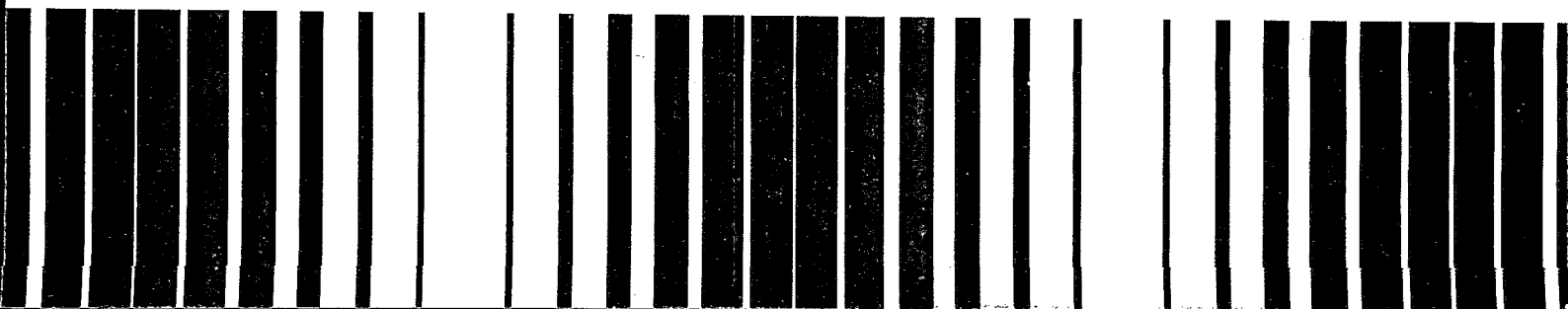
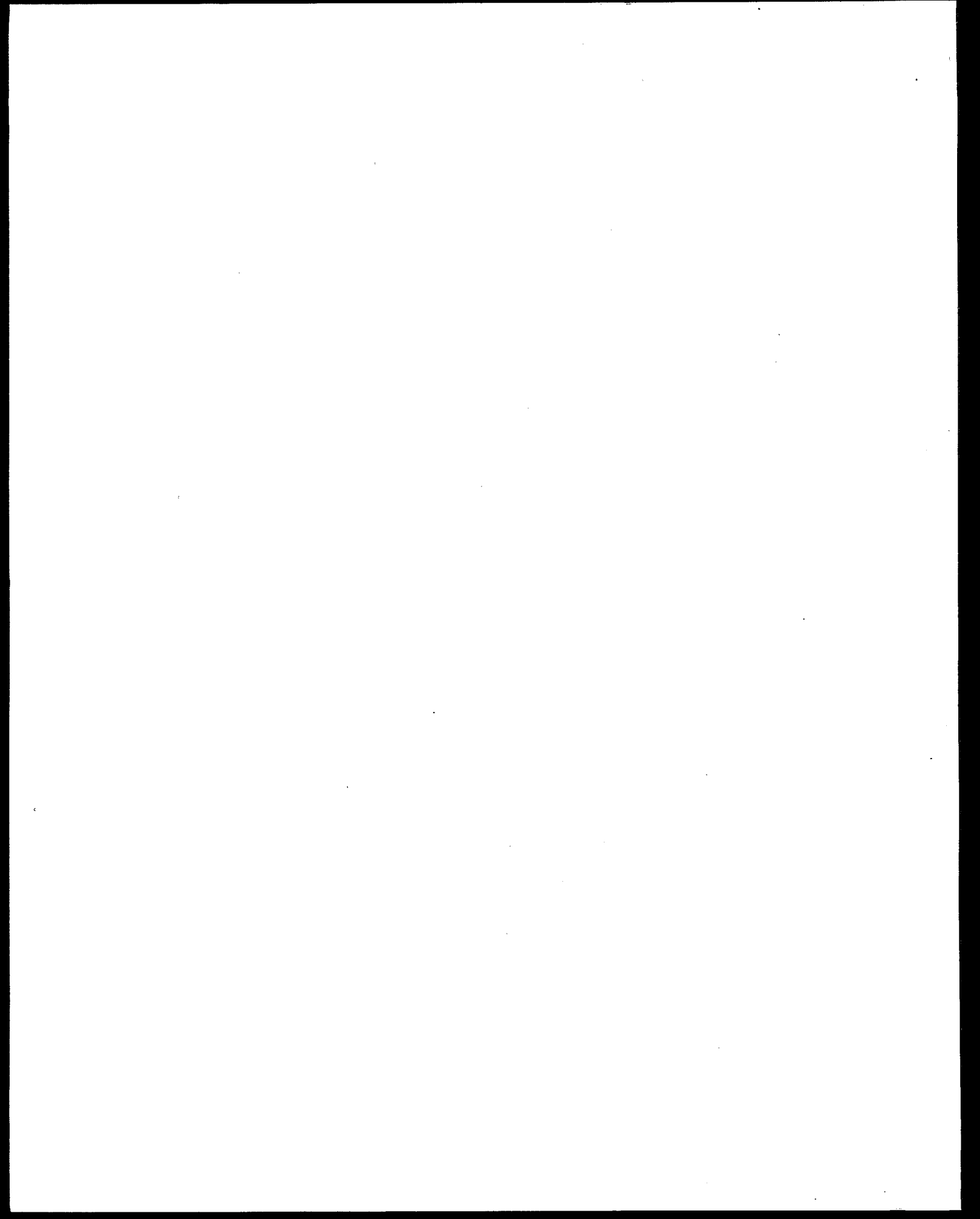




Workshop on Source Emission and Ambient Air Monitoring of Mercury

**September 13-14, 1999
Bloomington, MN**





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June 2000

**Workshop on Source Emission and
Ambient Air Monitoring of Mercury**
September 13 - 14, 1999
Bloomington, MN

National Risk Management Research Laboratory
National Exposure Research Laboratory
Office of Research and Development
US Environmental Protection Agency
Cincinnati, OH 45268



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List of Acronyms

AES	atomic emission spectrometry	DMA/CNC	Digital Machine Automation/Computer Numerical Control
AF	atomic fluorescence spectrometry	DO	dissolved oxygen
ALARA	as low as reasonably achievable	DOAS	differential optical absorption spectroscopy
AMS	alkaline mercury speciation	DOD	Department of Defense
AMS	Advanced Monitoring System	DOE	Department of Energy
ANPRM	Advance Notice on Proposed Rulemaking	EERC	Energy and Environmental Research Center
APCD	air pollution control devices	EMC	Emissions Monitoring Center
APPCD	Air Pollution Prevention and Control Division	EMEP	European Monitoring and Evaluation Program
ASTM	American Society of Testing Materials	EMR	Enhanced Monitoring Rule
ATO FMS	Aerosol Time-of-Flight Mass Spectrometry	EPA	Environmental Protection Agency
A&WMA	Air and Waste Management Association	EPRI	Electric Power Research Institute
BACT	Best Available Control Technology	ESP	electrostatic precipitator
BAT	Best Available Technology	ETV	Environmental Technology Verification
BIF	Boiler and Industrial Furnace	EU	European Union
°C	degrees centigrade	°F	degrees Fahrenheit
CAA	Clean Air Act	FETC	Federal Energy Technology Center
CAM	compliance assurance monitoring	FGD	flue gas desulfurization
CCC	chemical coordination center	GC/MS	gas chromatography/mass spectrometry
CEC	Commission for Environmental Cooperation	HAP	hazardous air pollutant
CEM	continuous emission monitor	HEPA	high efficiency particulate adsorption
CISWI	Commercial and Industrial Solid Waste Incinerator	HWC	hazardous waste combustor
CLRTAP	Convention on Long-range Transboundary Air Pollution	IC	ion capture
CVAA	cold vapor atomic absorption spectrometry	ICAP	inductively coupled argon plasma
CVAAS	cold vapor atomic absorption spectrometry	ICP	inductively coupled plasma
CVAFS	cold vapor atomic fluorescence spectrometry	ICR	Information Collection Request
CWA	Clean Water Act	INEEL	Idaho National Engineering and Environmental Laboratory
DEP	Department of Environmental Protection	ISO-IC	Isokinetic Iodated Carbon Method
DDT	dichlorodiphenyltrichloroethane	IVL	Swedish Environmental Research Institute

List of Acronyms (continued)

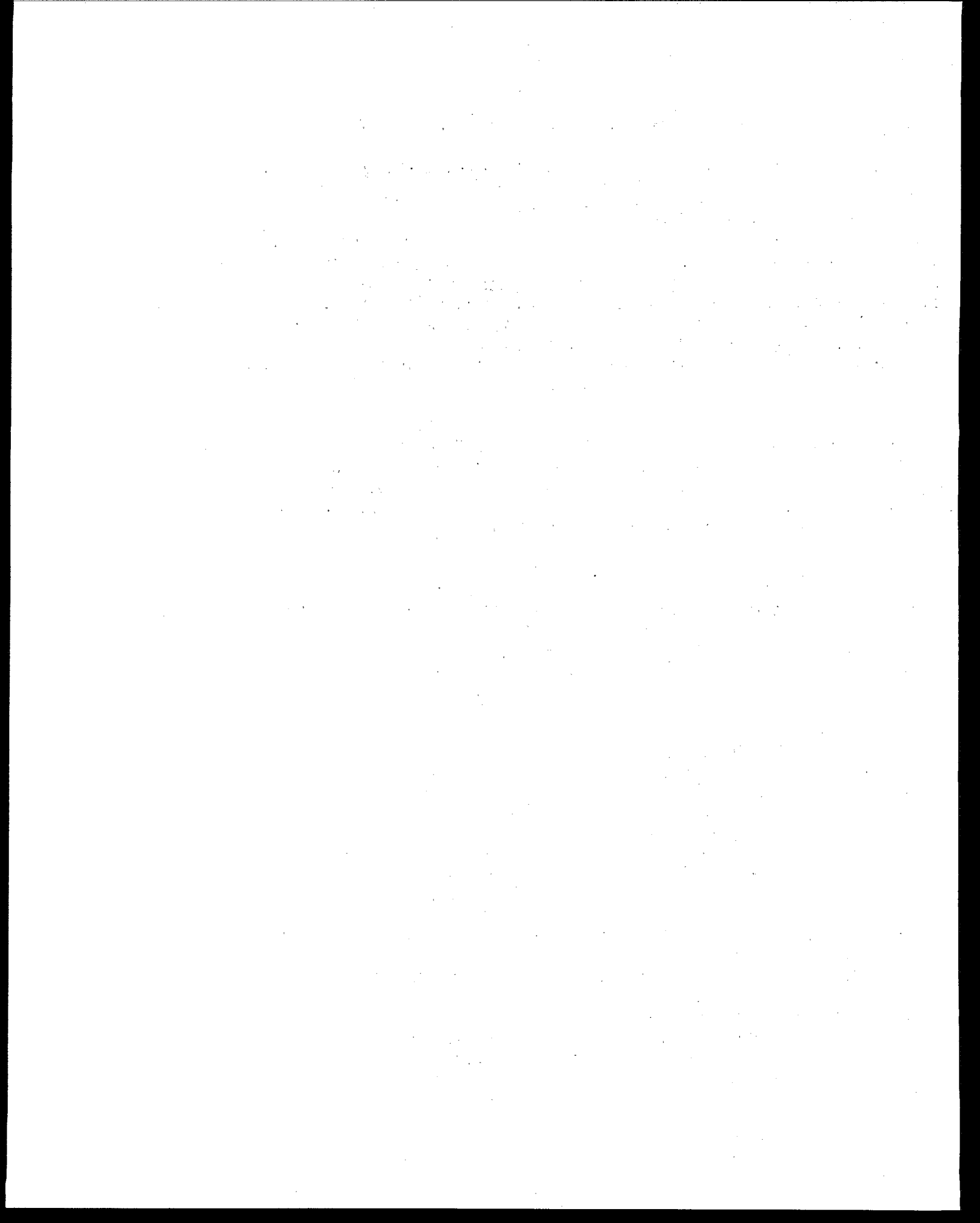
MAMCS	Mediterranean Atmospheric Mercury Cycle System		toxic substances
MDL	method detection limit	PCA	principal component analysis
MDN	Mercury Deposition Network	PCB	polychlorinated biphenyl
MM	multiple metals	PEM	particulate emission monitor
MOE	Mercury Over Europe	pg/m ³	picograms per cubic meter
MESA	mercury speciation adsorption	PM 10	particulate matter 10
MSC	meteorological synthesizing center	POP	persistent organic pollutant
MWC	municipal waste combustor	ppb	parts per billion
MWFA	Mixed Waste Focus Area	ppbv	parts per billion by volume
NAAEC	North American Agreement on Environmental Cooperation	ppbw	parts per billion by weight
NADP	National Atmospheric Deposition Program	ppm	parts per million
NAFTA	North America Free Trade Agreement	ppt	parts per trillion
NARAP	North American Regional Action Plan	PRB	Powder River Basin
NERL	National Exposure Research Laboratory	PS	performance specification
NESHAP	National Emission Standards for Hazardous Air Pollutants	QA/QC	quality assurance/quality control
NETL	National Energy Technology Laboratory	R _o	reproducibility
NIST	National Institute of Standards and Technology	RATA	Relative Accuracy Test Audit
NO _x	nitrogen oxides	RCRA	Resource Conservation and Recovery Act
NO/NO ₂	nitrogen oxide/nitrogen dioxide	RELMAP	Regional Langrangian Model of Air Pollution
NOAA	National Oceanic and Atmospheric Administration	REMSAD	Regulatory Modeling System for Aerosols and Deposition
NPRM	Notice on Proposed Rulemaking	RGM	reactive gaseous mercury
NRMRL	National Risk Management Research Laboratory	RSD	relative standard deviation
NSPS	New Source Performance Standard	RTP	Research Triangle Park
OAQPS	Office of Air Quality, Planning, and Standards	SBIR	Small Business Innovation Research
OPL	operating permit limit	scfm	standard cubic feet per minute
ORD	Office of Research and Development	SD	standard deviation
OSW	Office of Solid Waste	SEP	Supplemental Enforcement Project
PBTS	persistent bioaccumulative	SMOC	Sound Management of Chemical Initiative
		SoFAMMS	South Florida Atmospheric Monitoring Study
		SO _x	sulfur oxides
		SPDC	static plume dilution chamber
		STAR	Science to Achieve Results (an EPA research grant and fellowship program)
		STTR	Small Business Technology Transfer Program

List of Acronyms (continued)

SVOC	semi-volatile organic compound	UV	ultraviolet
TCLP	Toxicity Characteristic Leachate Procedure	UVDOAS	ultraviolet differential optical spectroscopy
TGM	total gaseous mercury	VOC	volatile organic compound
TMDL	total maximum daily load	XRF	X-ray fluorescence
TSCA	Toxic Substances Control Act	%	percent
$\mu\text{g}/\text{dscm}$	micrograms per dry standard cubic meter		
$\mu\text{g}/\text{m}^3$	micrograms per cubic meter		
$\mu\text{g}/\text{m}^2/\text{yr}$	micrograms per square meter per year		
TEAM	Total Exposure Assessment Model		
UN-ECE	United Nations Economic Commission for Europe		
UTS	universal treatment standard		

Acknowledgments

This Summary Report for the September 13-14, 1999 Workshop on Source Emission and Ambient Air Monitoring of Mercury was prepared by the Workshop Steering Committee consisting of Scott Hedges [U.S. Environmental Protection Agency (EPA), National Risk Management Research Laboratory (NRMRL)], Jeffrey Ryan (EPA, NRMRL) and Robert Stevens [Florida Department of Environmental Protection (DEP), formerly of EPA, National Exposure Research Laboratory (NERL)]. Gratitude is expressed to Science Applications International Corporation for their efforts in coordinating the workshop and for their assistance in preparing and assembling the report. Paper copies of the workshop presentation overheads and slides can be obtained from Mr. Scott Hedges (US EPA, NRMRL) at 202-564-3318.



Section 1

Introduction

1.1 Workshop Structure, Purpose, and Intended Audience

A workshop on Source Emission and Ambient Air Monitoring of Mercury was held on September 13 - 14, 1999, in Bloomington, Minnesota. The workshop was sponsored by the U.S. Environmental Protection Agency's (EPA's) Office of Research and Development (ORD). The EPA workshop was conducted in collaboration with the Air and Waste Management Association (A&WMA) International Specialty Conference on Mercury in the Environment, also held in Bloomington, Minnesota immediately following completion of the EPA workshop. Mercury monitoring issues were addressed at both meetings, and as such, many of the presenters at the EPA workshop also gave presentations at the A&WMA Specialty Conference.

The purpose of the workshop was to discuss the state-of-the-science in source and ambient air mercury monitoring as well as mercury monitoring research and development needs and the roles of EPA, the Department of Energy (DOE), other Federal and State agencies, and industry in addressing these needs. The workshop was open to the public and included both traditional presentations as well as interactive discussions addressing key research questions and needs.

In addition to a state-of-the-science review, the workshop focused on the following key issues:

- What are the needs for manual and continuous source and ambient mercury measurements?
- What steps are needed to demonstrate total mercury continuous emission monitor (CEM) performance so that their use for compliance assurance may be considered?
- What incentives are needed to develop reliable, accurate and cost effective CEMs and how can candidate facilities be encouraged to use them?
- Are there needs for speciated mercury CEMs for control technology research, process control monitoring, and to support site-specific risk assessments?
- Is there a need to conduct source emission and ambient monitoring research to investigate source/receptor relationships, atmospheric fate and transport considerations, and short-term plume transformations?

To facilitate discussions of these issues, the workshop included review presentations of the state-of-the-science in source emission and ambient air mercury monitoring technologies and associated performance criteria, on-going monitoring programs, and the status of EPA regulatory requirements. The workshop also included source and ambient mercury monitoring panel discussions to address the items listed above.

Presenters were from EPA, DOE, State agencies, industry, academia, monitoring equipment manufacturers, and consulting firms. The presentations were followed by two panel discussions: the first panel discussion addressed source monitoring and testing issues, and the second panel discussion addressed ambient monitoring issues.

This Workshop Summary Report provides a summary of: 1) the state-of-the-science in source emission and ambient air mercury monitoring; 2) key issues, findings, and results from the workshop, including the needs for developing total and speciated mercury CEMs; 3) policy and technical considerations and challenges associated with implementing mercury CEMs, 4) monitoring

data needed to support the development of source/receptor relationships, modeling, and risk assessment, and 5) recommendations by the EPA Workshop Steering Committee for future mercury monitoring research, performance evaluations and testing. In addition to the Summary Report, Appendix A provides the agenda and synopses of the individual presentations and panel discussions from the workshop, and Appendix B provides the list of workshop participants and contact information.

The intended audience for this summary report includes: the management and staff of EPA ORD and EPA Regions and Program Offices [particularly, the Office of Solid Waste (OSW) and the Office of Air Quality Planning and Standards (OAQPS)], the DOE and other Federal agencies, State and regional air regulators and scientists, the national and international mercury research community, developers of mercury monitoring instrumentation, and industry (i.e., representatives from the waste incineration and coal-fired electric utility industries).

The Summary Report was written by the Workshop Steering Committee consisting of Mr. Scott Hedges [US EPA, National Risk Management Research Laboratory (NRMRL)], Mr. Jeffrey Ryan (US EPA, NRMRL) and Mr. Robert Stevens [Florida Department of Environmental Protection (DEP), formerly of US EPA, National Exposure Research Laboratory (NERL)]. To prepare the report, the Steering Committee reviewed each of the presentation and panel discussion summaries from the workshop (summarized in Appendix A) and summarized the state-of-the-science in source emission and ambient air monitoring of mercury. The Committee then assessed and summarized the challenges and recommended steps they concluded are necessary (to be taken by EPA and others) to expedite the development, performance evaluation and implementation of mercury CEMs for compliance assurance, for process control, and for control technology research. In turn, the Committee also recommended source emission and ambient monitoring research which they concluded is necessary to further understand the ultimate fate and transport of mercury. The challenges, summaries, and recommendations presented in this Summary Report are based on the presentations and panel discussions from the workshop and the scientific expertise and judgement of the Steering Committee. They do not necessarily represent the opinions of the management of EPA ORD or the Program Offices.

1.2 Background

Mercury contamination, both nationally and internationally, has long been recognized as a growing problem for both humans and ecosystems. Mercury is released to the environment from a variety of human (anthropogenic) sources including plant effluent discharge, fossil-fuel combustors, incinerators, chlor-alkali plants, mining, and landfills. Other sources of anthropogenic mercury release include industrial processes and the disposal of products containing mercury. Since mercury does not degrade to simpler compounds, once it is released to the environment, it will always be present in one form or another.

