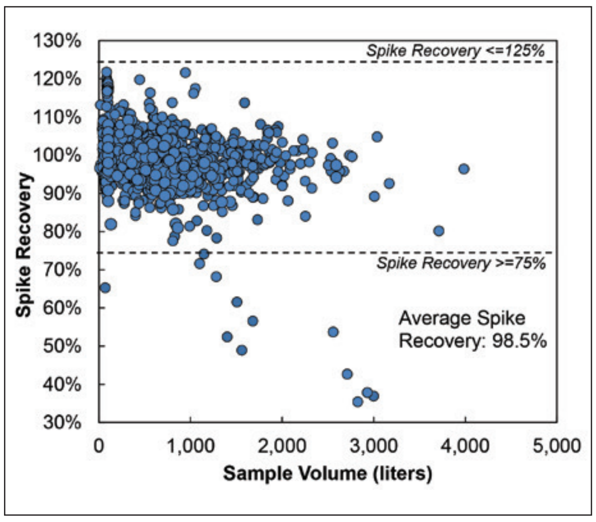

Figure 3. Spike recovery results over a three year monitoring period.

A good indicator of precision of each STMMS measurement is the agreement between the paired trap results, often expressed as relative deviation (RD). Figure 4 shows the precision of sorbent trap monitoring data over a period of over five months. Individual results of each of the two traps (A and B) of a STMMS used for weekly measurements at a utility firing Powder River Basin coal are displayed. During this period, the mercury concentrations measured ranged from 0.10 to 0.35 µg/m³. The chart shows the excellent precision of each measurement, with the RD between traps averaging 2.4%.

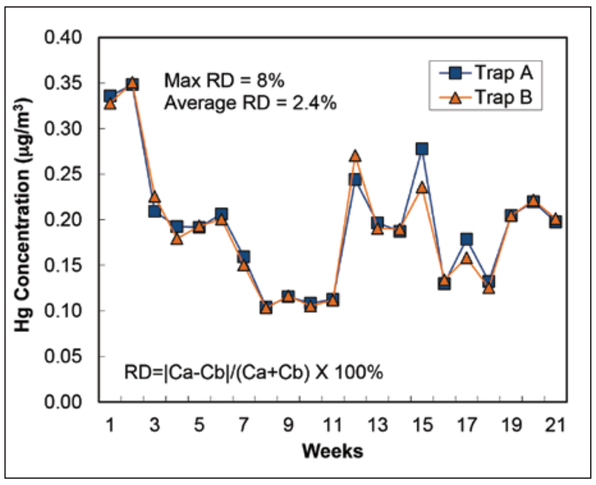

Figure 4. STMMS paired trap agreement expressed as Percent Relative Deviation (RD) for 21 trap pairs sampled at a Powder River Basin coal-fired facility. Ca and Cb refer to the mercury concentrations measured by trap A and B, respectively.

Measurement reliability is another area in which sorbent trap systems typically excel over other mercury monitoring approaches. Reliability can be assessed with "data availability", which is a measure of the number of hours in an operating period that the monitoring system provided reliable, quality-assured data. Data availability is generally expressed as a percentage of the operating hours. Figure 5 shows data from a STMMS operated continuously over a three-year period. During this time, the plant conducted 189 trap exchanges. Only one pair of traps failed the criteria for a valid data set in PS12B and resulted in missing data. Four trap runs resulted in only one of the two traps meeting the validation criteria. In those cases, the data is reported using a single trap adjustment factor, or STAF. Overall, the data availability for this unit was 96% over the three-year monitoring period.