Anthropogenic sources of mercury emissions to the atmosphere include fossil fuel combustion (containing trace amounts of mercury), municipal incineration, medical waste incineration, chlor-alkali plants, and landfills. These emission sources represent a significant contribution to the total mercury released (including natural and re-emitted) in the United States. The 1997 Mercury Study Report to Congress indicated that the deposition of atmospheric mercury has increased by a factor of two to five over pre-industrial levels [Mercury Study Report to Congress, Vols 1 - V111, EPA, 1997 (EPA Document No.: EPA-452/R-97-003 through 010, URL Address:

<http://epa.gov/oar/mercury.html>]. Additionally, most atmospherically-deposited mercury is in the form of gaseous or particulate-phase inorganic mercury. Unfortunately, the inorganic mercury released into the environment can be converted, by naturally-occurring biological processes, into the highly toxic methyl mercury species.

Understanding the relationship between source emissions and ambient air concentrations is a necessary step to understanding the fate and transport of mercury. Ambient monitoring is a key component in understanding these relationships and in the development and validation of mercury source/receptor models, and atmospheric fate and transport models. The ambient forms of stack-emitted mercury measured by ambient measurement methodologies are elemental mercury, reactive gas-phase mercury (primarily in the form of mercuric chloride) and particle bound mercury. (Methyl mercury can also be measured in the atmosphere but this is thought to be due to the mercury cycle and not to stack emissions directly.) These three forms of mercury have distinctly different chemical and physical properties which result in different atmospheric fates. For example, elemental mercury has a half-life of 6 months to a year due to its low reactivity and insolubility in water and is known to be globally transported before being converted and subsequently deposited on soil or water. Mercuric chloride has a half-life of hours due to its high sticking coefficient and high water solubility, and can be expected to deposit locally (i.e., within a 30-mile radius of a source) as well as regionally. Particle-bound mercury can also be deposited locally and regionally.

When Congress mandated mercury emission studies in 1990 [Clean Air Act (CAA) Amendments], researchers and regulators did not realize that mercury speciation plays such a significant role in the fate and transport of mercury. As a result, it is important to study source/receptor relationships in part through source emission/ambient air monitoring and wet/dry deposition monitoring of speciated mercury compounds, and through source/receptor modeling (developed and validated from these monitoring data) in order to further understand the origin (source), form (species), and quantity of mercury entering water bodies that can potentially become available for methylation and bioaccumulation in fish.

1.3 Need for Source Emission and Ambient Air Monitoring of Mercury

Improved source emission and ambient air monitoring data are needed to assure compliance with regulations promulgated to reduce the impact of mercury contamination in the environment, to assess and reduce mercury emissions and associated risks, and to further the understanding of the fate and transport of atmospheric mercury. Improved source emission and ambient air monitoring data, including speciated mercury data, are also needed to develop, validate and employ the air dispersion/deposition models used to assess mercury fate, transport and risk. (There are other reasons EPA is interested in these data, e.g., long-term trends, but these additional reasons are beyond the scope of consideration of this workshop.)

Currently, there is a need for continuous mercury emissions data to support alternative methods of compliance with hazardous waste combustor (HWC) regulations. The use of total mercury CEMs represents a promising approach to meeting this data need. There may also be a need in the future to use total mercury CEMs for coal-fired electric utility compliance (pending the outcome of a decision this year on whether to regulate mercury emissions from coal-fired electric utility boilers). Finally, there is also an increasing need for speciating mercury CEMs: to assist in the design, development, and evaluation of mercury combustion control technologies; and as a process control monitor for coal-fired electric utility boilers.

EPA's mercury stack emission limits for municipal solid waste, medical waste, and HWCs are based on the measurement of total (combined vapor and particle phase) mercury. EPA's recently released Phase I Maximum Achievable Control Technology (MACT) rule for HWCs sets total mercury stack emission limits for cement kilns, incinerators, and lightweight aggregate kilns that burn hazardous waste. These combustors will need to measure mercury concentrations in their feedstreams, preferably on a more continuous basis than infrequent manual method techniques. In addition, new rules will be forthcoming which address mercury emissions from non-hazardous waste cement kilns, hazardous waste boilers, and commercial and industrial solid waste incinerators. Each of these combustor rules have been or will be promulgated by OSW or OAQPS. They are designed to encourage the use of total mercury CEMs by providing permit incentives. For these waste combustion regulations, total mercury CEMs are or likely will be identified as options for compliance assurance.

EPA will be making a decision on or before December 15, 2000 on whether to regulate electric utility boilers for hazardous air pollutants, including mercury. To inform this decision, as well as to better understand the forms of mercury present and to evaluate existing control strategies, OAQPS sent a request for mercury emissions data (referred to as an Information Collection Request or ICR) to the utility industry for a variety of boiler configurations and types of coal. These mercury emissions data are due to EPA by June 1, 2000. If the decision is to regulate, the use of total mercury CEMs likely will be encouraged as a possible regulatory compliance tool.

Accurate ambient air and source emission monitoring data (including the use of CEMs) are also needed to support the development of air dispersion, deposition and Total Maximum Daily Load (TMDL) models for atmospheric mercury deposited onto water bodies. A TMDL is a calculation of the maximum amount of a pollutant that a water body can receive and still meet water quality standards, and an allocation of that amount to the pollutant's sources.

TMDLs are required by section 303(d) of the Clean Water Act (CWA). This section requires States to identify waters not meeting water quality standards and to establish TMDLs. (EPA is required to do this if States do not.) Initially, as States and EPA concentrated on major point source chemical discharges, TMDLs were usually referred to as wasteload allocations and served as the basis for effluent limits for point source permits. As the water program grew and the permitting program was implemented, it became apparent that water quality problems still remained. The remaining water quality problems resulted from the cumulative effects of a number of pollutants and the effects from pollutants from nonpoint sources.

The water quality based approach, of which TMDLs are a key element, relies upon analysis of receiving water quality and the contributions of the pollutant causing the impairment from all sources. The TMDL is the mechanism by which each pollutant source is given an "allocation" of the amount of pollutant it can discharge and water quality standards to be attained. It is important to note that the largest problems causing impairments are clean sediment, nutrients and fecal coliform. Most of these pollutants are from nonpoint source discharges and the TMDL provides a mechanism to develop control plans that allow for technical and economic tradeoffs.

Mercury TMDLs will be developed from risk assessments and from the forthcoming water quality criteria for mercury due out in 2000. An accurate understanding of the amount of atmospheric mercury deposited onto water bodies (due to wet and dry deposition) will be crucial to the development of appropriate TMDLs for mercury.

Section 2

Source Emission Monitoring

As indicated, mercury source emission monitoring data are needed to assure regulatory compliance, to better characterize source emissions, to evaluate the performance of mercury control technologies, and to further the understanding of the fate and transport of mercury. The following is a discussion of the state-of-the-science in source emission monitoring technologies as well as a discussion of the research needs and challenges associated with developing and implementing these technologies.

2.1 State-of-the-Science in Manual Methods for Measuring Total and Speciated Mercury Stack Emissions

EPA currently employs four manual methods for measuring mercury emissions: Methods 29/0060, 101, 101A, and 102 for measuring total mercury (gaseous and particulate emissions) and the Ontario Hydro Method (draft) for measuring speciated mercury. Method 101A was specifically developed for National Emission Standards for Hazardous Air Pollutants (NESHAP) in 1991 to measure mercury at sewage sludge incinerators. Method 29/0060 was developed to measure multiple metals including mercury.

The Ontario Hydro Method was developed outside EPA specifically to perform speciated mercury measurements from coal-fired sources and is currently being used to provide emissions data to the ICR project. Once this method is approved by the American Society of Testing Materials (ASTM), EPA can incorporate it by reference as an approved manual method for measuring speciated mercury.

The above mentioned manual methods are based on the same principle, the Method 5 sampling train. An extractive sample is withdrawn from the stack isokinetically and the gaseous and particulate mercury emissions are captured using a filter and series of impingers. The only major differences are the solutions used in the impingers to capture gaseous mercury. The collected samples are acid digested and then analyzed specifically for mercury using cold vapor atomic absorption (CVAA) or atomic fluorescence spectrometry (AES).

2.2 State-of-the-Science in CEMs

There have been significant strides over the last few years to develop reliable and commercially viable mercury CEMs. Use of CEMs provide the following advantages:

- Real-time emission data
- Direct pollutant measurements
- Potentially less reliance on waste feed characterization (i.e., for incinerators)
- Operational data for system optimization
- Improved process control
- Greater public assurance

In addition, facilities may also realize a significant cost benefit from reduced feed characterization costs (for waste incineration applications), improved throughputs, and avoided upgrade costs as a

result of voluntarily implementing CEMs.

Mercury CEMs are similar to most combustion process CEMs in that the emission sample typically must be extracted from the stack and then transferred to the analyzer for detection. However, mercury monitoring is complicated by the fact that mercury exists in different forms (particulate, oxidized, elemental) and that quantitative transport of all these forms is difficult. In fact, because the particulate form is difficult to transfer and is also often a measurement interferant, the particulate is typically filtered out and remains unmeasured. Similarly, there are known complications with the quantitative transfer of mercuric chloride as well.

Typically, CEMs can only directly measure (detect) elemental mercury. CEMs measure total mercury through the use of a conversion system that reduces the non-elemental mercury (oxidized form that is primarily mercuric chloride) to elemental mercury for detection. Although the particulate mercury can also be reduced to the gaseous elemental form, particulate sample delivery issues make this impractical. As a result, for most commercially available CEMs, the total mercury measured is in fact total gaseous mercury (TGM). The conversion of the nonelemental mercury is commonly accomplished using a liquid reducing agent (e.g., stannous chloride). In addition to the more established wet chemistry conversion methods, dry chemistry or thermal cracking conversion methods are also being developed.

In general, mercury CEMs can be distinguished by their mercury measurement detection systems. Detection systems include: cold vapor atomic absorption spectrometry (CVAAS); cold vapor atomic fluorescence spectrometry (CVAFS); in-situ ultraviolet differential optical absorption spectroscopy (UVDOAS); AES; and laser induced fluorescence spectrometry (LIFS) for multiple metals.

The majority of mercury CEM systems employ CVAAS or CVAFS as the detection technique. These systems are only able to measure elemental mercury and rely on the conversion of oxidized forms to measure TGM. In addition, these detection techniques are susceptible to measurement interferences resulting from the presence of common combustion process emissions. Gases such as sulfur dioxide, hydrogen chloride, hydrogen fluoride, and nitrogen oxides (present in the flue gas of coal-fired utility boilers) can act as spectral interferants as well as degrade the performance of concentrating devices (e.g., gold amalgams). As such, conditioning systems need to be developed that remove these interfering gases prior to sample delivery to the detector.

An alternative to the elemental mercury measurement approach is AES. With this technique, the mercury is ionized by a high energy source (e.g., plasma) and the emission energy detected. The advantage to this technique is that all forms of mercury, including particulate-bound mercury, are capable of being ionized and detected. However, the sample delivery issues still remain. Unless the particulate fraction can be delivered, this type of system will also be limited to TGM.

Total mercury CEMs appear to be more mature than has been widely perceived in the past. The units are becoming simpler to operate and maintain. The techniques employed to reduce oxidized species to the detectable, elemental form are less reliant on wet chemical approaches. In addition, techniques for managing potential interferants are also more advanced.

Currently, while there are no commercially available CEMs that directly measure the various speciated forms of mercury, many total gaseous mercury CEMs can be used to indirectly measure speciated mercury (the elemental and oxidized forms) by determining the difference between

elemental mercury and total gaseous mercury. This difference is recognized as the oxidized form. Separate mercury measurements are made before and after the conversion step in order to calculate the oxidized form. This indirect speciation method is referred to as "speciation by difference." Although the true identity of the oxidized form is not known, mercuric chloride is currently considered the major oxidized form of interest. However, recent research indicates that other nonchlorinated, oxidized forms may also exist.

The development of direct speciating mercury CEMs will help expedite and enhance mercury control technology research and process control evaluations for coal-fired electric utility boilers. Speciating CEMs will also help improve the accuracy of site-specific risk assessments required under EPA's HWC Combustion Strategy. It is assumed that most speciating CEMs will be based on mass-spectrometry methods or laser-based techniques (e.g., photo-dissociation and fluorescence). Development of these CEMs will be a challenge, since at first they will likely be complex and expensive.

2.3 Challenges to Implementing CEMs

At this time, EPA regulations require only periodic total mercury emissions measurements (using the manual methods) for regulatory compliance. In order for total mercury CEMs to be considered for regulatory compliance assurance, acceptable performance will need to be demonstrated. It is this lack of demonstrated performance that caused OSW to use total mercury CEMs for compliance assurance only as an option in the Phase I MACT rule for HWCs. EPA is not likely to require facilities to install mercury CEMs unless sufficient performance data are available to justify the promulgation of a CEM-based standard. Without a mandatory requirement for mercury CEMs, CEM manufacturers and regulated facilities are reluctant to invest in their further development. In addition, few opportunities to demonstrate CEM performance exist, and those demonstrations that have been conducted have not been sufficiently robust to fully support mandatory use of mercury CEMs in EPA regulations. As a result, the developmental progress of mercury CEMs has been slower than originally anticipated. Further challenges still remain.

One is that few total mercury CEMs truly measure total mercury emissions. This is because most systems do not measure particulate-bound mercury. The particulate fraction is often filtered out and remains unmeasured. As a result, the total mercury measurement is in fact total gas-phase mercury, and this could potentially impart a negative bias to the total mercury measurement. This bias could be further amplified as certain types of particulate may actually capture gas-phase mercury. It should be noted that the procedure for evaluating mercury CEM performance compares the total mercury CEM measurement to that of the manual method which truly measures total mercury (i.e., both particulate-bound and gas phase). Any potential particulate mercury measurement bias may be able to be identified by examining the particulate measurement of the manual method. This may not be a significant issue for sources where particulate-bound mercury is not present in appreciable quantities, but may be significant for high particulate-emitting sources (e.g., sources with minimal particulate control). Therefore, the ability to measure the particulate component is important and should not be ignored.

2.4 CEM Performance Evaluation

Draft Performance Specification 12 (PS 12) entitled "*Specifications and Test Procedures for Total Mercury Continuous Monitoring Systems in Stationary Sources*" is the specification to be used for

evaluating the performance of total mercury CEMs at the time of or soon after CEM installation. In accordance with PS 12, total mercury CEMs that are evaluated need to be capable of measuring the total mercury concentration (regardless of speciation) of both vapor and solid phase mercury. PS 12 provides specifications for locating and for installing CEMs and for evaluating performance, as well as provides procedures to be used during testing and data reduction. The specification outlines reference method tests to determine relative accuracy, as well as tests for calibration error, calibration and zero drift, and interference checks.

Many of the techniques contained in PS 12 are useful tools for evaluating mercury CEM performance. However, in its current form, the appropriateness of PS 12 is questioned. Certain aspects presented in PS 12, such as gaseous standards for elemental mercury and oxidized mercury, cannot be implemented since the tools are not currently available. Also, the acceptance criteria presented may not be appropriate for every application, and therefore, performance still needs to be determined on an individual (case-by-case) basis following the data quality objectives outlined in PS 12. EPA recognizes that PS 12 can be improved upon, and that PS 12 may be updated in the future. However, these improvements would need to be demonstrated prior to incorporation into a revised PS 12. Mercury CEM performance evaluation/data collection demonstrations would be a means to examine viable modifications and improvements to this performance specification.

It is important for future mercury CEM demonstration testing to be open to alternative and improved methods for evaluating measurement performance. For example, the European TUV performance certification programs may provide alternative approaches that can be considered when performing mercury CEM performance demonstration testing. It may be possible that lessons-learned, evaluation techniques and/or direct advice from the TUV certification program can be used to assist EPA mercury CEM performance evaluation testing. In addition, EPA's Environmental Technology Verification (ETV) Program should also be considered as a resource to evaluate/verify CEM performance.

As part of the performance evaluation and data collection (demonstration) process, it is suggested that combustion sources be selected where the probability of measurement success is high. Initially, this can be accomplished by selecting sources where the measurement environment is less severe (e.g., facilities with low particulate matter/acid gas/interferences), prior to demonstration on a more severe source (e.g., cement kiln, coal-fired utility). In addition, for emission environments of a more severe nature, a high probability for field measurement demonstration success can be achieved by performing more cost-effective, pilot-scale evaluations under controlled conditions where individual measurement issues can be examined in detail prior to undertaking costly field evaluations. ORD's NRMRL - Air Pollution Prevention and Control Division (APPCD) combustion research facility has successfully been used in such a manner to conduct pilot-scale investigations of both multiple metal and mercury CEMs. Similarly, pilot-scale research performed at the University of North Dakota's Energy and Environmental Research Center (EERC) has focused on mercury CEM measurement issues specific to coal combustion emissions. Finally, for use in MACT regulations, facilities with MACT control technologies already installed should be given preference as demonstration sites for mercury CEMs if at all possible. This will provide optimal support for the regulatory use of mercury CEMs in MACT regulations.

2.5 Mercury CEM Implementation

The implementation of mercury CEMs as an alternative means of compliance assurance under the EPA HWC MACT regulations will likely require an incremental or phased approach. Among other things, progress will depend on the cooperation of regulators (regional and State), the facility, and vendors to demonstrate mercury CEM performance. Progress toward CEM implementation can be made only if these cooperative arrangements are mutually beneficial. OSW is interested in defining what incentives (regulatory or otherwise) and steps need to be taken to encourage facilities to install CEMs. However its focus is not directed at undertaking research, but protecting the public and meeting the demand for real-time monitoring.

Although the HWC MACT regulations provide for an option to use mercury CEMs for compliance assurance, facilities may be dubious about the benefits (including enhanced process control) that would result. Also, it is not currently known if mercury CEMs are in fact appropriate for compliance with mercury standards that were based on manual method data, at least without some type of translation of those data into parallel continuous emission data or data ranges. This is due, in part, to the absence of sufficient information on the full range of emissions that may be encountered and measured on a continuous basis by a mercury CEM.

It is also unknown whether a single measurement-range analyzer will be able to cover the range in emissions necessary. Alternatively, dual-range mercury CEMs may be necessary - one for routine emissions and one to account for spikes. In addition, even if CEMs were used for compliance assurance, the requirement to characterize and limit the mercury in waste feed is likely to continue. If so, this may undercut one incentive for a facility interested in using mercury CEMs - the reduction of mercury waste feed testing requirements. However, if CEMs are installed and their reliability demonstrated, approaches should be considered to reduce waste feed testing requirements. Using CEMs may also allow compliance emphasis to be shifted to stack emission limits, thus enhancing public assurance.

Flexibility in the interpretation of the performance specification procedures is also needed to further the implementation of mercury CEMs. However, there needs to be a balance between this flexibility and the need of EPA regional permit writers and regulators for standardized and validated measurement methodologies to support regulatory compliance. Implementation of mercury CEM measurement procedures will require technical support (from ORD and the Program Offices) to the permit writers and regulators to assist in the interpretation and review of test plans and performance evaluation approaches. Although ORD does provide limited technical support in this area, it is expected that the level of support will need to be increased to meet the needs of the permit writers and regulators.

The immediate need is to evaluate the current levels of mercury CEM performance at various sources and not necessarily place performance in a pass/fail category. These performance data can then be used to determine the suitability of CEMs for regulatory application. Use of mercury CEMs for compliance assurance monitoring could then be based on the monitoring objectives or requirements of the regulated source.

Unfortunately, few opportunities exist for demonstrating mercury CEM performance. EPA is currently not funding field performance demonstrations. The past OSW performance demonstration test was limited in its usable results, primarily due to the complexity of the source tested. Additional EPA

performance demonstrations have not been considered due to the expense. Although EPA is not currently funding field performance demonstrations, the ETV Program, in collaboration with NRMRL, is planning a pilot-scale mercury CEM evaluation program that may ultimately include field demonstrations. This pilot-scale program will evaluate promising monitoring technologies that could, in the future, be used for a variety of applications, including compliance assurance.

The DOE Mixed Waste Focus Area (MWFA) has also sponsored a limited number of mercury CEM performance evaluations. While these tests have been relatively successful, they are still limited in scope and application. Clearly, furthering the development and performance demonstration of mercury CEMs will require a coordinated and cooperative effort of EPA researchers and regulators, DOE and other Federal agencies, regional, State and local regulators, industry, and mercury CEM vendors/developers. This cooperative effort must be mutually beneficial, requiring that incentives be provided to a facility to encourage participation and cooperation. Assuming a HWC owner/operator is willing to install a mercury CEM, incentives and benefits that could be explored include:

- Obtaining continuous data to improve a facility's own understanding of process variability within its system
- Potential tool for the facility itself to evaluate alternative compliance options
- Increased averaging times to reduce inappropriate influence of emission spikes
- Potentially less stringent waste feed characterization and testing program
- Potential for regulatory implementation extension if needed to install the CEMs and have them reach a state of operability
- Less performance stack testing and enforcement quality testing of operating permit limits (OPLs)
- Less monitoring of OPLs for compliance assurance
- Improved public assurance
- Potential proactive response to anticipated State regulations
- Improved ability to characterize legacy waste.

Many of these types of incentives and benefits may also have application to electric utility boilers should a decision be made to regulate hazardous air pollutants from these sources.

2.6 Speciating CEMs for Control Technology/Process Control Evaluations

Because waste combustor regulations (e.g., HWC combustor MACT) limit total mercury emissions, the use of total mercury CEMs is a logical option for compliance assurance. In contrast, the need for speciating mercury CEMs from a regulatory perspective is uncertain. However, there is a need for a speciating mercury CEM both as a mercury control technology research and evaluation tool and

possibly as a process control monitor.

A need currently exists for speciating CEMs to support control technology field demonstration research for coal-fired utility boilers. Speciated CEMs are needed to determine the species of mercury emitted from the wide variety of coals burned in utility boilers, and subsequently to evaluate and select appropriate technologies to reduce the species of mercury emitted. To support the regulatory determination process for coal-fired utility boilers, EPA ORD, in cooperation with DOE, will be supporting a series of field studies to evaluate and demonstrate potential mercury control technologies.

These control technology demonstrations will require comprehensive speciated mercury measurements as a function of process variation and control technique employed. Most importantly, this will offer an opportunity to optimize these candidate technologies. To do so will require timely speciated measurements. The use of manual speciation methods such as the Ontario Hydro Method (which measures elemental, oxidized, and particle-bound mercury from coal-fired utility boilers) is not practical due to the time and cost of sampling and analysis, even if the analysis is done onsite. A speciating mercury CEM is the most viable option for providing these time sensitive data.

A speciating mercury CEM may also be useful as a process control monitor. The approach to control mercury emissions is based on the mercury form present, and because fuel types and characteristics can vary substantially, the mercury species will also vary. Aspeciating monitor would be an effective tool to utilize the most effective mercury control technique(s) and ensure the cost-effectiveness of the technique(s).

Based on the current understanding that the oxidized species of primary interest is mercuric chloride and that mercuric chloride is the dominant form of oxidized mercury present, the "speciation by difference" technique is an acceptable approach to obtaining speciated mercury measurements. The "total" measurement actually represents the total gaseous component and typically does not include the particulate matter fraction. This approach is dependent on the reliability of the elemental and total gaseous mercury measurements. Unlike total mercury CEMs, direct speciating mercury CEMs are not commercially available. Much of the advances in "speciation by difference" mercury CEMs have come about largely due to individual research needs and not because of a regulatory driver. As a result, the state-of-the-science for speciating mercury CEMs is clearly not as advanced as that for total mercury CEMs. However, research conducted by the University of North Dakota EERC has clearly demonstrated the viability of this technique. Because of the relatively small demand for a fully-speciating research instrument, there has been limited commercial interest in its development. However, should mercury emission regulations be promulgated for the utility industry, it appears that a commercial market for a speciating mercury CEM as a process control tool may well develop.

2.7 Workshop Steering Committee Recommendations for Demonstrating the Viability of Mercury CEMs

Clearly, many obstacles must be overcome in order to fully demonstrate the viability of mercury CEMs for regulatory compliance, control technology research and for process control. Although EPA is not currently funding field performance evaluations, the ETV Program (as previously indicated) may ultimately provide a mechanism for these types of field demonstrations.

EPA also provides funding through the Small Business Innovation Research (SBIR) Program to

develop and demonstrate new and innovative technologies such as CEMs, and through the "Science To Achieve Results" (STAR) programs to enable the academic community to sponsor monitoring research. In addition, DOE's Small Business Technology Transfer Program (STTR) provides funding to develop mercury CEMs as well as techniques to resolve specific mercury measurement issues. Similarly, various State agencies have furthered the development of CEMs through their own funding initiatives. These initiatives typically focus on the research and development of promising, less mature technologies rather than the commercially available technologies currently considered for emissions monitoring application. As a result, technologies developed under these initiatives require more time (usually several years) to reach the level of maturity needed for demonstration in the field. However, each of these programs and initiatives is needed to develop and evaluate the wide variety of technologies required to further the CEM implementation process.

Also, the Steering Committee concluded that in order to demonstrate the viability of CEMs for potential use as a compliance assurance tool:

- EPA should take the initiative in seeking and developing cooperative relationships between the regulator/permittee and the facility in an effort to encourage voluntary CEM use. The Agency should also encourage any interested stakeholders to participate in this cooperative effort.
- Facilities should reach out to their communities and get them involved in the compliance assurance process. CEM data can then be used to communicate a facility's ability to comply with mercury limits.
- A clear message needs to be sent to mercury CEM vendors/developers as to what application and performance will be expected from total mercury CEMs. Specifically, what measurement ranges are needed (HWC versus coal utility), desired performance requirements, system on-line duration, and equipment durability.
- Research should be performed at the pilot-scale to investigate and resolve known or suspected mercury CEM measurement performance issues. This approach provides a controlled environment to conduct parametric investigations of diverse measurement environments [HWC, municipal waste combustor (MWC), cement kiln, coal-fired utilities] prior to conducting more costly field performance evaluations. Most importantly, this approach will reduce the time needed to conduct a field demonstration and will greatly improve the probability for a successful demonstration once in the field.
- The role of EPA's ETV Program and the testing of total mercury CEMs should be defined with respect to specific EPA Program Office, State or regional needs. Any potential testing should be in direct consultation with these groups. The benefits to the CEM vendor of participating in the ETV Program should also be clearly identified.
- Funding should be identified to support field performance demonstration efforts. Additional EPA and DOE funding and possibly funding by other sources [e.g., Department of Defense (DOD), State agencies] is necessary to support these demonstration programs. Collaborative efforts that leverage resources should also be considered.
- Research is needed to investigate the development and application of mercury gas

standards. Such calibration standards are called for in PS 12 and would be valuable as part of CEM operation (i.e., calibrations, calibration drift checks).

The following recommendations are also provided for the development of speciated mercury CEMs for control technology evaluations and process control applications:

- Research indicates that certain types of fly ash exhibit catalytic properties that can oxidize elemental mercury under certain conditions, including those associated with heated particulate filters. This conversion can lead to an overestimation of the oxidized form of mercury, which in turn can erroneously impact the interpretation of mercury control data. Research is needed to minimize or eliminate this bias.
- Currently, control technology research, primarily for coal-fired utility boilers, represents the current market for speciating mercury CEMs. Until such time as a demand for a speciating mercury CEM as a process control monitor exists, the advancement of this technology will be driven by EPA and DOE's control technology research needs. To expand opportunities for process control application, speciating CEM vendors/developers should seek collaboration with DOE and EPA. Applying for control technology research grants under the EPA SBIR and DOE STTR programs is one avenue to foster this collaboration.

Section 3 Ambient Air Monitoring

As previously discussed, in addition to source emission monitoring, there is also a need for accurate and comprehensive ambient air monitoring data for mercury (including deposition monitoring). These data are needed to support the development and validation of air dispersion and deposition models, the development of TMDLs, and in turn to further the understanding of mercury fate and transport. The following is a discussion of the state-of-the-science in ambient air monitoring technologies as well as a discussion of the ambient monitoring research needs relative to the fate and transport of mercury.

3.1 State-of-the-Science in Methods To Measure Mercury in Ambient Air

Manual sampling of ambient mercury can be used in routine projects (to support monitoring networks), exploratory projects (for fugitive emission monitoring), special projects (for aircraft measurements and chlor-alkali facilities), and to support quality assurance/quality control efforts. EPA Method IO-5 is the standard manual method for measuring vapor and particle phase mercury in ambient air. The method for collection and analysis of elemental mercury takes advantage of the amalgamation property of mercury to pre-concentrate ambient air in a gold-coated bead trap prior to thermal desorption and detection using CVAFS. The method for collection and analysis of particulate-bound mercury consists of collecting the particulate on a pre-fired glass-fiber filter which is microwave-digested in nitric acid prior to extraction and detection using CVAFS. A complete description of EPA Method IO-5 can be found in the "EPA Compendium of Methods for the Determination of Inorganic Compounds in Ambient Air, EPA/625/R-96/01a, July 1999"

Examples of currently available manual methods for the speciation of mercury include: impregnated (ion exchange) filters; refluxing mist chambers; and annular thermal denuders. Annular thermal denuders are the most promising methodology for avoiding artifact formation.

Annular denuders provide ambient speciation of elemental, reactive, and particulate mercury without known interconversion problems. Denuders are not a new technology. Tubular denuders were previously used in Europe to speciate mercury in stacks and annular denuders have been used for decades for sulfur dioxide and ammonia determinations. However, in order to use denuders for ambient mercury speciation, two key modifications have been made to previous designs. A single annulus quartz denuder was constructed and coated with potassium chloride to efficiently capture reactive gaseous mercury or RGM (i.e.; oxidized or ionic mercury), and rather than perform a wet chemical extraction and subsequent analysis, the quartz denuders are thermally desorbed. At approximately 500 degrees Centigrade (°C), RGM is quantitatively converted to elemental mercury vapor and purged directly into a CVAFS detector. Once desorbed, the denuder is regenerated and ready for reuse.

In addition to being relatively easy to use, tests show that annular thermal denuders are capable of obtaining high collection efficiencies [over 97 percent (%) in the 5 to 2,000 nanogram per cubic meter range]. Denuders can also be used to perform high-resolution sampling at relatively low method detection limits (MDLs). Furthermore, the manual sampling configuration is relatively inexpensive, simple, and mobile.

An automated system that houses a CVAFS detection system and utilizes thermal annular denuder technology has also been introduced by Tekran, Inc. The Tekran 2537A analyzer is capable of continuously measuring both elemental mercury and oxidized or ionic mercury. In addition, recent advances in particulate mercury measurement technology have been made which utilize a quartz filter housed in a quartz chamber. The chamber is heated to convert the captured particulate mercury to elemental mercury prior to measurement in the CVAFS detector. Research is underway to incorporate this thermal quartz filter technology into the Tekran instrumentation. As a result, oxidized, elemental and particulate mercury will be able to be measured at ambient levels.

Deposition monitoring is also integral to understanding the relationships between air emission sources of mercury and the concentration of mercury in water bodies. A Mercury Deposition Network (MDN), coordinated through the National Atmospheric Deposition Program (NADP), has been designed to study and quantify long-term trends associated with atmospheric fate and deposition of mercury. MDN collects weekly samples of wet deposition (rain and snow) for analysis of total mercury and at some sites, methyl mercury. MDN sites are currently located in the Eastern United States and in Canada. A goal of the MDN program is to expand network coverage to the entire United States, as is the case for the NADP network. Expanding the network will help provide additional data needed to further understand source/receptor relationships and the ultimate fate of mercury.

3.2 Source/Receptor Relationships, Atmospheric Fate and Transport Considerations, and Short-Term Plume Transformations

Recent ambient air monitoring research has attempted to link mercury emissions from combustion processes to ambient speciated mercury measurements. A major uncertainty is the degree to which standard combustion source speciated mercury measurements (as measured in the stack) compare to ambient speciated mercury measurements. Although both source and ambient monitoring systems measure elemental, oxidized (RGM), and particulate-phase mercury species, many factors exist that likely result in measurements that are not comparable.

For example, the filter component of the source method is operated at a highly elevated temperature [250 degrees Fahrenheit (°F)]. As a result, the level of mercury condensed on particulate will differ from that condensed at ambient temperatures. Another concern with the source method is that some fly ashes for coal-fired utility boilers exhibit catalytic properties that can oxidize elemental mercury under certain conditions. This condition results in a positive bias in the RGM component of the speciated measurement. This potential disparity impedes the ability to model source/receptor, fate and transport relationships. Clearly, for atmospheric modeling purposes, source data need to be collected in a form comparable to the ambient data.

A significant disparity between source and ambient mercury measurements is that source measurements do not account for the short-term atmospheric transformations that take place in the stack gas plume. Accounting for this is needed since the conversion of mercury species is likely to occur rapidly from the stack to plume as a result of changing chemical and physical conditions. Dilution techniques have been demonstrated to simulate these transformations to the ultimate ambient forms. Source data that account for these combustion plume transformations are needed to improve the accuracy of atmospheric models.

Plume dilution systems have been designed to characterize these short-term plume transformations. One such system is the "Static Plume Dilution Chamber" or SPDC. The SPDC acts as a large inert (Teflon-coated) reaction chamber to form controlled combustion emission plumes by isokinetically introducing a small volume of flue gas (e.g., 20 liters) into a large volume (e.g., 500 to 1,000 liters). The SPDC has several variables that can be easily controlled: 1) temperature, 2) dilution ratios, 3) reaction time, 4) light input, and 5) rainwater. Both dry deposition (on the sides of the walls) and mercury washout by rainfall can also be assessed with a SPDC. This allows users to assess deposition in the environment and to identify which atmospheric mercury species are removed into aquatic ecosystems. In addition to using a mercury filter pack system to collect a sample from the chamber for particulate mercury, RGM and elemental mercury analysis, the instrumentation is also set up to measure (via a probe) mercury speciation in the flue gas. Total mercury in the SPDC is measured to calculate a SPDC mass balance.

With speciated source and ambient mercury measurements that are directly comparable, valid source apportionments and modeling can occur. Obtaining source data in its transformed form (i.e., in the stack plume) will also provide more accurate information for site-specific risk assessments. Such source-specific data can also support the understanding of TMDLs, including the need for regulatory action. We need to improve our identification of differences between source and ambient measurements, so that mercury source/receptor relationships can be better defined, and accurate source/receptor models can be developed.

3.3 Fate and Transport Research Recommended by the Workshop Steering Committee

The following monitoring research is recommended to define the relationships between the sources of mercury and ambient concentrations:

- Research by EPA ORD and others should be conducted to establish the speciated data relationship(s) between conventional, in-stack, mercury speciation measurement methods and ambient mercury speciation measure methods. To do so will require the simulation of the short-term atmospheric transformations taking place in the plume and ambient environment as combustion process emissions exit the stack. This can be accomplished using dilution techniques, although other approaches could exist. Ambient speciated measurements made directly from diluted combustion emissions can then be compared with conventional source speciating measurements to establish relationships between elemental, RGM and particulate-phase mercury measurements. These relationships should be determined for multiple combustion source categories. Ultimately, this would improve the quality of data used by modelers to determine source/receptor relationships.
- Once this relationship has been established, source profiles and speciated mercury measurements should be obtained from representative types or categories of emission sources, including resource recovery and medical waste incinerators at different geographical locations. If the ratio of elemental mercury to mercuric chloride to particle-bound mercury to total mercury was known for a representative group of sources, it would be possible to more conclusively model mercury fate and transport relationships and perform TMDL calculations.
- EPA should support the operation and expansion of the MDN program where possible. In addition, a minimum of three to four new air quality monitoring stations should be established

to measure speciated mercury and related elements in the atmosphere in the short-term. These new monitoring stations should be located at sites considered receptors for emissions from stationary sources. These sites should be maintained for a minimum of 5 years to assess the impact of mercury emission controls. Wet deposition samples should also be collected concurrently with atmospheric measurements. Currently two sites are being setup by EPA ORD: one in Florida and one in Ohio. These sites should be operational in mid 2000. If the ambient mercury speciation instrumentation from these sites proves to be reliable and provides data on source/receptor relationships important for TMDL validation, it would then be advantageous to allocate additional funding to expand the number of monitoring sites and to sustain these sites beyond the 5 year period. This short-term sampling may also help interpret the long-term results of the MDN program, and potentially demonstrate new monitoring technologies that may in the future be used by the MDN program.

- Future ambient air and deposition monitoring programs should be developed based in part on the need to develop, validate, and refine air dispersion and wet/dry deposition models. Both monitoring and modeling needs to be addressed simultaneously.

Section 4

Workshop Summary and Conclusions

As discussed, the state-of-the-science for both source emission and ambient air mercury monitoring has advanced substantially over the last several years, particularly in the case of total mercury CEMs. Research is now needed to develop direct speciating mercury CEMs, to address total mercury CEM interference and bias, and to investigate and finalize procedures for the evaluation of mercury CEMs. Research is also needed to further the understanding of the fate and transport of mercury, particularly an understanding of the short-term transformations that occur in combustion plumes. This will require additional and precise speciated mercury monitoring at the source, at the receptor, and most importantly, measurements that account for the stack gas plume atmospheric transformations. This monitoring is also needed to develop, validate and refine air dispersion and deposition models, and to accurately calculate TMDLs. Lastly, collaboration is needed between EPA, DOE, other Federal and State agencies, and vendors to perform full-scale demonstrations of these source emission and ambient air monitoring technologies.

In order to promote the development of mercury monitoring systems (particularly CEMs), the Workshop Steering Committee suggests that EPA continue to provide assistance and guidance to:

- Manufacturers to develop mercury monitoring systems and for industrial sources to install these systems.
- The academic community through research grants.
- Federal Agencies through Interagency Agreements.

It is also suggested that EPA ORD continue to inform the EPA Program Offices and Regions, State and local permit permitting authorities, industry, and the international community about the latest developments in manual and continuous systems to measure source and ambient levels of mercury.

Appendix A - Workshop Agenda, Speaker Presentation Summaries, and Panel Session Summaries

This appendix contains a copy of the workshop agenda followed by summaries of the presentations and panel discussions from the workshop. This appendix does not constitute an actual proceedings, since the presentations were informal, and no written versions were required. Furthermore, speaker and session summaries are organized according to the order in which they were presented.

Agenda
Workshop on Source Emission and
Ambient Air Monitoring of Mercury

Day 1 -Morning

7:30 Registration

8:30 Workshop Purpose/Opening Remarks (Scott Hedges, US EPA, NRMRL)

Session 1 - Need for Source and Ambient Mercury Measurement (Jeffrey Ryan/Robert Stevens Session Chairs)

8:45 Part A - The Regulatory Perspective

Regulatory Perspective on Mercury Monitoring (Fredric Chanania, US EPA, OSW - 20 min)

Need for Source and Ambient Mercury Measurement: A Regulatory Perspective (William Maxwell, US EPA, OAQPS - 20 min)

The Mercury Problem: What Is It? (Thomas Atkeson, PhD, Florida DEP - 20 min)

9:45 Part B - Transboundary Considerations

The Commission for Environmental Cooperation (CEC) and the North American Regional Action Plans (NARAPs) on Mercury in the North American Environment (Andrew Hamilton, PhD, CEC - 20 min)

10:05 Part C - Fate and Transport/ Exposure Considerations

Mercury Modeling and Measurements and Their Source Control Implications (Russell Bullock, US EPA, NERL - 20 min)

10:25 Break

11:00 Part D - Process Control Applications

Measurements To Evaluate Emission Controls for Utilities (Thomas Brown, DOE, National Energy Technology Laboratory (NETL), formerly Federal Energy Technology Center (FETC) - 30 min)

Process Monitoring in DOE Mixed Waste Thermal Treatment Systems (Stephen Priebe, PhD, Bechtel B&W Idaho, Contractor for DOE, Idaho National Engineering and Environmental Laboratory (INEEL) - 20 min)

11:50 Lunch

Day 1 - Afternoon

Session 2 - State-of-the-Science in Measuring Mercury Emissions (Jeffrey Ryan/Thomas Brown Session Chairs)

1:00 Part A - Mercury Measurement Methodologies

Manual Methods for Measuring Total and Speciated Mercury (John Bosch, US EPA, OAQPS - 20 min)

CEMs for Measuring Total and Speciated Mercury (Nina French, PhD, Sky + Inc. - 20 min)

Industrial Applications of Ultraviolet Differential Optical Absorption Spectroscopy (DOAS) Systems for Mercury Measurements (Carl Kamme, Opsis Inc, Lunde, Sweden - 20 min)

Problems/Issues Associated with Mercury Measurements (Thomas Brown, DOE, NETL - 20 min)

Merits of Dilution Source Sampling: Measurement of Mercury Emissions James Schauer, PhD, University of Wisconsin - 20 min)

2:30 Break

3:00 Part B - Mercury Measurement Research and Development Activities

Mercury Measurement Research at the EERC (Dennis Laudal, University of North Dakota EERC - 30 min)

Mercury Measurement Research at EPA/NRMRL (Jeffrey Ryan, US EPA, NRMRL - 30 min)

Use of a Dilution Chamber To Measure Stack Emissions and Near-Term Transformations (Eric Prestbo, PhD, Frontier Geosciences - 20 min)

4:20 Session 3 - Mercury CEM Performance and Evaluations (Jeffrey Ryan/Scott Rauenzahn Session Chairs)

Part A - Methods for Evaluating/Certifying CEM Performance

EPA Performance Specifications: Optional Use of CEMs (Scott Rauenzahn, US EPA, OSW - 20 min)

Suitability Testing of CEMs for Mercury (Carsten Röllig, TUV -Rhineland, Cologne, Germany - 30 min)

EPA's ETV Program: An Avenue for Testing of Mercury CEMs (Thomas Kelly, PhD, Battelle - 15 min)

5:35 End of Day 1

Day 2 - Morning

8:00 Part B - CEM Performance Evaluations and Demonstrations

Mercury CEM Field Demonstrations (Nina French, PhD, Sky + Inc. - 30 min)

Evaluation of CEMs for Mercury Speciation (Dennis Laudal, University of North Dakota EERC - 30 min)

9:00 Break

9:30 Session 4 - Panel Discussion of Source Monitoring / Testing Needs (Jeffrey Ryan/Nina French Session Chairs)

Panelists

Russell Bullock-US EPA, NERL; Scott Rauenzahn-US EPA, OSW; Stephen Priebe-Bechtel B&W Idaho; Thomas Brown-DOE, NETL; Ronald Baker-Aldora Corp.; John Bosch-US EPA, OAQPS; Catherine Massimino-US EPA, Region X

Topics/Questions

- 1) Do you believe total mercury CEMs are capable of cost-effectively monitoring emissions for compliance assurance?
 - Why or why not?
 - Which technologies are forerunners, and why?
 - Which technologies are you less sure of and why?
- 2) What are the greatest concerns associated with CEM operation?
 - What are the risks?
 - What are the technical obstacles (e.g., interferences, filter artifacts, durability, biases)?
- 3) How should CEM performance be evaluated?
 - What are the most important considerations with respect to CEM performance (e.g., drift, calibration technique, sensitivity, precision, durability, etc)?
 - Is PS 12 still considered to be the appropriate method for evaluating total mercury CEM performance?
 - Why or why not?
 - Should PS 12 be revised? Who will do it? When?
 - What tools (e.g., gas standards, reference materials, comparison methods, techniques) are needed to fully evaluate CEMs?
 - Are existing reference methods (i.e., Methods 101A and 29) satisfactory as an accuracy check or reference point for total mercury CEM (averaged) data?