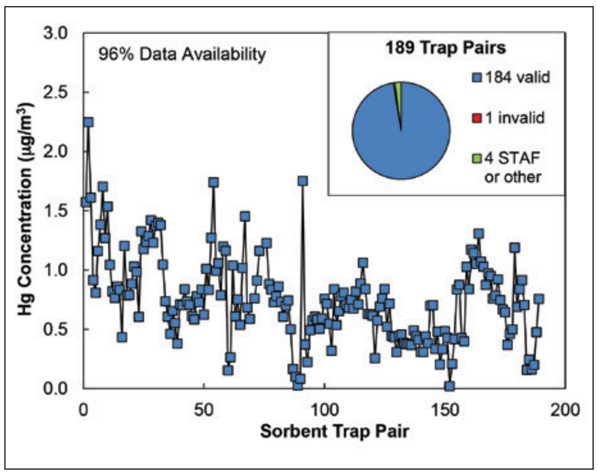

Figure 5. Reliability data for a CleanAir MET-80 Sorbent Trap Monitoring System, showing data availability and mercury concentration for 189 trap exchanges over a period of three years. Each data point represents results for a sample period of 30 minutes up to several days.

Conclusions

The cement and electric utility industries have come under increased pressure to control and reduce their mercury emissions. As a result, regulations have been implemented in the U.S. that significantly limit the amount of mercury that is emitted into the atmosphere by both industries. An integral part of these regulations is the ability to accurately and precisely measure mercury emissions to ensure compliance with the existing regulations. This is complicated by the low mercury levels resulting from new emission controls that were installed as a response to the promulgated regulation. Although within the analytical range of a continuous mercury analyser, this technology falls short when including the measurement uncertainties introduced by the sample extraction, conditioning, and transport system. The resulting sensitivities are not sufficient to accurately quantify mercury at the prevalent low mercury levels. In addition, there are still ongoing concerns about the ability to quality-assure the resulting real-time data in a NIST traceable manner at these low levels.

Sorbent trap-based mercury monitoring systems, on the other hand, have proven their ruggedness and reliability for compliance monitoring at numerous installations at coal-fired power plants and cement kilns. Their inherent ability to accurately measure very low levels of mercury, combined with the fact that the generated results are NIST traceable, have made the sorbent trap-based monitoring approach the preferred monitoring approach.

References

[1]National Emission Standards for Hazardous Air Pollutants for the Portland Cement Manufacturing Industry and Standards of Performance for Portland Cement Plants; Final Rule, 2013. U.S. Environmental Protection Agency, Federal Register 78FR10005 (https://federalregister.gov/a/2012-31633).

[2]Reconsideration of Certain New Source Issues: National Emission Standards for Hazardous Air Pollutants from Coal- and Oil-fired Electric Utility Steam Generating Units and Standards of Performance for Fossil-Fuel-Fired Electric Utility, Industrial-Commercial-Institutional, and Small Industrial-Commercial-Institutional Steam Generating Units; Final Rule – Notice of final action on reconsideration, 2013. (http://epa.gov/airquality/powerplanttoxics/pdfs/20130328notice.pdf).

[3]Technologies for Control and Measurement of Mercury from Coal-Fired Power Plants in the United States: A 2010 Status Report, 2010. Northeast States for Coordinated Air Use Management (NESCAUM) (http://www.nescaum.org/documents/hg-control-and-measurement-techs-at-us-pps_201007.pdf).

[4]Performance Specification 12B – Specifications and Test Procedures for Monitoring Total Vapor Phase Mercury Emissions From Stationary Sources Using a Sorbent Trap Monitoring System, U.S. Environmental Protection Agency, (http://www3.epa.gov/ttn/emc/prompspec12B.html), accessed October 2015.

About the Authors

James Wright (B.S., Chemical Engineering, Virginia Tech, Blacksburg, VA, U.S.A.) is currently CleanAir's Chief Operations Officer. He has been with the company for over 20 years and managed the development of CleanAir's MET80 sorbent trap monitoring system.

Volker Schmid (Ph.D., Environmental Sciences: Physics, Portland State University, Portland, OR, U.S.A.) is the technical leader of CleanAir's Advanced Monitoring Group. He has been with CleanAir since 2002 and was responsible for the development of CleanAir's mercury monitoring services.