- 4) What type of field demonstrations and/or technology improvements/cost reductions are necessary to reduce the risk of implementing total mercury CEMs?
 - What type and how many field demonstrations will be required to fully demonstrate CEMs?
 - What are the types of sources that must be considered?
 - Can nominal and/or worse case monitoring conditions be defined?
- 5) Where are speciating CEMs needed?
 - Is speciation by difference adequate or are direct speciating techniques needed?
 - Are performance specifications needed for speciating CEMs?
- 6) Does the CEM technology available today provide an accurate description of the chemical and physical forms of mercury introduced into the ambient air after the stack emissions have diluted and cooled to ambient temperatures?
- 7) What is EPA's role in the development of mercury CEMs? What are the roles of others (e.g., DOE, vendors, State, and local)?
- 8) What actions or outcomes are required to move towards implementing mercury CEMs for compliance assurance?

11:30 Lunch

Day 2 - Afternoon

1:00 Session 5 - State-of-the-Science in Ambient Air Monitoring (Robert Stevens/Gerald Keeler Session Chairs)

International Monitoring/Measurement Activities for Atmospheric Mercury (John Munthe, PhD, Swedish Environmental Research Institute, Goteborg, Sweden - 20 min)

Source/Receptor Relationships for Mercury: Monitoring and Modeling - (Gerald Keeler, PhD, University of Michigan - 20 min)

Manual Speciation Methods for Measuring Atmospheric Mercury: Applications/Implementation (Matthew Landis, PhD, US EPA, NERL - 20 min)

2:00 Break

2:30 Session 5 - State-of-the-Science in Ambient Air Monitoring (Continued)

Automated Mercury Speciation Methods and Demonstrations (Robert Stevens, State of Florida DEP - 30 min)

Wet Deposition Sampling - Applications/Implementation (Timothy Dvonch, PhD, University of Michigan - 20 min)

Atmospheric Wet Deposition of Mercury in North America (Clyde Sweet, PhD,
Illinois State Water Survey - 10 min)

3:30 Session 6 - Panel Discussion of Ambient Monitoring Needs (Robert Stevens/Carl Kamme Session Chairs)

Panelists

Gerald Keeler-University of Michigan; Eric Prestbo-Frontier Geosciences;
John Munthe-Swedish Environmental Research Institute; Thomas
Atkeson-Florida DEP; Matthew Landis-US EPA, NERL; Clyde Sweet-
Illinois State Water Survey; Russell Bullock-US EPA, NERL

Topics / Questions

- 1) What is the state-of-the-science in measurement methods?
- 2) What are the needs for representative and comparable data?
- 3) Do we need to expand the wet deposition and aerosol mercury monitoring network and add additional atmospheric mercury measurements?
- 4) What are the needs for method standardization and ambient reference method?
- 5) Use of manual vs. automated sampling techniques.
- 6) What are the needs for speciation?
- 7) What ambient and source inputs are needed for dispersion modeling?
- 8) What is EPA's role in the development of ambient monitoring techniques? What is the role of other groups?
- 9) What does EPA need to do and when?

4:30 Summary and Concluding Remarks (Scott Hedges, US EPA, NRMRL)

4:45 Adjourn

Workshop Purpose/Opening Remarks

Presented on September 13, 1999 by Scott Hedges, US EPA, ORD, NRMRL

Problem Statement

This workshop was developed because mercury contamination, both nationally and internationally, has long been recognized as a growing problem for both humans and ecosystems. Mercury is released to the environment from a variety of human (anthropogenic) sources including fossil-fuel combustors, incinerators, chlor-alkali plants, and landfills. Since this metal does not degrade to simpler compounds, once it is released to the environment, it will always be present in one form or another.

The 1997 Mercury Study Report to Congress indicated that mercury deposition has increased by a factor of two to five over pre-industrial levels. In general, anthropogenic emissions constitute the most significant releases of mercury in the United States. Emissions include fossil fuel combustion (containing trace amounts of mercury), municipal incineration, medical waste incineration, chlor-alkali plants, and landfills. Other sources of anthropogenic mercury include industrial processes and the disposal of products containing mercury. Additionally, most atmospherically-deposited mercury is in the form of gaseous or particulate-phase inorganic mercury. Unfortunately, inorganic mercury released into the environment can be converted, by naturally-occurring biological processes, into the highly toxic methyl mercury species.

In order to assess and control future mercury emissions, improved emission estimates from major sources are needed, along with an improved understanding of the transport, transformation, and fate of the mercury emitted from these sources. As a result, accurate source emission and ambient air measurements of mercury species are needed to address these research requirements and to ensure compliance with regulations promulgated to reduce the impact of mercury contamination in the environment.

Purpose of Mercury Monitoring Workshop

In addition to providing information on the latest developments in speciated and total mercury monitoring methods and instrumentation, this workshop was designed to address monitoring research needs and data quality objectives for the EPA Program Offices (in particular the OSW and the OAQPS) and Regional Offices, the international community, the DOE, the DOD, State agencies, developers of monitoring equipment, and industry.

The workshop was broken down into six sessions, including two panel discussions on source emission measurements and ambient air measurements, in support of these goals. Additionally, lists of questions/issues were developed and forwarded to the participants prior to the meeting to help focus the panel discussions towards areas of particular interest to the workshop organizers (see Panel Discussion Summaries for these questions). The panel discussions were intended to examine points of controversy and develop consensus for future efforts.

Regulatory Perspective on Mercury Monitoring

Presented on September 13, 1999 by Fredric Chanania, US EPA, OSW

Mercury Monitoring

Mercury monitoring is of particular interest to the solid and hazardous waste industries. In general, source emission monitoring techniques are used to assess treatment related issues, both within and at the end of a treatment process. Ambient monitoring techniques, on the other hand, are frequently used to support risk assessment efforts.

Ambient air monitoring can be divided into two categories: ambient air and ambient monitoring. Ambient air measurements are used to examine post-stack transport and transformation issues (i.e., between the stack and the ultimate receptor), while ambient measurements are used to address receptor site transport and transformation issues (i.e., from uptake or bioaccumulation to fish or human receptors). Although OSW uses air quality control data from treatment processes to perform ambient air risk assessments, most of its efforts are focused on ambient receptor site transport issues (e.g., mercury transport within a water body) and mercury transformations associated with uptake and bioaccumulation, including exposures to human and ecological receptors.

Monitoring Result Use

Monitoring results are used to:

- Set national regulatory standards (e.g., treatment standards, stack emission limits, and other regulatory limits) - After a national treatment standard is set, facilities typically have to comply with the standard following State adoption. Thermal burning is usually regulated through stack emission limits/actions; hazardous waste site delisting petitions and other regulatory limits, however, are set by OSW.
- Develop methods - OSW develops methods which can be used to accurately and precisely measure mercury concentrations in different matrices.
- Assess facility compliance - Compliance with the standards is determined through monitoring, sampling, and analysis.

Mercury Monitoring of Thermal Waste Treatment Systems

Mercury monitoring data are often used to assess the performance of combustion or other thermal treatment systems. Performance is frequently measured relative to compliance with the following: stack emission standards, process monitoring OPLs; the Phase I MACT Combustion Rule, Boiler and Industrial Furnace (BIF) Regulations, permit-specific OPLs, and thermal desorber monitoring requirements under Subpart X. Detailed discussions of process monitoring OPLs and the Phase I MACT Combustion Rule include:

Process Monitoring OPLs - Process monitoring OPLs were developed in response to high stack emission testing and compliance costs and can be used to ensure that stack emissions meet regulatory limits. OPL types include:

- Feedstream monitoring - When feedstream OPLs are used, it is assumed that almost none of the mercury entering the stack is captured within the system. Thus, the feedstream data are used to set the outer boundaries for the unit.
- Combustion chamber conditions - Temperature and other operating conditions in the combustion chambers can be controlled to reduce/control mercury emissions from certain regulated facilities.

- Performance parameters - Since many common Air Pollution Control Devices (APCDs) have difficulty capturing mercury, OPLs for APCD performance parameters are less likely to be used.

Phase I MACT Combustion Rule - The Phase I MACT Combustion Rule was recently released for HWCs. This rule sets new stack emission limits for total mercury [i.e., 47 micrograms per dry standard cubic meter ($\mu\text{g}/\text{dscm}$)] for lightweight aggregate hazardous waste kilns, 120 $\mu\text{g}/\text{dscm}$ for incinerators, and 130 $\mu\text{g}/\text{dscm}$ for cement kilns]. Under this rule, facilities with cement kilns, incinerators, and low weight aggregate kilns will need to measure mercury concentrations in their feedstreams on a more continuous basis. Facilities with wet scrubbers will also need to monitor for a host of system-related parameters on a semi-continuous basis (e.g., hourly or daily). Facilities which use activated carbon injection or carbon beds to control mercury emissions will also need to monitor additional parameters related to these APCDs. Although approximately 80% of thermal facilities are not regulated under the MACT Rule, a new rule is just coming out which addresses non-hazardous waste cement kilns. Furthermore, the Commercial and Industrial Solid Waste Incinerator (CISWI) rule is approaching proposal.

Mercury Monitoring of Non-Thermal Waste Treatment Systems

Non-thermal waste treatment systems will need to monitor their residuals for compliance with the following total mercury concentration standards:

- 0.2 milligrams per liter (mg/L) Toxicity Characteristic Leachate Procedure (TCLP) for mercury retort nonwastewater
- 0.025 mg/L TCLP for all mercury non-retort nonwastewaters
- 0.15 mg/L for mercury wastewater
- 10 times the universal treatment standard (UTS) for soils or 90% reduction.

For these numerical standards, total mercury consists of non-speciated mercury obtained from the TCLP extraction. Also, there are no OPLs for non-thermal waste treatment systems and the focus is primarily on the output of the treatment system (unlike thermal systems). Furthermore, facilities with "high mercury nonwastewaters with organics" typically use incineration /retorting, and facilities with "high mercury inorganic wastewaters" typically use retorting only.

Key Regulatory Drivers of the Future

Future standards and regulations will most likely follow present patterns. Therefore, since mercury CEMs will probably not reach the final stages of development for some time, it is unlikely that regulators will commit to developing a proposal for CEMs in the near future. A Phase II MACT Combustion Rule for boilers and halogen acid furnaces, however, will probably be enacted. Finally, an Advance Notice on Proposed Rulemaking (ANPRM) and Notice on Proposed Rulemaking (NPRM) has been issued stating that EPA will be examining the mercury treatment standards for all non-thermal and applicable thermal treatment systems. This may have a significant impact on incineration and retorting systems.

Implications for Mercury Monitoring

Although there is a policy preference for using continuous sampling and analysis methods, it is important to balance a facility's need to control monitoring costs against the regulator's need for certainty. The Agency must be able to justify continuous sampling and analysis from a "value added" perspective. In the future the Agency will also need to determine whether total and/or speciated mercury measurements will be used to monitor feedstreams (both process and remedial), waste treatment residuals (e.g., ash and sludges), and soils.

Within combustion systems, a cooperative effort may be needed to determine whether total or speciated mercury measurements are more useful. Currently, total mercury measurements are used to determine MACT compliance from the exit stack. During risk assessments, however, emphasis is often placed on obtaining speciated ambient measurements (e.g., methyl mercury). In the future, EPA will need to determine whether speciated mercury monitoring should be done at the end of the stack or only at the receptor site. The Agency will also need to determine whether multiple metal or mercury monitors are more sensible from a regulatory perspective. It currently appears that EPA is leaning towards using multiple metal CEMs, probably because they are more developed and because many toxic metals other than mercury are already regulated.

Need for Source and Ambient Mercury Measurement: A Regulatory Perspective

Presented on September 13, 1999 by William Maxwell, US EPA, OAQPS

CEMs are needed to determine compliance with given regulations. CEMs can also be used for control device evaluations, permit compliance, and to obtain data for models.

A study of electric utility steam generating units for air toxics was mandated by Section 112(n)(1)(A) of the CAA. Under this Act, EPA must determine whether regulations are appropriate and necessary based on the results of the study. The final report to Congress was issued in February 1998. In this report, the hazardous air pollutant (HAP) of greatest concern was mercury from coal fired utilities. The current due date for regulatory determination is December 15, 2000. If the determination is positive, regulations must be proposed by November 2003 and promulgated by November 2004. If mercury emission limits are established, CEMs are believed to be the Agency's preferred method of determining compliance, assuming they are available, cost effective, etc.

There are two types of mercury CEMs: 1) units that measure total mercury; and 2) units that determine the oxidized fraction by the difference between elemental and total mercury. Speciation is important to understanding and modeling dispersion, fate, deposition, and exposure potential of mercury. Speciated data will also help the Agency evaluate local, regional, and global impacts. Further, speciated mercury data may also be beneficial for future risk analyses. Speciation data can also be used to evaluate up-front control devices; however, once controls are in place, control device evaluations or risk evaluations may no longer be needed.

If total mercury measurements are regulated, then it may be more appropriate to measure total mercury. For example, many electric utilities burn more than one type of coal. Since different types of coal emit different species of mercury at different concentrations, mandatory speciated monitoring would not make sense for this industry from a regulatory standpoint.

In addition to the utility industry, the following source categories also need to be considered:

- Municipal waste combustors - Although the current rule does not include a mercury HAP CEM for MWCs, in part because no mercury HAP CEMs were available when the rule was developed, it is possible mercury CEMs could be required under future revisions. It is also possible that the required controls may prove as expensive as incineration.
- Medical waste incinerators - Mercury HAP CEMs were not specified for medical waste incinerators in the current HAP CEM rule and are not expected under future revisions due to cost considerations.
- Industrial/commercial boilers - HAP rules have not been proposed for industrial and commercial boilers.
- Commercial/industrial incinerators - HAP rules have not been proposed for industrial and commercial boilers, however, it is unlikely that mercury HAP CEMs will be specified in future rulings due to cost considerations.
- Chlor-alkali plants - Rules for chlor-alkali plants are still under development and the CEM requirement is unknown.
- Portland cement plants - Portland cement plants are still being disputed at this time and the litigation impacts are unknown.

At this time, total mercury CEMs appear to be the most likely candidate for compliance monitoring, although many factors are still subject to change. Total metal and speciated mercury CEMs are also of interest, and there are reasons for having either one or both of these systems. Regardless, a working version of the selected technology is needed by mid-2001, at which time this unit needs to be tested and compared to the manual methods. A commercial-ready version is also needed by the implementation deadline (i.e., within 3 years of promulgation or by November 2007). This leaves approximately 6.5 years from when data gathering starts to when implementation needs to occur.

In November 1998, EPA issued an ICR which requires that:

- All coal-fired utility units analyze coal for mercury content for the calendar year 1999
- Approximately 85 units are required to test for speciated mercury emissions using the Ontario Hydro Method
- All data are due to EPA by June 1, 2000.

The ICR data will be used to refine the mercury emissions estimates for utilities. These data will also be combined with other inputs (e.g., health studies and control options) to inform the Administrator for regulatory determination.

The Mercury Problem: What Is It?

Presented on September 13, 1999 by Thomas Atkeson, Florida DEP

The mercury coordinator for Florida DEP, Dr. Atkeson, noted that he has seen a lot of changes since 1992. During this period, private, Federal, and State cooperation has contributed to the development of a multimedia approach to the mercury problem. Over the next 5 years, however, Dr. Atkeson expects advances to occur that will allow concerned parties to understand the mercury problem on its various spatial scales and move toward control.

What Is It?

Mercury is the quintessential multimedia problem, affecting air, water, and soil. Global and regional emissions cycles are the primary transport mechanisms of mercury into most fresh waters. The aquatic cycling of mercury is also crucial to the "expression" of the mercury problem. Although inorganic mercury inputs have little consequence by themselves, when mercury is converted to methyl mercury it is frequently "biomagnified" in the aquatic food chains, to the point at which both humans and ecological resources are at risk. To effectively address the mercury problem, all three aspects of the problem need to be dealt with.

The discovery of high levels of mercury in the Everglades helped focus attention on the mercury issue in Florida. Lower concentrations of mercury in the coastal waters and rivers and lakes throughout the State are also problematic. Although Florida's monitoring efforts have been thorough, a lot of "in-fill" is still needed to form a more accurate picture of mercury contamination throughout the State. Although Florida was the first Southern State to describe the mercury problem, since then many other States in the South (specifically, the Southern Coastal Plain) have also recognized their mercury problems.

Is It Natural?

When Florida first found high mercury levels in Everglades fish this contamination was initially attributed to naturally occurring sources (e.g., peat soils), mainly because there were no anthropogenic point sources in the Everglades. Core study results from 1990, however, showed that the rate of mercury accumulation in Everglade soils had increased approximately 500% since 1900. This sharp rise in mercury deposition has been attributed to increased anthropogenic emissions to the atmosphere.

Where Does the Mercury Come From?

Once it is determined that increased levels are human-induced, it is necessary to determine where the contamination originated. This is a difficult issue to address, since there are three components to the atmospheric mercury cycle (global, regional, and local). Efforts are further hampered by an early general disinterest in monitoring and controlling mercury emissions. This can be attributed in part to the lack of political or legal mechanisms to control/reduce global emissions. With time, however, the scientific and regulatory community realized that mercury is not just a global problem and that local, State, and national efforts to reduce emission sources have a significant impact on levels within the US

Mercury operates on three different spatial scales (global, regional, and local). Global impacts are generally associated with elemental mercury entering an area from an unknown, outside source. In addition to being relatively inert, elemental mercury has a long atmospheric residence time and

circles the globe to average out to a fairly even background level. At the local level (100 kilometers of a source) and regional (1,000 kilometers of a source) level, however, speciated mercury forms drive the deposition patterns. For example, the majority of RGM or mercury(II) emissions are generally deposited locally, while fine particle-phase mercury emissions are deposited both locally and regionally. Therefore, in order to understand where mercury contamination is originating, the scientific and regulatory community needs to understand the nature of the sources, both locally and regionally, as well as the global impact. Good speciation data from a wide variety of sources (e.g., CEM data) are essential to understanding the atmospheric mercury cycle and selecting appropriate controls.

After several years of surface water monitoring, Florida was surprised to note that global, regional, and local atmospheric mercury inputs (the total atmospheric mercury budget) to water sources accounted for almost 20 times as much mercury (125 to 150 kilograms per year) as surface water inputs (4 to 6 kilograms per year). It is anticipated that this factor will grow to 30 to 50 times once scientists develop the ability to factor dry deposition into atmospheric estimates. Florida is currently trying to determine: 1) what proportion of the atmospheric budget is originating from different local and regional sources; and 2) how vigorously it can practically control these emissions to reduce deposition. Florida also needs to account for global impacts, since global inputs to coastal environments can be significant.

Speciation data obtained by EPA and the University of Michigan during a regional transport modeling pilot study in 1995 were then presented for four different types of sources. According to the results of this study, oxidized mercury emissions [observed as mercury(II)] from a cement kiln, a large regional medical waste incinerator, a municipal incinerator, and a coal-fired utility boiler averaged $25\pm 4\%$, $95\pm 5\%$, $78\pm 5\%$, and $67\pm 27\%$, respectively, over several runs. Since many medical waste incinerators have low stack heights and low exit velocities, the majority of the oxidized mercury from the medical waste incinerator was probably deposited near the source (i.e., in the Everglades). Furthermore, since South Florida has the highest per capita reliance on MWCs compared to other States, the high percentage (approximately 80%) obtained during the study for the MWC may call for a reassessment of the effect of these facilities on the Florida Everglades.

The Southern Florida Mercury Science Program is also focusing a significant portion of its research efforts toward the following:

- Atmospheric source apportionment - To include atmospheric chemistry and measurement techniques; the Regional Transport & Deposition Model; an EPA/DEP "Super Site" for intensive measurements; EPA/National Oceanic and Atmospheric Association (NOAA) airborne measurements; and a EPA/DEP 3rd Generation Regional Transport and Deposition Study
- Bioaccumulation in the aquatic food chain - Methyl mercury levels in Everglade fish are typically seven orders of magnitude above the average water concentration of 100 to 200 parts per quadrillion. This presents risks to wading birds and panthers.
- Aquatic cycling - To include cycling processes research and the development of the Mercury Cycling Model.

The CEC and the Development of NARAPs on Mercury in the North American Environment

Presented on September 13, 1999 by Andrew Hamilton, CEC

Two new North American institutions have been established: the North American Agreement on Environmental Cooperation (NAAEC) and the CEC. The CEC was established in 1994 under the NAAEC, which was negotiated by the governments of Canada, Mexico, and the United States as a parallel side agreement to North American Free Trade Agreement (NAFTA). The top three objectives of the NAAEC are to: "a) foster the protection and improvement of the environment in the territories of the parties for the well being of present and future generations; b) promote sustainable development based on cooperation and mutually supportive environmental and economic policies; and c) increase cooperation between the parties to better conserve, protect and enhance the environment, including wild flora and fauna."

The CEC is made up of three parts: the Council, Joint Public Advisory Committee, and the Secretariat. The Council consists of cabinet level appointees and acts as the governing body. The Joint Public Advisory Committee advises the council and is made up of five representatives of each country. The third component is the Secretariat, which is staffed by representatives of each country and carries out the work on behalf of the Commission.

The Sound Management of Chemicals Initiative (SMOC) is a major program established under Council Resolution 95-05. SMOC established a framework for cooperation in addressing chemical pollution in North America. The resolution established a working group made up of senior government officials to work with the CEC to implement the decisions and commitments contained in the resolution. Council Resolution 95-05 deals mainly with persistent bioaccumulative toxic substances (PBTs). The Working Group, in consultation with the Secretariat, initially selected four chemicals [i.e., mercury, dichlorodiphenyltrichloroethane (DDT), chlordane, and polychlorinated biphenyls (PCBs)] and established Implementation Task Forces for each. These task forces oversee the implementation of a NARAP. Additionally, the Substance Selection Task Force was established, which oversees the implementation of the process for identifying candidate substances for regional action under the SMOC initiative.

The substance selection process involves three major steps. Stage I is the nomination stage, during which governments nominate additional chemicals to the Working Group for inclusion as PBTs. The evaluation stage, or Stage II, has two steps: the screening evaluation and the mutual concern evaluation. Stage III is the discussion/decision stage. In this stage, the Working Group prepares recommendations to ministers for preparation of a NARAP. Beginning this year, the Substance Selection Task Force is looking to develop a NARAP for dioxin/furans and hexachlorobenzene over the next 2 years.

Article 13 of the NAAEC allows the Secretariat to prepare a report on any matter within the general scope of the annual work plan or, in most instances, within the scope of the Agreement. The Continental Pollution Pathways Report was developed under Article 13 and is a public document containing a mercury case study. The report emphasizes that pathway issues are a cross-media issue (air, land, water, and biota) and that integrated approaches are required. Also, the Air Issues Program has evolved out of the Continental Pollution Pathways Initiative.

There were two Council Resolutions in 1999. The first was #99-01, developing a NARAP on dioxins/furans and hexachlorobenzene. The second was #99-02, developing a NARAP on environmental monitoring and assessment.

A concept paper was also developed defining the monitoring program. Among other things, this paper discussed having monitoring and long-term ecological research experts review draft documents and provide input on monitoring efforts in North America which could be useful for the Initiative.

The Phase I NARAP on mercury was approved in October 1997. Phase II is currently out for public review and comment and formal governmental approval is expected in early 2000.

Key elements of the NARAP on environmental monitoring and assessment include: 1) to promote more and better collaboration among the parties; and 2) to facilitate effective and sustained trilateral cooperation in generating adequate, comparable, and continuing data. At the heart of NARAP is the commitment to develop a coherent system of index and/or reference sites for the three countries. This system would provide pertinent monitoring and assessment data. Sampling protocols are also needed to improve the comparability of methods and procedures applicable to quality assurance/quality control (QA/QC) and data assessment.

Mercury Modeling and Measurements and Their Source Control Implications

Presented on September 13, 1999 by Russell Bullock, US EPA, NERL

Mr. Bullock asked the audience a broad question "What makes mercury so special?" Or, in other words, "Why is mercury getting so much more attention than arsenic?" He then answered this question by providing the following information about mercury.

- Mercury has a predominant gaseous fraction in the atmosphere; other atmospheric metals are found almost exclusively in the atmosphere as solid aerosols.
- Mercury has a wide variation in water solubility depending on its chemical form. Also mercury's wet deposition efficiency depends on its physical and chemical state. Other metals are all effectively wet-scavenged as aerosols. (Note: Since chemical form has a large impact on solubility and other factors, speciated measurements are very important, particularly as inputs to models designed to improve our understanding of the mercury cycle.)
- Mercury is mostly found in the atmosphere in its elemental state whereas other atmospheric metals are almost always found as compounds.
- Mercury must convert to a methylated form and bio-accumulate in the food chain in order to become a serious human health risk. Even though researchers and scientists see the atmosphere as the first step in the transport of this toxic substance to areas of damage, they need to understand how damage occurs within an ecosystem to really understand the human health effects.

Global atmospheric mercury speciation averages were then presented. Based on these averages, approximately 98% of mercury is found in the gaseous state; greater than 90% of this gaseous fraction as elemental mercury and the remainder as mercury(II) compounds (e.g., mercuric chloride and other compounds with high vapor pressures). The remaining 2% of mercury associated with aerosol particulate matter (presumably mercuric sulfides, mercuric oxides, and other compounds with low vapor pressure) or more volatile mercury(II) compounds sorbed to ambient aerosols in the atmosphere. Based on this information, it is reasonable to conclude that mercury that is released as gaseous mercury compounds can later be sorbed to pre-existing particulate aerosols. Furthermore, particulate mercury may represent more than 2% of the total atmospheric mercury burden in industrial and urban areas. There is also very little information regarding the oxidation state of atmospheric mercury at higher altitudes.

Mr. Bullock then discussed the mercury emissions inventory used in Regional Langrangian Model Air Pollution (RELMAP) modeling for the Mercury Study Report to Congress. Speciation percentages for elemental mercury, mercury(II), and particulate mercury were: 50%, 30%, and 20%, respectively, for electric utility boilers (coal, oil, and gas) and 58%, 20%, and 22%, respectively, for HWCs. Speciation percentages were also presented for a number of different source types (e.g., MWCs, commercial and industrial boilers, residential boilers, chlor-alkali factories, Portland cement facilities, pulp and paper plants, sewage sludge incinerators, areas sources, and other point sources). The percentages for HWCs were based on plant-specific emission rates for elemental mercury, mercury(II), and particulate mercury. All other percentages presented were based on modeling assumptions.

Mr. Bullock then discussed simulation of the deposition of elemental mercury gas and divalent

mercury gas in the US. After noting that elemental mercury gas emissions are roughly distributed across the US according to population, Mr. Bullock then noted that simulated wet deposition for elemental mercury from US sources was extremely low, less than or equal to 1 microgram per square meter per year ($\mu\text{g}/\text{m}^2/\text{yr}$) across the US. Furthermore, divalent mercury gas emissions were also distributed across the US according to population, though there were some rural areas with higher levels due to large combustion sources in these areas (i.e., coal fired boilers or HWCs). Simulated wet deposition levels of divalent mercury gas in the US were extremely high relative to elemental mercury wet deposition.

The annual mercury mass budget (in metric tons) published in the EPA's Mercury Study Report to Congress was then presented, including total elemental mercury, mercury(II), and particulate mercury deposition across continental US. These results were generated using a 1-year RELMAP simulation. According to these results, almost all measured anthropogenic elemental mercury emissions (62.3 of 63.5 metric tons) were transported out of the model domain by the wind without depositing to the surface. But, for the mercury(II) in gas form, only about 15.5 of 52.3 metric tons emitted left the model domain without depositing within the continental US. However, the methods used to model dry deposition of gaseous mercury(II) may have been too simple since there are currently no operational methods to directly measure this phenomenon over vegetated land surfaces.

Vapor pressure and water solubility constitute the primary differences between mercury species. For elemental mercury and mercuric chloride, the vapor pressures are high enough at atmospheric conditions for gas formation. Furthermore, only a limited amount of atmospheric modeling has been done on methyl mercury due to certain chemical and photolytic reactions that are assumed to quickly degrade this species back to the elemental form. This may change, however, if extreme levels of methyl mercury emissions and/or ambient concentrations are found in the future.

After briefly discussing the global mercury cycle, Mr. Bullock noted how the quality work done by schematic developers over the last 5 years has shown that there is much more to tell in the story. In addition to chemical reactions in plumes from natural sources (e.g., volcanos), researchers and scientists are just now starting to understand species deposition on trees, vegetation, and wetlands. It is now also known that this mercury is primarily re-emitted as elemental mercury and that there are more gaseous reactions and heterogeneous reactions dealing with gas to particle chemistry. Aqueous chemistry also needs to be better understood, especially what happens to mercury in various types of cloud formations. Mr. Bullock then presented several cloud-water oxidation reactions involving mercury (ozone, photochemical, and especially over oceans by chlorine) and several cloud-water reduction reactions [by sulfur (IV), photoreduction, and by the hydroperoxyl radical].

Mr. Bullock concluded with another question, "What does all this mean?" He explained that if significant oxidation of elemental mercury is occurring in the gas and/or aqueous phases then all forms of mercury in air emissions must be controlled to reduce atmospheric deposition from wet and dry processes. If significant reduction of mercury compounds to the elemental form is occurring in cloud water, then the scientific community must be underestimating the rate of emission of reactive oxidized mercury, since observed mercury wet deposition rates are too large to be from elemental mercury scavenging alone. If a strong reduction/oxidation equilibrium is maintained by all atmospheric processes, then the control of all forms of mercury is equally important. And lastly, if chemical reactions of mercury in air and cloud water are generally slow and insignificant, then control of RGM and particulate mercury is warranted and life would become much easier for numerical modelers.

Measurements To Evaluate Emissions Controls for Utilities

Presented on September 13, 1999 by Thomas Brown, DOE, NETL, formerly FETC

Mr. Brown began his presentation with by verbally illustrating the difficulties associated with measuring mercury in coal fired flue gas. He asked his audience to imagine a 250,000-mile-long pipeline extending from the moon to the earth. If this pipeline contained flue gas from coal-fired power plants, the "plug" of mercury representative of its concentration in power plants would only be 18 inches long. As expected, the measurement of these low concentration emissions, normally 1 part per billion by volume (ppbv) in flue gas, have proven difficult. Measurement efforts have been further complicated by the need to measure mercury speciation, defined as total speciation of ionic or oxidized, or non-elemental mercury that is somewhat soluble in water or in media in coal fired operations.

Most US coals have mercury concentrations that range from 20 to 120 parts per billion by weight (ppbw), although some coals range from 200 and 300 ppbw. The ratio of vapor-phase elemental mercury to oxidized mercury varies from 10:90 with a nominal 70:30. This ratio is dependent on the coal type and interactions between the solid- and vapor-phase constituents in the flue gas. Thermochemical equilibrium calculations have been used to predict the mercury species resulting from the combustion of different ranks of coals. These equations incorrectly predict that post-combustion mercury will most likely be present as mercuric chloride and as elemental mercury at higher temperatures for bituminous and subbituminous coals. Field sampling results were used to develop the following percentages for mercury(II) in three ranks of coal: 70 to 88% in bituminous coal, 15 to 50% in Powder River Basin (PRB)/subbituminous coal, and 30% in lignite coal. Furthermore, gas-phase equilibrium for mercury-containing species is not valid in coal-fired systems

Research has indicated that mercury oxidation is influenced by interactions between the solid and vapor-phase constituents in the flue gas. Mr. Brown then discussed the mechanisms involved in the oxidation of mercury. If coal combustion is tracked from the lump, through combustion, to vaporization, and then to conversion or to ash formation, the distribution does not follow thermodynamic equilibrium. There are various species of mercury formed but there are no methods to measure them other than by measuring the distribution between elemental and oxidized forms.

Mr. Brown then discussed a "typical" air pollution control system for coal-fired utilities. These systems typically consist of a boiler, followed by a particulate removal system [electrostatic precipitator (ESP), baghouse, cyclones, etc.], a flue gas desulfurization (FGD) system (wet or dry), and a stack. When operating these systems, it is very important to know the configuration of the boiler, the rank of the coal, and the chlorine, sulfur, trace metal, and mercury contents both before and after the coal is cleaned and between the boiler and the particulate removal. Approximately 65% of industry only use an ESP for particulate removal. Ten percent instead use a baghouse and the remaining 25-30% use a FGD system (95% of which are wet). Mercury distribution and the amount of control across each system varies. Furthermore, based on Method 29 data, the highest reductions were found using wet FGD (90%) systems.

A comparison between Method 29 and the Ontario Hydro Method at the inlet and outlet of a wet FGD scrubber indicated comparable total mercury results. Outlet elemental mercury concentrations obtained using Method 29 were significantly higher than similarly measured inlet concentrations.

This can be attributed to the sulfur dioxide in peroxide impingers, resulting in an overestimation of the oxidized form. Both of these methods also show that mercury is oxidized across the FGD system.

The following collaborative efforts for "Mercury Method Development" were then noted:

- Development and validation of mercury speciation methods for coal-fired utilities, in part to address inconsistency issues.
- DOE/Electric Power Research Institute (EPRI) funded a 2-year, 3 million dollar program with the University of North Dakota EERC to develop this method.
- The Ontario Hydro Method has been validated at the pilot-scale and full-scale level and the protocol is being finalized through ASTM.
- EPA is also on the advisory team and ASTM committee to recommend the method as a standard for utility flue gas.
- Ontario Hydro is the method of choice for EPA's ICR.
- Coal-fired utilities are required to report coal mercury concentrations and approximately 85 power plants are required to report mercury speciation and emissions by June 2000. This will help provide information for the database and will help to develop more accurate emission modification factors for field control equipment.

Sampling study data for six facilities over 2 years were then discussed. All six facilities used wet scrubbers and similar coal ranks. The data showed that the elemental mercury was approximately the same in the inlet as the outlet except for 8 to 20% which measured an increase. This increase could be due to the control system, measurement errors, or off-gassing. In the six plants, an average of 60 to 70% of the total mercury was removed and 80 to 90% of the oxidized mercury was removed. It can be assumed from these results that most scrubbed plants do remove the oxidized mercury that would otherwise be put into the environment.

In facilities using Western coal with no enhancement to the removal process, as the temperature, loss on ignition (LOI), and carbon content increased, so did mercury's affinity for capture. The efficiency of various power plant operations strategies for the removal of oxidized and elemental mercury indicate the following:

- Coal cleaning operations remove a median of 37% of the elemental mercury and an unknown amount of oxidized mercury
- ESP systems remove a median of 15% of the oxidized mercury and 15/30% of the elemental mercury
- Fabric filters remove a median of 30% of the oxidized mercury and 65% of the elemental mercury
- Scrubbers remove a median of 55% of the oxidized mercury and unknown amount of the elemental mercury
- Spray dryers remove a median of 60% of the oxidized mercury and 60% of the elemental mercury.

These ranges are heavily affected by coal ranks.

Mr. Brown concluded with a brief discussion of a novel mercury control operation that uses nonactivated carbon up front.

Process Monitoring in DOE Mixed Waste Thermal Treatment Systems

Presented on September 13, 1999 by Stephen Priebe, Bechtel B&W Idaho, (Contractor for DOE, INEEL)

Dr. Priebe's discussion included the goals of process monitoring, a description of DOE mixed wastes, types of DOE treatment systems, DOE monitoring concerns, and raised the question regarding how monitoring can be used to overcome barriers.

Goals of Process Monitoring

The goals of DOE's process monitoring are simple and not unique. They are simply to demonstrate the control of mercury emissions to below recent and/or future MACT requirements, and to ensure compliance with the regulatory limits and the demands of public stakeholders.

DOE Mixed Waste

DOE mixed waste is a combination of hazardous and radioactive wastes. As a result, it is regulated by both EPA and the Nuclear Regulatory Commission. Since EPA and the Nuclear Regulatory Commission sometimes have mutually exclusive requirements, management of these wastes can be complicated. Since DOE is not able to select which requirements it would like to meet, DOE must meet them all.

DOE waste is the legacy of 40 years of nuclear weapons production. It is present at almost 50 sites distributed across numerous congressional districts. DOE waste often contains Resource Conservation and Recovery Act (RCRA) pollutants, Toxic Substances Control Act (TSCA) pollutants, and/or radionuclides; however, the dominating pollutant (from a regulatory perspective) depends on the type of waste. This waste is frequently very heterogeneous and often is not well characterized. Since DOE first began storing this waste in the 1940s, storage has been inconsistent (e.g., in barrels or drums, above ground or below ground). Furthermore, since mercury is nearly ubiquitous in these wastes, they are automatically assumed to contain mercury, whether it is actually present or not.

DOE Treatment Systems

DOE has a variety of thermal treatment systems, including a high-level liquid waste calciner located in Idaho and incinerators located in Oak Ridge, Tennessee; Savannah River, South Carolina; and Idaho. There are also steam reformers and various joule-heated and plasma melters. All of these systems have the potential to volatilize mercury.

DOE Monitoring Concerns

Even though tests have shown mercury reductions of 5 to 95%, concerns regarding monitoring inaccuracies force DOE to assume that all the mercury in the waste is emitted in the offgas (i.e., no control). Furthermore, compliance is based on comprehensive testing and limiting the waste feed to 0.5 to 2 parts per million (ppm) mercury (under new MACT incineration rules). This will be difficult to achieve, since accurate analysis of mercury to ppm levels is extremely hard to obtain, and sampling and analysis of the waste feed is very expensive. Also, in addition to being expensive, waste feed sampling and analysis increase the risk of personnel exposure to radionuclides. To address risk concerns, DOE operates under a system called ALARA (as low as reasonably

achievable). Unfortunately, worker safety can be difficult to guarantee since the wastes often have to be sorted by hand.

DOE Monitoring Uses

DOE could use monitoring technologies for waste feed characterizations (to non-intrusively monitor "what's going in") or for offgas characterizations (to measure "what's coming out"). Ideally, feed characterization will replace sampling and analysis, which is often costly, time consuming, and unacceptable to the public. These systems must be capable of non-intrusively monitoring liquid and containerized solid waste so that the waste can be monitored without having to be taken out of its containers. Currently, systems are being developed which use gamma ray activation; these systems have been successfully tested at the 100 ppm range on homogenous waste. Unfortunately, however, these units have problems with consistency and can currently only be used to analyze streams with uniformly distributed concentrations.

It is possible that the new rules may support replacing feed characterization with offgas characterization for compliance. This technology could show some mercury removal from offgas in lieu of control technology. In other words, it may allow for mercury control without using a mercury control technology. It may also improve the performance of the control technology. Stakeholder assurance is also an area of primary current focus. For example, when a new waste treatment facility was proposed in Idaho, residents from Jackson, Wyoming (100 miles away) called for the Idaho facility to hold public meetings across the border in Jackson. When Idaho DEP refused, the residents of Jackson sued the Idaho DEP, halting progress on the new facility.

Barriers to Implementation

Current barriers to implementation include an uncertain future for DOE facilities. Even though a facility is currently being built, there are other facilities that EPA says should not even be opened. Since the baseline changes so frequently, facilities are unsure whether they will be operating 5 years from now.

There is also no regulatory driver to install and operate monitoring technologies at facilities. EPA is not requiring facilities to use these technologies. Facilities are also fearful that CEMs will eventually be tied to waste feed cutoffs and that their systems could be shut down if these are ever exceeded. CEM use is also hindered by the lack of demonstrated performance in the US, although there have been a number of applications in Europe. As is often the case with limited government budgets, cost is a major issue and taxpayers are not willing to spend the extra money for these systems. There are also significant reliability and maintenance issues.

Dr. Priebe ended his presentation by discussing his desires for the future, including testing CEMs at operating facilities. DOE has tested a CEM in Oak Ridge and, if the funding is approved, DOE plans to perform a longer test (4 to 8 months) at an incinerator in Oak Ridge, Tennessee next year. Dr. Priebe would also like to work with: 1) EPA to define specific performance goals and levels of acceptability; and 2) permittees to develop a phased approach to implement operation.

Manual Methods for Measuring Total and Speciated Mercury

Presented on September 13, 1999 by John Bosch, US EPA, OAQPS Emissions Measurements Center (EMC)

Mr. Bosch's presentation was divided into two parts. The first part discussed EMC's impact on mercury monitoring methods and programs, namely "who they are, what they do, and why they do what they do." The second half discussed the manual methods for measuring mercury and their applicabilities.

EMC

EMC is in the business of approving emission measurement methods and performance specifications for regulatory purposes. Although many of the local, State, and regional regulatory and permitting agencies negotiate their own emission methods, performance specifications, etc, EMC is often asked to approve, certify, and/or review the methods, technologies, or performance specifications implemented by these agencies to comply with State/Federal regulations and to address permitting authority questions. (Note: Periodic monitoring requirements are responsible for 50 to 80% of the difficulties/decisions associated with the permitting process.)

EMC is located within the Emissions Monitoring and Analysis Division of OAQPS. EMC's "sister groups" within Emissions Monitoring and Analysis Division focus on emission inventories, ambient air monitoring, and modeling. These organizations are tasked with approving nationwide processes for modeling or strategy development (e.g., AP 42) based on research obtained from a variety of internal and external sources. Furthermore, many of the models discussed thus far come from research developed through the modeling group. The ambient monitoring group is responsible for defining approximately 8 million dollars of ambient monitoring of toxics throughout the States, 5 million of which is scheduled to occur this year. Individuals with suggestions regarding "what needs to be done, where, and when" were encouraged to contact the monitoring group and those interested in formulating emission factors were encouraged to contact program representatives in the early planning stages so that the factors can be added, for example, as an approved method for emission inventories.

EMC performs a number of functions. The EMC group conducts testing on a number of source categories in order to obtain data that regulators can use to develop standards and requirements. It also advises the regulators on available compliance monitoring techniques and technologies. EMC also develops new emission methods and performance specifications although, in the future, it plans to concentrate on fostering advances in emission monitoring technologies through collaborative efforts with the DOD, academia, and grant programs. EMC has official authority, delegated by the Administrator, to approve new methods and emission monitoring performance specifications. This authority interfaces with other programs, such as EPA's ETV Program and DOD's Inductively Coupled Argon Plasma (ICAP) Program.

EMC's primary customers are the emissions Standard Division within OAQPS (which is responsible for developing the regulations), OSW, the Office of Enforcement and Compliance Assurance, and State and local permitting authorities. EMC engineers are also working on the ASTM committee for ASTM Test Method D 22-03, which addresses ambient and emissions monitoring. Whenever possible, EMC approves ASTM methods for use in compliance monitoring for Federal and State

environmental regulations. In fact, ASTM methods for opacity, electrical chemical monitoring, NOx monitoring, etc., have already been incorporated in EMC regulations.

Mr. Bosch encouraged those developing new emission monitoring methods or technologies and seeking EPA approvals in the future to get EMC involved early in the approval process (i.e., during test plan development).

Manual Methods for Measuring Total and Speciated Mercury

EPA currently employs four manual methods for measuring mercury: Methods 29, 101, 101A, and 102 for measuring total mercury and the Ontario Hydro Method (draft) for measuring speciated mercury. Method 101A was specifically developed for NESHAP in 1991 to measure mercury at sewage sludge incinerators. In contrast, Method 29, which measures multiple metals and mercury, was revised from an existing method (i.e., Method 5) in 1996. The Ontario Hydro method was developed outside EPA for coal fired sources and is used primarily for the ICR project. Once this method is approved by ASTM, it could be incorporated by reference by EPA as an approved manual method for measuring speciated mercury. All of these methods are available on the EMC website at www.epa.gov/ttn/emc. (Note: EMC is amenable to modifying any of its methods or performance specifications, assuming it agrees with the intent of the change and is involved in the process of designing and implementing the changes.)

After noting that all of these methods employ CVAAS and are extractive and isokinetic with stack traverse, EPA Method 29, EPA Method 101A, and Ontario Hydro Method sampling trains were briefly discussed. Mr. Bosch then noted that detailed instructions of the various components/steps in these trains are available on the EMC website.

Mr. Bosch closed by noting that a significant amount of work and funding has been invested in developing and testing the Ontario Hydro Method. Although this method is not perfect, there is much information available on how well it performs including significant quantities of field test data. Since this method is only applicable to coal-fired power plants, field testing and validation testing would need to be performed before EMC could approve using this method for other source types.

CEMs for Measuring Total and Speciated Mercury

Presented on September 13, 1999 by Nina Bergan French, Sky+ Inc.

Dr. French began by briefly listing the following topics to be discussed during her presentation: advantages of mercury CEMs; who makes them; how they work; how to use them; characteristics of speciating mercury CEMs; CEM cost/benefits (and how to put a dollar value next to a facility's decision to utilize a CEM); how mercury emission CEMs compare to multimedia CEMs; and how a facility and EPA can work together to implement these systems.

Advantages of Mercury CEMs

The advantages of mercury CEMs include:

- Real-time emission data
- Direct pollutant measurements
- Less reliance on waste feed characterization
- Operational data for system optimization.

Who Makes Them

Currently six European vendors (mostly German) offer commercially available mercury CEMs. These vendors include: Seefelder Messtechnik; Sick Instruments (which has taken over Perkin Elmer/Bodenseewerk); Opsi, Inc; Semtech Metallurgy AB; Verewa (i.e., Durag); and PS Analytical. Several CEMs are also currently under development including a microwave-based technology for coal fired utilities from Princeton Plasma Physics Lab and a surface acoustic wave sensor technique from Sensor Research and Development, Inc. Tennessee Valley Authority and ADA Technologies are also developing CEMs, however, these companies are not currently funded. Finally, Techran has an ambient monitor which could possibly be used as a CEM.

How They Work

In general, CEMs can be distinguished by the detection systems used to measure mercury. These methods include: CVAA: in-situ UVDOAS; AES; and LIFS for multiple metals. Although the majority of detection systems employ CVAA, this method only measures elemental mercury and is relatively expensive. Also, since many systems (e.g., CVAA) can only measure elemental mercury, a conversion step may also be needed to convert the speciated mercury (which has already been separated from interferences) into elemental mercury. In addition to wet chemistry, dry chemistry or thermal cracking can be used to convert the mercury. Although wet chemistry methods are currently more common, Dr. French believes that thermal cracking methods are the "wave of the future."

How To Use Them

The following steps need to be followed to use a mercury CEM:

- Get the sample
- Convert sample to elemental mercury
- Separate vapor from particles
- Separate elemental mercury from other vapors (e.g., using a gold trap)
- Desorb elemental mercury from gold trap (e.g., using a thermal desorber)
- Detect elemental mercury
- Calibrate the detector and reactor.

This process is complicated by the fact that CEM developers rarely use the same combination of separating, converting, and measuring subsystems.

Speciating CEMs

When addressing the question "What is a speciating mercury CEM?", it is important to note the confusion over the term "speciating". According to Dr. French, speciating CEMs "measure" the difference between elemental mercury and total mercury (i.e., the difference in the amount of total mercury that is not elemental). Since most mercury CEMs only measure total mercury, a conversion step must be used to change non-elemental mercury to elemental mercury, if the detector used in the CEM can only measure elemental mercury. As a result, measurements must be taken before and after the conversion step in order to be able to calculate the difference between elemental and total mercury.

The need for speciating mercury CEMs was then questioned. It is assumed that these units will be based on mass-spectrometry methods or laser-based techniques (e.g., photo-dissociation and fluorescence). As a result, they will probably be expensive, complicated, time-consuming to operate, and pose a high technical risk. Furthermore, before proceeding with development, it is important to first determine whether real-time chemical speciation data are needed. To do this, scientists, engineers, and regulators need to address the following questions/issues:

- Is chemical speciation a transient phenomena and does speciation change with time?
- Do emissions vary with facility conditions (feed, temperature, pressure, etc.)?
- Can chemical speciation be inferred from "sample-and-analyze data"? Is it possible to infer these data by coupling total speciating monitors with Ontario Hydro Method data?
- Is it worth the cost/development time?

CEM Performance

The following sources of CEM performance data were then identified:

- 1997 DOE/EPA mercury CEM long-term test
- 1997 DOE/EPRI mercury CEM tests at the University of North Dakota EERC
- European TUV certification test results (five CEMs have been tested thus far)
- European field installation data
- Direct discussions with vendors.

Based on the TUV certification tests, Sick Instrument's CEM (MERCCEM) appears closest to meeting US performance requirements. Unfortunately, however, this system is complex (it uses a wet conversion system) and is expensive to operate. Ideally, simpler and less expensive alternatives which utilize dry conversion chemistry and other relatively simple techniques [e.g., batch X-ray fluorescence (XRF) or simple AES] need to be developed. In fact, a number of companies (Seefelder Mebtechnik and others) have already replaced their wet chemistry conversion systems with dry chemistry processes. Furthermore, SRI International has also developed a "2-laser in-situ system" which measures particle/vapor partitioning and concentrations in the part per trillion (ppt) range.

Costs/Benefits

Dr. French then provided the results of a cost/benefit analysis for facilities that voluntarily implement CEMs. Based on this analysis, these facilities could realize a total cost/benefit of 70 million dollars on an annualized basis, not including savings associated with improved public relations and reduced lawsuits. These gains were associated with reduced feed characterization cost, improved

throughput, and avoided upgrade costs. With the public relations benefits, gains could be upwards of 100 million dollars.

Mercury Emission Versus Multimedia CEMs

In general, multimedia CEM systems are just combinations of other measurement techniques [e.g., inductively coupled plasma (ICP) and AES; laser and AES; microwave and AES; spark and AES; and XRF]. Since these units do not use CVAA, they rarely rely on separation or conversion techniques. Furthermore, most multiple metal CEMs have not been tested for mercury and are usually more expensive to use than dedicated mercury CEMs.

Implementation

Dr. French closed with the following suggestions regarding implementing mercury CEMs:

- Develop realistic performance specifications - Revisit daily absolute calibration, on-site calibration, and calibration standards.
- Perform validation testing at realistic facilities - Compare the results of these tests to EPA requirements, which still need to be defined.
- Perform site specific cost/benefit analyses - These data allows facilities to make low-risk decisions about the costs/benefits of CEMs.

Even on a voluntary basis, the likelihood of success for any of these techniques is high.

Industrial Applications of Ultraviolet DOAS Systems for Mercury Measurements

Presented on September 13, 1999 by Carl Kamme, Opsis Inc.

Mr. Kamme began his presentation by describing a DOAS system. During operation, light [in the deep ultraviolet (UV) to infrared range] is sent from a light emitter mounted on the side of the stack through the stack to a receiver mounted on the other side of the stack. The beam is then transmitted from the receiver through a fiberoptic cable to an analyzer containing a multiplexer and a spectrometer. Elemental mercury concentrations are calculated by applying spectrometer measurements taken approximately every 0.01 seconds to the Beer-Lambert Law, which states $I_2 = I_0 e^{-c\alpha_2 l}$ and $\ln(I_2/I_1) = c(\alpha_1 - \alpha_2)l$. Since measurements are based on the responses that occur as the light passes through the monitoring path (e.g., stack), sample collection and conditioning systems are unnecessary.

Next Mr. Kamme described the configuration used to span and zero calibrate the DOAS system. During system calibration, a reference gas is sent through the calibration bench and calibration cells (with mercury vapor pressures), and vented to the outdoors. Calibration measurements are taken across the length of the calibration bench, similar to how measurements are taken across a stack. Although the schematic showed an external manual calibration system, Mr. Kamme noted that some systems have integrated calibration systems within their systems. Mr. Kamme then noted that the calibration systems are strongly temperature dependent.

DOAS applications include: power plants, waste incinerators (to mainly monitor mercury), sulphuric acid production, chemical industry, mineral wool production, cement industry, fertilizer production, aluminum smelters, and steel mills. According to German standards, these systems must comply with a minimum mercury measurement range of 0 to 150 micrograms per cubic meter ($\mu\text{g}/\text{m}^3$) and a minimum measurement time of 10 seconds when installed on boilers above a certain size. These minimums also comply with the US EPA requirements. In the US, however, installations are certified according to 40 CFR Part 60 and 40 CFR Part 75.

Mr. Kamme then summarized performance data (Method 29) obtained using an AR 600 Analyzer at a MWC in Florida. Results were provided for elemental mercury and sulfur dioxide. For mercury, the maximum measurement range for a 1 m path was 0 to 1,000 $\mu\text{g}/\text{m}^3$, the lowest TUV-approved measurement range was 0 to 150 $\mu\text{g}/\text{m}^3$, the minimum detectable quantity for a 1 meter path and 30 seconds was 3 $\mu\text{g}/\text{m}^3$, and the zero drift for 1 meter path maximum per month was +/- 6 $\mu\text{g}/\text{m}^3$.

Similar performance data were also reported for parameters regulated in Europe according to German standards for waste incinerators. In this configuration a combination of UV (AR600) and infrared (AR650) spectrometers are used to measure nitrogen oxide, nitrogen dioxide, sulfur dioxide, ammonia, water, hydrogen chloride, hydrogen fluoride, carbon monoxide, carbon dioxide, and mercury.

When DOAS and Method 29 elemental mercury concentrations measured over 4 days at the stack of an incinerator were compared, elemental mercury concentrations obtained using Methods 29 were higher than the DOAS results on the first and last day of the test and lower on the days in between. Comparison of sulfur dioxide and mercury concentrations obtained hourly over an 8-day period

indicates that there is some correlation between sulfur dioxide and mercury concentrations, frequent variations complicated the comparison.

Mr. Kamme then discussed the application of a heated DOAS CEM which used an elemental mercury converter to monitor total mercury at a chlor-alkali factory. During this application, the DOAS system was set up to continuously monitor elemental mercury concentrations ranging from 0 to 500 $\mu\text{g}/\text{m}^3$ over an optical path length of 10 to 100 meters. Since the unit was installed in an area containing strong magnetic fields, the DOAS system also had to be electromagnetically protected.

Mr. Kamme concluded his presentation by stating that the DOAS system provides reliable elemental mercury measurements in stack monitoring applications. After noting that the DOAS system can be modified (e.g., using a converter and employing an extractive mode) to monitor total mercury, Mr. Kamme also noted that the DOAS system can be used to provide continuous in-situ measurements of elemental mercury in chlor-alkali factory applications.

Problems/Issues Associated with Mercury Measurements

Presented on September 13, 1999 by Thomas Brown, DOE, NETL (formerly FETC)

Mr. Brown's presentation addressed a variety of issues associated with sampling mercury in flue gas from coal-fired utilities, including "high particulate loadings prior to the initial APCD, and low loadings after the primary particulate control device" (70% of the industry), and emission measurements "at the stacks of wet FGD systems" (approximately 30% of the industry). Although, in general, greater than 98.5% of the particulate from coal-combustion is removed by the APCDs, the fine particulate that escapes should be considered before mercury CEMs can be used for compliance in the future. Mr. Brown then noted that the data to be presented during his presentation was collected as part of the air and waste management critical review on mercury measurement and control written by NETL, formally FETC. (Brown, T.D., Smith, D.N., Hargis, R.A., and O'Dowd, W.J., "Mercury Measurement and Its Control; What We Know, Have Learned, and Need to Further Investigate," Presented at the Air & Waste Management Association's 92nd Annual Meeting and Exhibition, St. Louis, Missouri, June 1999.)

Mercury Measurements

Measuring mercury from coal-fired power plants and other sources is complicated by the fact that mercury concentrations need to be measured to parts per billion (ppb) or even ppt levels. Measurement methods are further complicated by the presence of sulfur dioxide, hydrogen chloride, and other vapor-phase compounds. Mr. Brown then noted that mercury speciation also plays an important role, as demonstrated by the impacts associated with volatilization, oxidation, and particulate reactions (e.g., the adsorption and catalysis of elemental mercury to oxidized mercury). It is important to consider the different stages impacting the mercury species and whether the mercury is in the vapor or particle-phase.

The distribution of different trace metals associated with the particulate (i.e., less than 5 microns in diameter) obtained from the stacks of two utilities (a facility firing a western or PRB coal and a facility firing an eastern bituminous coal) was then presented. The first facility used a fabric filter for particulate control and the second facility used an ESP system, respectively. The unit with the fabric filter produced approximately 1,000 pounds per year of HAP as compared to the facility with the ESP system, which produced 6 tons per year. (Note: The ESP system was under-operated and was eventually replaced with an ESP system which is 99.5% effective at removing particulate.) The distribution demonstrated that fine particulate is being emitted at low levels and has trace levels of metals associated with it. When developing monitoring methods for mercury it is important to address particulate impacts, since particulate matter can adsorb mercury and/or oxidize elemental mercury, even when present at levels equal to or below the current New Source Performance Standard (NSPS) level for particulate emissions of 0.03 pound per British thermal unit.

After noting that DOE funded researchers have determined that the presence of iron in the fly ash and certain iron-based compounds impacts the oxidation of elemental mercury (especially in eastern coals), percent elemental mercury results captured and oxidized across a fixed bed over time were then presented. These data were collected from a study in which elemental mercury in a simulated flue gas was delivered to a fixed bed containing a specific iron-based catalysts. The data showed that mercury adsorption was initially observed (i.e., within the first 200 to 400 hours of the test), but eventually stopped. Not surprisingly, a similar, but opposite trend (a "mirror image") was observed

as the elemental mercury was converted to an oxidized form. Based on this study and others, it was concluded that an oxidized form rather than elemental mercury is emitted once the equilibrium adsorption capacity of the media in the fixed bed (certain iron-based compounds, fly ashes, etc.) is reached. This conclusion may have a significant impact on future mercury measurements, particularly for facilities that need to measure total mercury concentrations at ppt or ppb levels. Particulate impacts also need to be better understood in order to develop appropriate control strategies/technologies for the coal-fired utility industry, if regulations are required.

Mr. Brown then presented mercury data from a power plant which burned PRB coal. The data represents the mercury as measured using two versions of the Ontario Hydro Method. The first version of the Ontario Hydro Method (OH-1) was operated normally, with the nozzle turned in the direction of the flow of flue gas (and fine particulate). In the second version of the Ontario Hydro Method (OH-2), however, the probe was turned opposite to the flow of the flue gas and a particulate matter 10 (PM 10) cutter and an oversized nozzle were used to minimize the amount of fine particulate entering the nozzle. Although the OH-1 filter had an order of magnitude more particulate than the OH-2 filter, particulate from both filters contained particulate-bound mercury. It should be noted, however, that it is not known if the mercury was associated with the particulate as it entered the filters or if the mercury was adsorbed on the particulate as the particulate was collected on the filter. Further, the observed grain loadings of the OH-2 filter are probably indicative of the grain loadings on the outlet (i.e., extremely low); this could impact particulate and vapor-phase concentrations while utilizing mercury CEMs. Since CEMs only measure vapor-phase mercury, not particulate-bound, this could "bias low the amount of mercury exiting the stack." Mr. Brown then noted that coals and fly ashes with relatively fine particulate are more likely to exhibit higher particulate impacts/effects (e.g., adsorption and conversion of elemental mercury), but more research is required to reach a final conclusion.

Mr. Brown then compared the percent of elemental mercury oxidized and/or adsorbed across a fixed bed for a variety of fly ashes (subbituminous or PRB, bituminous, lignite, and oil-fired). Results obtained from two locations within an ESP system (i.e., from the first ESP field, where coarser particles are collected, and from the fifth ESP field, where fine particles are collected) indicate that the bituminous coal fly ash collected from the fifth field indicated more oxidization (and adsorption) than the fly ash from the first field. These results support earlier findings indicating that finer particulate may have a tendency to adsorb and oxidize more mercury than coarser particles. Mr. Brown then stressed that this conclusion needs to be further addressed from both a method utilization (e.g., for Method 29 or the Ontario Hydro Method) and compliance perspective (CEMs for coal fired utilities, HWCs, MWCs, and other sources).

Carbon in the fly ash may also cause difficulties when collected at the front-end of the mercury CEM sampling probe. The sorption capacities for both elemental mercury and mercuric chloride at different LOIs were then presented along with a comparison of the fly ash results obtained for a highly mercury adsorbent and an oxidizing activated carbon (FGD carbon or LAC from a lignite coal). All the tests were conducted with either mercury form being carried in a simulated flue gas to a fixed bed containing different LOI fly ashes. According to Mr. Brown, the LOI for this fly ash varied from 0 to 82% with the fly ash being collected from different locations within the power plant. The data presented imply a correlation between an increase in LOI and an increase in mercury (both elemental and mercuric chloride) adsorption. Like the previously presented study results, the data indicated the possibility of another fly ash constituent having an impact on obtaining accurate total measured mercury concentrations. Again, Mr. Brown noted that this impact needs to be addressed and resolved if mercury CEMs are to be required for compliance by coal-fired utilities, since a

significant amount of mercury could be captured on the sampling probes of CEMs. The captured mercury would need to be accounted for when trying to meet ppt and ppb level emission requirements.

Mr. Brown then presented sulfur dioxide concentrations from the inlet and outlet of a FGD system installed at a power plant. After noting that the mercury concentrations appeared to vary with the sulfur dioxide and other flue gas constituents, Mr. Brown mentioned NETL's ongoing efforts to develop correlations and trends for mercury to these and other flue gas constituents. Furthermore, since sulfur dioxide is problematic for most mercury CEMs, Mr. Brown stressed that conditioning systems need to be developed which can remove the sulfur dioxide and other interferences before the flue gas is delivered to the detectors (which have been proven to work well in the absence of these gases). Finally, in order to develop speciating mercury CEMs or total mercury CEMs, either: 1) a conditioning system needs to be developed which can convert total speciated mercury into elemental mercury; or 2) the development of a detector which can measure speciated forms of mercury providing total mercury measurements in the presence of the interfering gases (although this may prove much more expensive than developing a conditioning system).

Mr. Brown closed by noting that mercury CEM detectors work well in the absence of the interfering gases, but that "front-end systems" need to be developed which can remove vapor-phase compounds (e.g., hydrogen chloride, hydrogen fluoride, sulfur and nitrogen oxides, and other gases). These compounds could preclude effective operation and accurate measurement of total mercury concentrations for most of the current suite of mercury CEMs under development. The conditioning systems developed to remove these compounds need to work without altering the form of the mercury or the total concentration of the mercury. After reiterating the importance of particulate-phase mercury measurements (particularly for coal-fired utilities), Mr. Brown then noted current difficulties associated with effectively calibrating mercury CEMs (calibration is not typically problematic with other CEMs, for example sulfur dioxide or nitrogen oxides). According to Mr. Brown, accurate and stable calibration techniques need to be developed for both elemental and oxidized mercury (e.g., mercuric chloride) at the ppb and ppt levels, before CEMs can be used as a compliance tool. Although some headway has been made (e.g., regarding particulate impacts and field calibration techniques), acid gases and other interferences need to be addressed before a workable mercury CEM can be deployed which is robust, near maintenance free, and accurate for measuring mercury in the ppt and ppb range from coal-fired utility flue gas streams.

Merits of Dilution Source Sampling: Measurement of Mercury Emissions

Presented on September 13, 1999 by James Schauer, Water Chemistry Program, University of Wisconsin-Madison

According to Dr. Schauer, dilution source sampling techniques have been well developed to address fine particle issues that have received significant attention with the new fine particle standard. Although in general these methods have not been used for mercury emissions testing, Dr. Schauer anticipates that this approach will be used more frequently. This increase is expected in part because the sampling method can easily be modified for mercury measurements, but also because the scientific and regulatory community needs a more advanced sampling technique to allow it to be able to characterize particle-phase mercury data and collect complete mercury speciation data.

Motivation

Measurement of emissions from air pollution sources is often motivated by: 1) a need to comply with regulatory or process control requirements; or 2) a desire to relate emissions to the presence of pollutants in the environment (via their application in receptor and transport models). Furthermore, the emissions from many important air pollution sources are injected into the atmosphere in hot exhaust plumes. Significant physical and chemical sampling artifacts associated with chemical reactions, gas/particle partitioning, and particle size distribution can also occur during the collection of these hot stack emissions.

Objectives of Source Emission Characterization

Source emission testing is needed to obtain emissions measurements which are: 1) chemically and physically consistent with ambient measurements; and 2) are integrated with broad-based emissions characterization measurements (both chemical and physical). In addition to providing a real-world measure of air pollution (via portable samplers), source emission tests can also provide data that can be used as inputs to state-of-the-art air pollution models to develop a description of the pollutants located in the downwind plume.

Portable Dilution Source Sampler

Portable dilution source samplers can be used to take real-world measurements in the field. The dilution sampler turbulently mixes the hot exhaust emissions with cleaned dilution air to bring the diluted exhaust to near ambient pressure and temperature conditions, simulating the atmospheric dilution that occurs downwind of the plume. The diluted exhaust passes through a residence time chamber where the semi-volatile compounds are allowed to partition between the gas and particle phases. The diluted exhaust can then be sampled from the residence time chamber by the same techniques used for ambient sampling. In addition to being modular and field portable, the sampler can also be used for ultra-trace level measurements.

Dilution source sampling has been used extensively to sample for organic emissions, including particle-phase organic compounds [by gas chromatography/mass spectrometry (GC/MS)], semi-volatile organic compounds or SVOCs (by GC/MS), and volatile organic compounds (VOCs). It has also been used to sample for the bulk chemical composition of particulate matter (including trace metals by XRF and organic and elemental carbon), particle size distribution measurements (including

particle size- resolved chemical composition using MOUDI impactors), and to perform advanced real-time single-particle analyses using an Aerosol Time-Of-Flight Mass Spectrometer (ATOFMS).

The dilution source sampler was originally developed at Caltech for fine particle emissions. It has been adapted over the last 5 to 6 years to sample semi-volatile, gas-phase pollutants, and, most recently, to perform ultra-trace metal analyses. During operation, a sample is withdrawn from the stack through a heated inlet line that is measured with a Venturi meter. Downstream of the Venturi meter the hot exhaust emissions are turbulently mixed with cleaned-up dilution air. The dilution air is cleaned with a high efficiency particle adsorption (HEPA) filter and an activated carbon bed. Most of the diluted exhaust is expelled across a high volume filter where a "high volume of mass is collected." A portion of the diluted exhaust is pulled into the residence time chamber upstream of the high volume filter. The diluted exhaust resides in the residence chamber for approximately 1 minute prior to being sampled.

The following sections of the sampler were then briefly addressed:

- Dilution Air Conditioning Zone - The dilution air condition zone is composed of a variable speed blower, cooler, HEPA-filter, activated carbon bed for removal of contaminants, flexible steel ducts, and an orifice meter (1,000 liters per minute). In general, the cooler is not needed for most operations.
- Sample Inlet Zone - Near isokinetic sampling is performed in the sample inlet zone using a PM10 cyclone to remove larger particulate matter. Stack probes (80 centimeters up to 2 meters) in the sample inlet zone utilize automated temperature controls to heat the probes to 5 to 10 °F above the stack temperature. The inlet zone is also equipped with a Venturi meter (to measure the flow rate of the stack gas entering the system), pressure tapes, and temperature controls.
- Turbulent Mixing Zone - Stack gas mixing with the dilution air typically occurs at a very high Reynolds number (e.g., 10,000). Sample and dilution air flow rates typically range from 10 to 50 and 750 to 1,200 liters per minute, respectively. Depending on the sampling requirements, the sampler can be operated over a dilution range of 15:1 to 200:1. Finally, most of the air is expelled outside of the high volume filter and the remainder proceeds to the residence time chamber.
- Residence Time Chamber - The 12 inch diameter by 54.5 inch tall residence chamber yields a 60 second residence time at a sample flow rate of 100 liters per minute. It is also possible to extract samples from parallel sampling systems.
- Sample Collection Zone - Samples can be withdrawn from the residence time chamber using ambient air sampling equipment (of virtually any type), including real-time particle measurements and particle size distributions. Furthermore, sample rates control residence times.
- Particle-size Distributions - Real-time particle size distributions can also be performed using the Digital Machine Automation/Computer Numerical Control (DMA/CNC) combination and larger particles can be counted using a laser optical particle counter. A pair of MOUDI impactors can also be used to measure: 1) mass and chemical composition as a function of size; 2) elemental and organic carbon; 3) trace metals by neutron activation; and 4) inorganic ions by ion capture (IC) and colorimetry. Single particle analyses can be performed using an ATOFMS.

Source Tests

The dilution source sampler has been used to test the following sources:

- Catalyst-equipped gasoline-powered vehicles

- Non-catalyst automobiles
- Diesel trucks
- Food cooking operations
- Cigarette smoke
- Fireplace combustion of wood
- Wood burning stoves
- Spray coating operations
- NG-fired boilers
- Fuel oil boilers
- Coal-fired boilers
- Roofing tar pots.

A coal-combustion test is scheduled for the Fall 1999; unfortunately this test does not include mercury measurements.

Sampler Configurations

The versatile sampler has been used to collect samples from a number of sources using a number of configurations, as described below:

- Stack sampling from boilers, incinerators, and fireplaces
- Motor vehicle sampling using a pre-dilution sampler and dynamometer tests
- Pre-diluted open source sampling associated with agricultural burning
- Pre-diluted closed source sampling associated with cigarette smoke, candle smoke, and resuspended particulate matter.

Performance Evaluations

Dilution samplers have undergone extensive performance evaluations to measure particle losses, comprehensive blank tests, and to assess SVOCs and particle losses. Dilution samplers have also been tested for comparison to other source sampling measurements [e.g., motor vehicle VOCs and trace gases from NG boilers] and for sampling equipment characterization.

Application of Mercury Emissions

In order to apply the dilution sampler to mercury emissions, the sampler will need to be Teflon-coated and the dilution air cleaning system may need to be modified. Furthermore, virtually any type of ambient mercury sampling equipment would need to be installed on the system. Opportunities are also available to measure total mercury, mercury speciation (of both the gaseous and particulate phases), and particulate mercury (as a function of size) using dilution samplers.

Conclusions

Dr. Schauer concluded that dilution samplers have been shown to be an effective strategy for measuring and speciating emissions from air pollution sources. Furthermore, the application of a dilution sampling strategy for the measurement of mercury emissions is expected to enhance emissions monitoring efforts by allowing:

- Direct application of ambient sampling and analysis techniques to stack sampling (e.g., gaseous and particulate species)
- Integration of mercury emissions data with other advanced emissions characterization efforts that will ultimately aid in mercury modeling efforts.

Mercury Measurement Research at the EERC

Presented on September 13, 1999 by Dennis Laudal, University of North Dakota EERC

Initial EERC pilot-scale testing used EPA Method 301 protocols to validate EPA Method 29 as a mercury speciation method. This testing, which was funded by EPRI and the DOE, took place on the inlet side of a fabric filter (i.e., the high dust side) during Blacksville bituminous coal combustion. (Note: EPA Method 301 uses a quatrain, four samples, and six repetitions. The resulting data are compared internally to determine the bias and precision.) The results clearly showed that the elemental mercury added to the flue gas stream was not being measured as elemental mercury by EPA Method 29.

The EERC pilot-scale test combustor was then described; it is composed of an electric preheater, combustor, heat exchanger, pulse-jet baghouse (containing 99% efficient Gore-Tex bags composed of Teflon), and a cyclone. The combustor burns approximately 75 pounds of coal per hour and generates 130 standard cubic feet per minute (scfm) of flue gas.

Before EERC could conclude that EPA Method 29 was not correctly speciating mercury, it first had to rule out whether "something else was going on." As a result, EERC began examining the following mercury speciation methods: the Mercury Speciation Adsorption (MESA) Method, the Tris-Buffer Method, the Acetate-Buffer Method, and the Ontario Hydro Method. After initially examining these methods, EERC returned to the lab to further study fundamental mercury reactions, measurements, and controls at the bench-scale level. EERC found that mercury had a strong tendency to interact with sulfur dioxide, nitrogen dioxide, and hydrogen chloride.

EPA Method 301 provides a statistical basis for determining precision and bias of the method, but not method accuracy. It is an acceptance method which is defined by a percent relative standard deviation (RSD) of less than 50% and a bias correction factor of greater than 0.7 but less than 1.3. While verifying the Ontario Hydro Method, EERC noted that mercury injected into the system at the outlet of the baghouse was unchanged by the process. This finding enabled EERC to measure method accuracy.

The Ontario Hydro Mercury Method is a complicated method which uses a series of potassium chloride, peroxide, and permanganate impingers. This method is currently being used in the field to generate legal data through the ICR. The method is on the EPA web page at www.epa.gov/ttn/emc/prelim.html.

The Ontario Hydro Method is a very difficult and complex method, requiring substantial experience or training to ensure high quality data. A correction action plan is needed to ensure good data; this plan is usually based on field blank and field spike results. An independent field audit also helps ensure quality results. There are currently a number of labs that are qualified to observe the testing.

Mr. Laudal closed by noting that the following mercury CEMs have been tested at EERC's facility: the Perkin Elmer MERCEM, the PS Analytic Sir Galahad, and the Sintac Mercury 2000. Furthermore, EERC has also conducted bench-scale, pilot-scale, and field tests to examine mercury control techniques at a power plant in Michigan (with CEMs), the 3M Oak power plant, and at a plant

in the Midwest. The bench-scale tests were performed using the PS Analytical and Sintac CEMs. Field tests were performed using the Ontario Hydro Method.

Mercury Measurement Research at EPA NRMRL

Presented on September 13, 1999 by Jeffrey Ryan, US EPA, NRMRL

EPA NRMRL maintains a program to conduct fundamental and applied combustion Hg emissions control research. High quality bench-, pilot-, and field-scale mercury measurements are a critical component of this research. To support this goal, EPA NRMRL has established a separate research component specifically designed to evaluate manual and CEM methods used to measure speciated and total mercury. NRMRL has also recently expanded its "mission" to provide measurement support to the Program Offices and Region Offices.

Research Approach and Interests

The main goal of EPA NRMRL's Hg measurements research is to test the application and performance of manual mercury methods and determine how well they perform under diverse conditions (e.g., in-house research/field demonstrations, coal/chlorinated wastes). Although EPA NRMRL is primarily focusing on chlorinated waste combustion sources (e.g., HWCs and MWCs), NRMRL is also targeting the development of quality tools to evaluate speciating and total mercury CEMs. NRMRL is also investigating techniques for measuring other mercury species (e.g., elemental mercury), particularly using direct measurement techniques. EPA NRMRL has also tried to use and benefit from the University of North Dakota EERC data and to further the abilities in speciating research for utility boilers and coal combustion.

Understanding Manual Methods

Two years ago, EPA NRMRL began investigating the fundamentals of high temperature mercury speciation in combustion systems. In an effort to better understand this process, EPA NRMRL attempted to use several methods [e.g., Draft Method 101B, Ontario Hydro Method, Alkaline Mercury Speciation (AMS) Method] to speciate mercury during these pilot-scale combustion experiments. Unfortunately, only poor results were obtained. After performing some fundamental testing, EPA NRMRL concluded that the poor results could be attributed to the oxidation of elemental mercury in the sampling trains. Since NRMRL was primarily concerned about the reactivity of chlorine and elemental mercury, dynamic spiking tests with chlorine and elemental mercury were performed to determine where the oxidation was occurring. These tests indicated that oxidation was occurring in the impinger solution.

This research expanded to the examination of potential interferences and oxidation properties in solution during a series of liquid-phase mercury oxidation tests. During these tests, different concentrations of sulfur oxides (SO_x) and nitrogen oxides (NO_x), and hydrogen chloride and chlorine were used. Mercury was measured during these tests using the Ontario Hydro Method and AMS Method. Based on the results, EPA NRMRL concluded that: 1) NO_x and SO_x by themselves did not "present a significant artifact" on the methods; and 2) liquid-phase oxidation of elemental mercury as much as 50% was observed as a function of increased chlorine concentrations (e.g., from 1 to 10 to 100 ppm). Furthermore, although less pronounced reactions were observed when HCl and SO₂ were added to the 10 ppm chlorine tests, no oxidation occurred when sodium thiosulphate was added to a 100 ppm chlorine solution. Since the most recent update to Method 26 calls for the addition of sodium thiosulphate to the alkaline impinger, this was a very significant finding to take into the field.

Future pilot-scale combustion experiments (under chlorinated waste conditions) are also planned to evaluate the effectiveness of sodium thiosulphate addition and to compare the Ontario Hydro Method and Method 29. Although it has already been shown that there is a positive bias of the oxidized Hg form using Method 29 under coal combustion conditions, EPA NRMRL is interested in examining how these methods perform under chlorinated waste combustion conditions. Ultimately, EPA NRMRL intends to use Method 301-type experiments (with dynamic spiking) to evaluate the suitability of the Ontario Hydro Method under pilot-scale chlorinated waste combustion conditions. Although preliminary information indicates that the Ontario Hydro Method may be suitable for performing speciated Hg measurements from chlorinated waste combustion conditions, further research is needed to substantiate this belief.

Tools To Evaluate Measurement Performance

EPA NRMRL efforts to evaluate measurement performance include the following:

- Characterizing the overall measurement quality (calibration, digestion and capture)- In addition to comparing the Ontario Hydro Method and Method 29, EPA NRMRL is also investigating appropriate acceptance criteria.
- Developing elemental mercury and mercuric chloride dynamic spiking systems for manual trains and CEMs- Efforts thus far indicate that dynamic spiking with elemental mercury needs to occur beforehand and that spiking/delivering mercuric chloride will prove challenging.
- Evaluating the reliability and uncertainty of elemental mercury permeation devices Elemental mercury permeation devices may have a significant impact on the quality of CEM calibrations. Unfortunately, the evaluation of these devices has been complicated by: 1) poor/incomplete records on "perm ovens" and 2) confusion associated with the fact that permeation tubes are factory-certified using purely gravimetric methods.
- Collaborating with Spectra Gases to evaluate elemental mercury compressed gas cylinders - This work will support the development of a gas standard for calibration at several different concentrations.
- Configuring a combustion test facility for precise control of mercury concentration and species (elemental and mercuric chloride) as well as independent control of hydrogen chloride, chlorine, SOx, NOx, and moisture levels- The EPA NRMRL Rotary Kiln Mercury Measurement Test Facility is unique because it is able to exert control over the concentration and species of mercury in a combustion atmosphere as well as NOx, sulfur dioxide, hydrogen chloride, chlorine, and moisture. This facility has been used as a testing area for multiple metal CEMs. The Ontario Hydro Method performed very well during multiple tests, with replicate measurements within 5% for total mercury and 7% for speciated mercury.

Mercury CEM Evaluations

Speciating and total mercury CEMs are needed for mercury control research. Currently both Program and Regional Offices support efforts to identify and create opportunities where viable mercury CEMs can be made available for evaluation, as both a research tool and potential compliance monitor. Pilot-scale testing performed under controlled, varied, representative conditions needs to be performed, however, before testing can proceed from the lab to the field. This is an essential step in developing an effective approach to identifying and investigating problem areas and improving the probability for successful field demonstrations for chlorinated waste combustion conditions. Thus far, EPA NRMRL's approach has been to compare mercury CEM measurements (speciated and total mercury) to Ontario Hydro Method speciated measurements; this approach is consistent with the PS 12 approach. This approach also affords EPA NRMRL the opportunity to investigate issues relative to PS 12 (i.e., drift checks and interference checks).

Potential Mercury CEM Evaluations

Since past mercury CEM evaluations have been constrained by limited mercury CEM availability and funding, a cooperative evaluation of mercury CEMs during control technology research is needed. To succeed, participation must be mutually beneficial and CEM vendor participation is essential. If employed, this approach will provide an opportunity to investigate and address measurement issues in controlled, realistic combustion environments in preparation for possible field demonstrations.

Measuring Other Mercury Species

EPA NRMRL is interested in directly measuring other mercury species in addition to elemental mercury and mercuric chloride. Currently, however, EPA NRMRL is focusing its efforts on measuring elemental mercury, since very little is known about this compound and it is difficult to measure using heat diffusion methods and ionization testing. EPA NRMRL is also interested in new techniques to determine the effect of nitrogen dioxide on elemental mercury and "where it goes."

Summary

Bench-scale experiments indicate that the Ontario Hydro Method shows promise as a mercury speciating method for chlorinated waste combustion conditions; however, planned pilot-scale combustion evaluation tests (with dynamic spiking) will help determine actual suitability. EPA NRMRL is interested in evaluating viable speciating and total mercury CEMs as research tools and for potential field demonstration. Finally, it is critical to know the quality of the tools used to perform evaluations.

Use of a Dilution Chamber To Measure Stack Emissions and Near-Term Transformations of Mercury

Presented on September 13, 1999 by Eric Prestbo, Frontier Geosciences Inc.

From Flue to the Plume

There is a data gap between mercury speciation in flue gas emissions and ground-based measurements of mercury air concentrations and wet deposition. Although engineers and scientists are currently making good mercury speciation measurements in the stack, and researchers are making good ground-based measurements of mercury speciation and deposition, our understanding of the chemical and physical transformations of mercury in the near-term emission plume is limited. Filling this data gap will be critical as the process to determine the need and extent of mercury control regulations for point source combustion sources moves forward. In addition to understanding mercury transformations in the plume, the hypothesis that emissions of RGM [mercury(II)] and particulate mercury from a combustion source are efficiently scavenged by rain on a local scale needs to be experimentally confirmed. Although there are good reactive plume models for mercury point source emissions, these models are handicapped by a lack of good experimental measurements of mercury speciation in the near-term plume.

Numerous chemical and physical changes take place as emissions proceed from the stack to the plume. These changes are impacted, in part, by different conditions in the stack and atmosphere. For example, temperatures in the stack range from 70 to 175 °C, while plume temperature ranges from -30 to 38°C. Plume reaction times are also typically much longer (hours as compared to seconds) and the available deposition surfaces outside of the stack are more diverse (e.g., water, trees, soil). Further, plumes are exposed to both light and oxidants, such as ozone (at concentrations of 0 to 50 ppbv) associated with photochemical cycles in the atmosphere, both of which may influence the speciation and transformations of mercury. Condensed water is not present in the stack, while often there is immediate droplet formation as the plume forms and of course the possibility for the plume to interact with clouds, fog and rain. Particle behavior/characteristics are also more complex in the plume, particularly with regards to gas to particle conversion.

RELMAP Limitations and Data Gaps

The EPA Mercury Study Report to Congress identifies a number of current limitations and data gaps for RELMAP. In this report, EPA notes that additional data are needed, particularly local exposure assessment data. According to EPA, "there is a lack of adequate mercury measurement data near the anthropogenic atmospheric mercury sources considered in this report." Additionally, "the lack of such measured data precludes a comparison of the modeling results with measured data around these sources." To further his discussion of RELMAP limitations, Dr. Prestbo then noted that there is a large difference between the base case mercury emission profiles and the alternative case mercury emission profiles in total deposited anthropogenic data (i.e., 77.9 tons and 48.2 tons, respectively). The point being that mercury deposition to sensitive ecosystems can be strikingly different depending on the assumptions made in the model. It is the goal of the following research on mercury speciation in emission plumes to replace the assumptions made in atmospheric models with high quality experimental data.

Why Measure Mercury in Combustion Plumes?

It is important to measure mercury in combustion plumes since the conversion of mercury species is likely to occur rapidly from the stack to plume as a result of changing chemical and physical conditions. Furthermore, combustion plume data will contribute to the improvement and accuracy of atmospheric models, which will be one of the primary tools used to help determine if emission regulations are needed.

SPDC

The SPDC acts as a large inert (Teflon-coated) reaction chamber to form controlled combustion emission plumes by isokinetically introducing a small volume of flue gas (e.g., 20 liters) into a large volume (e.g., 500 to 1,000 liters). The SPDC has several variables that can be easily controlled: 1) temperature, 2) dilution ratios, 3) reaction time, 4) light input, and 5) rainwater. Both dry deposition (on the sides of the walls) and mercury washout by rainfall can also be assessed with a SPDC. This allows users to assess deposition in the environment and to identify which atmospheric mercury species are removed into aquatic ecosystems. In addition to using a mercury filter pack system to collect a sample from the chamber for particulate mercury, RGM [mercury(II)] and elemental mercury analysis, the experiment is also set up to measure (via a probe) mercury speciation in the flue gas. Total mercury in the SPDC is measured to calculate a SPDC mass balance. The capability to mass balance a SPDC experimental run is the most powerful QA assessment. All the mercury introduced must be accounted for to provide a confident data interpretation. Finally, mercury speciation is also measured using mist-chambers that can mimic cloudwater plume interactions.

An "in-stack" comparison of TGM using the MESA Method and the In-Stack Isokinetic Iodated Carbon Method (ISO-IC) following a coal flue gas plume test in Unit #8 showed very little disparity, with a relative percent difference between the means of 1.65% for 12 different events. Furthermore, an examination of the in-stack speciation [elemental mercury vs mercury(II)] using the MESA Method supports the consistency of both the method and the boiler controls. A mass balance comparing total mercury to the sum of the species measured with the SPDC showed good agreement in general. It is also possible to conclude, based on a comparison of injected and SPDC measured elemental mercury and mercury(II) data, that: 1) there was a rapid transformation of mercury(II) to elemental mercury in the simulated plume; or 2) the flue gas speciation was incorrect and nearly all the mercury entering the SPDC was in the elemental form. Furthermore, some mercury removal was observed when simulated rain was injected into the SPDC; however, the resulting values do not support rapid mercury(II) removal. Predominantly the very minor amount of RGM [mercury(II)] was seen as dry deposition and some gas-phase concentrations.

The mass balances performed for a waste incinerator were not as good as those found at Unit #8, but were reasonable. When no "rain" was added, more mercury(II) was observed in the air and dry deposition fractions than the amount injected, indicating a possible conversion from elemental mercury to mercury(II) in the plume. When "rain" was added, injected mercury(II) was nearly equal to measured mercury(II), with the majority being removed to the dissolved rainwater fraction. Furthermore, nearly all of the mercury(II) observed in the SPDC was found in the dissolved dry deposition or dissolved simulated rainwater fractions. Finally, although the absolute concentrations were low, there was significant conversion of gas-phase mercury to particulate mercury from the flue to the plume.

Conclusions

The following conclusions were made:

- The SPDC method works and is a valuable tool to further understand the probable fate of mercury emissions from combustion sources.
- Modelers need more data close to sources. SPDC experiments can provide valuable input to help refine local, regional and continental scale models as well as complement source-receptor field studies. It may be beneficial to plan for concurrent SPDC and source-receptor field studies.
- When gaseous mercury(II) is present in the flue gas, its fate is tied to dry deposition and scavenging by rain. Although this result was predicted by mercury models, it is important to confirm the models with experimental data.

Additional Research Efforts

The following SPDC research efforts were then mentioned:

- Frontier/Center for Air Toxic Metals-EERC/USDOE/EPRI in the Fall 1999 - The purpose of this study is to challenge the SPDC method using the EERC Pilot-Scale Power Plant capabilities to generate a well- characterized flue gas matrix with mercury species spiking and real-time measurements.
- Frontier/ERM/Minnesota Department of Natural Resources Event-Based Deposition Study, Summer/Fall 1999 - Rainwater samples from a waste incinerator and an eastern coal plant (i.e., the Dickerson Power Plant) will be used to confirm SPDC results showing rapid rainwater washout of mercury(II) emissions.
- Improvements in the SPDC Method - To use a Tekran 2537 and the new 1130 speciation module to obtain real-time measurements of mercury speciation in order to generate mercury species conversion curves.
- Confer with atmospheric modelers [e.g., Total Exposure Assessment Model (TEAM), RELMAP, ADOM-TCM]
- Combine SPDC experiments with flue gas control technology studies and high-frequency, local-scale, ground-based mercury speciation campaigns.

EPA Performance Specification: Optional Use of CEMs

Presented on September 13, 1999 by H. Scott Rauenzahn, US EPA, OSW

HWC Phase I MACT Rule

Mr. Rauenzahn opened his presentation by discussing the HWC Phase I MACT rule. This rule addresses hazardous waste combustion sources including incinerators, cement kilns, lightweight aggregate kilns, and others. When the MACT rule was developed, Section 63.8(f) was included to encourage alternative monitoring approaches. This section, specifically 63.1209(1) or (2), allows any alternative monitoring approach for OPLs. It also allows permits to require alternative monitoring and encourages facilities to use CEMs, if the CEMs are at least as good an indicator of compliance as the OPLs required by the rules.

The MACT rule also proposed a number of performance specifications including: PS 10 for multiple metals (MM), PS 12 for mercury, PS 13 for hydrogen chloride, and PS 14 for chlorine. Currently, however, there are no plans to finalize these specifications, mainly due to concerns whether the data quality objectives in the specifications are achievable. (Note: For mercury CEMs at cement kilns, it was found that the specifications were not achievable. PS 13, however, has been demonstrated at a MWC.) Unfortunately, without a promulgated performance specification for these monitors, performance must be demonstrated on a site-by-site basis by individual plants which chose to use CEMs.

Plans are being made, however, to finalize PS 11 and Procedure 2 for particulate matter CEMs, and Method 5i is final. (Note: PS 11 is determined based on a correlation between the manual method and the output from the CEMs, and Procedure 2 specifies how and when testing needs to be performed.) Also, the performance of particulate matter CEMs has been shown to meet the performance specifications.

Why Would a Facility Elect To Use CEMs?

Some facilities have decided to voluntarily use CEMs to evaluate compliance options. One pharmaceutical company is installing CEMs on its incinerator to assess MACT compliance and to avoid buying millions of dollars of air pollution control equipment in the future. Furthermore, facilities that install CEMs now will only need to meet a 0.08 grain particulate matter standard, which is much easier to meet than the future standard of 0.05 grain.

CEMs can also be used as particulate emissions monitors (PEMs) to identify better approaches for traditional monitoring. One study looked at PEMs on a lime kiln. It took over 600 samples to model how system variabilities affected final particulate matter emissions. With CEMs, the characterization process becomes much simpler (less samples and stack time), resulting in cost savings.

There is a need to reach out to the community and get it involved. CEM data can be used to communicate a facility's ability to stay within the limits at any given time. CEMs may also prove to be important for permitting and State statutes and regulations. As MACT starts requiring CEMs (e.g., PS 11, for particulate matter CEMs), States can be expected to become proactive about requiring CEMs. In fact, one State has already required CEMs in its regulations.

Finally, CEMs can be used to fulfill Supplemental Enforcement Project (SEP) requirements. For example, CEMs are an important alternative for a utility company with a wet stack that cannot use an opacity monitor.

Submittal of Alternative Monitoring Request

To get approval for alternative monitoring with a CEM, a facility needs to coordinate with its permitting authority before purchasing and testing the CEM to: 1) ensure that the permitting authority is agreeable to CEM use; 2) answer any questions it may have; and 3) determine what data are needed to obtain approval from the regulating agency. For some performance specifications (e.g., PS-11), the facility may also need to collect data above the emissions standard to test for possibly exceeding the standard and testing agreements. It is also important to receive approval of the demonstration approach and agree on the criteria for accepting the CEMs data for compliance before proceeding with testing.

Demonstration of CEMs

Facilities interested in demonstrating CEMs need to follow the procedures found in the promulgated performance specification. However, these facilities need to use the data acceptance criteria shown to be achievable at the facilities, rather than the acceptance criteria proposed in the specification. The timeline associated with the CEM demonstration process should be expected to take 1 to 2 years. There is a "shakedown phase" which can take 3 to 6 months, followed by a "demonstration phase" which can take 6 to 12 months. This, in turn, is followed by an "evaluation phase" that usually lasts 3 to 6 months. Of course, these timeframes are approximations that can change with the complexity of the facility and the CEM being tested (e.g., a multiple metal CEM will probably take longer than a hydrogen chloride CEM).

Are CEMs Better than the Status Quo?

Before a CEM can be substituted for an existing compliance methodology, facilities first need to confirm that the CEM is at least as good as the current compliance methodology. To determine this, facilities need to compare the uncertainty of the current compliance approach with the uncertainty of the CEM. This can be accomplished, ideally during the demonstration test, in a number of ways, including: 1) comparing manual method stack data to CEM data and incorporating this information in OPLs; and 2) via a "sum of the errors" approach, in which the individual errors associated with the devices, methods and procedures are summed. Furthermore, CEMs are usually better at detecting higher emissions than OPLs.

Incentives for Using CEMs

Facilities which use CEMs are not required to do performance testing (stack testing) for mercury. These facilities are able to avoid enforcement quality testing of OPLs while their CEM is operating. This could have big implication for field streams that are difficult to characterize. Finally, facilities with operating CEMs do not need monitoring OPLs for enforcement.

Future CEMs Test Failure

If a facility fails to meet a Relative Accuracy Test Audit (RATA), the data obtained prior to the CEMs test failure should not be impacted/compromised. Most likely, the facility will be required to repair the monitor and retest or establish a new correlation curve, which may result in more frequent maintenance requirements. The failure may also cause the data acceptance criteria to be modified (to reflect the new data), assuming the level of performance is still better than using OPLs.

Suitability Testing of CEMs for Mercury

Presented on September 13, 1999 by Carsten Röllig, TUV Rheinland Sicherheit und Umweltschutz GmbH

TUV testing is performed under the German QA/QC Measures Program. Only TUV tested and approved instruments are allowed to be used for official measurements. Instruments are tested onsite after they are installed at a plant. The three part test procedure includes: maintenance testing; an annual function test conducted by an independent measuring institute; and comparison measurements every 3 to 5 years by an independent measuring institute. Data acquisition and reporting are accomplished by an emission computer installed on-site at the plant. This computer, which is linked to the CEM being tested, evaluates and reports all the test data collected. In some newer plants, the plant can be controlled through a direct link with the local authority.

TUV Approval-Test Scheme

TUV testing is driven by a need to comply with Federal emission limits for different types of plants. The objectives are set by a group of experts responsible for establishing test requirements. The test procedure is executed by an authorized institute and the data obtained are evaluated by a State committee and published by the ministry. Finally the instrument (the CEM) can be installed onsite under the QA/QC Measures Program and periodically monitored by the local authority.

Main Performance Characteristics

The TUV test procedure is divided into two parts: a laboratory test and a 3-month field test in which two devices are installed in the same stack. The following performance characteristics are evaluated and/or established during a TUV CEM test:

- Setup of analysis function (calibration curve)
- Linearity and interferences
- Detection limit and response time (plant)
- Drift behavior (zero and reference point) (plant)
- Availability and maintenance interval (plant)
- Reproducibility (i.e., the uncertainty between two instruments).

The TUV field application is used to obtain information on the gaseous matrix (type of plants) and to identify the smallest full-scale range configuration (typically 1.5 to 3 times the emission limit).

During the laboratory test, the following must be tested on two complete systems:

- System function - Every function has to be tested.
- Instruction manual - The manual needs to be comprehensive and in German.
- Linearity - Linearity is checked over the full measuring range and needs to be within $\pm 2\%$ of the measuring range.
- Measuring range - The measuring range needs to be very close to or within 1.5 to 2 times the emission limits.
- Temperature range - The temperature range must be checked for the difference of indoor or outdoor installation. The temperature range needs to be within $\pm 5\%$.
- Line voltage fluctuation - Line voltage fluctuation needs to be within $\pm 2\%$.
- Interference error - Both positive and negative deviations associated with interferences are used to determine interference error; however, these interferences need to be added separately. The interference error needs to be within $\pm 4\%$.

The majority of these parameters are tested at zero and near 70% of the measuring range.

Mercury test gases are generated using a HOVACAL unit. This unit uses an evaporator to combine mercuric chloride (in solution) and carrier gas. Both the concentration of the mercuric chloride solution and the flow rate of the carrier gas can be modified to achieve the concentrations (e.g., 100 µg/m³) and flow rates (e.g., 2 to 6 liters per minute) needed for testing.

During the field test two independent systems are tested at one plant for a minimum of 3 months. The following parameters are evaluated during a field test:

- Detection limit - The detection limit needs to be at least 5% of the daily mean emission limit for the plant.
- Response time - The response time must be two hundred seconds for 90% of the time.
- Availability - The unit must be available 95% of the measuring time the unit is in the field.
- Drift behavior - Drift behavior is tested using test standards. Drift is determined based on the zero point (at 2 to 3% of the measuring range reference point).
- Analytical function - Analytical function is very important and is based on a correlation to the manual reference method.
- Reproducibility - Reproducibility is the difference between the two instruments.
- Maintenance interval - An instrument needs to be able to operate at least 1 week without maintenance.

Manual Reference Method According to CEM

In most cases, the manual reference method according to CEM employs an in-stack filter and a low concentration potassium permanganate adsorption solution (2%). Although more impingers can be used, usually only two impingers are needed to collect the total mercury. The choice of materials used on the sampling train is also very important. Although a glass sampling train is the best, stainless steel works well. (Note: titanium sampling trains should not be used for mercury.) Finally, relatively low flow rates are employed (1 to 2.5 liters per minute).

Performance Characteristics CEM - Methods

The results of two CEM tests performed at two waste incineration facilities were presented. The results were fairly good, with mean concentrations of 6 and 100 µg/m³, respectively, and reproducibility at 3.5 and 36 µg/m³, respectively. Repeatability was 1.7 and 18 µg/m³, respectively. Better results would be difficult to obtain. Four institutes worked on the testing.

The Definition of the Reproducibility

Reproducibility is based on the standard deviation between the two tests and the standard deviation (SD) is related to the measuring range. Reproducibility (R_D) is defined as:

$$R_D = \frac{\bar{Y}}{SD \cdot t_{f;0.95}}$$

where,

$$SD = \sqrt{\frac{\sum_{i=1}^n (Y_{1i} - Y_{2i})^2}{2 \cdot n}}$$

The following six CEMs passed TUV testing for mercury: the OPSIS AB Lund AR 602 Z; the Sick Instruments MERCEM; the Seefelder Mebtechnik Hg Mat 2.1; the VEREWA HM 1400; the Semtech

AB Hg 2000; and the Mercury Instruments SM 3. The majority of these CEMs use wet chemistry methods to treat the sample. Since wet chemistry methods require a lot of maintenance (e.g., cleaning), some of the new units use dry chemistry sampling methods, which are relatively low-maintenance by comparison.

EPA's ETV Program: An Avenue for Testing of Mercury CEMs

Presented on September 13, 1999 by Thomas Kelly, Battelle

ETV Goals

The primary goal of the ETV Program is to promote commercially available environmental technologies, through EPA-supported performance verification testing. The main function of ETV is to provide credible, objective third-party performance data to purchasers and permittees of environmental technologies.

Twelve ETV Pilots

The ETV Program consists of 12 pilot programs having the following topic areas:

- Advanced Monitoring Systems (AMS)
- Drinking Water Systems
- P2, Recycling & Waste Treatment Technologies
- Site Characterization & Monitoring Technologies
- Indoor Air Products
- P2/Innovative Coatings and Coating Equipment
- EvTEC (any technology area)
- Air Pollution Control
- Greenhouse Gas Technologies
- Wet Weather Flow Technologies
- P2/Metal Finishing
- Source Water Protection.

Battelle is EPA's partner in the AMS pilot. This pilot verifies monitoring technologies for air (ambient, source, and indoor air), water, and soil. Thus far AMS verifications have been completed on portable nitrogen oxide/nitrogen dioxide (NO/NO₂) emission analyzers for combustion sources. Verifications are in progress on open-path optical monitors and on-line turbidimeters. Verification plans are being developed for fine particle monitors for ambient air, and for portable analyzers for metals and other contaminants in water. The AMS pilot is also interested in verifying mercury monitors, including CEMs.

Key Aspects of ETV

The ETV Program is a voluntary program for commercial-ready technologies; it does not verify prototypes or provide technical or monetary support to developers. Although most of the costs are currently supported by EPA funding, vendors are expected to pay a participation fee (which is expected to increase with time) and to cover "in-kind" costs (e.g., equipment operators and staff time to review test plans and reports). Further, ETV is not an approval or certification process; instead the outcome is a quantitative statement of performance during a specific test.

Mercury CEM Testing Through ETV

Data quality is a critical facet of the ETV Program. As a result, the program will capitalize on existing test procedures and reference methods during future mercury CEM testing. ETV will also try to collaborate with DOE, EPA, and other testing organizations in order to benefit from their knowledge and experience (i.e., lessons learned). The role of the AMS pilot is to involve CEM vendors, develop test plans, collaborate in testing, and to prepare verification reports. The product of an ETV test is a verification report and a summary statement signed by Battelle senior management and an EPA

lab director. These documents state quantitatively how the technology performed during testing. Since each technology is tested independently, the reports do not include comparisons between verification tests performed on similar instruments. The test data obtained are used by the AMS pilot solely to determine the performance of tested technologies, but a collaborative program could also be available for uses other than verification (e.g., evaluation of the performance of emission control technologies).

More information on the ETV Program is available at <http://www.epa.gov/etv>.

Mercury CEM Field Demonstrations

Presented on September 14, 1999 by Nina Bergan French, Sky+ Inc.

While working on a project that examined applications and implementations of mercury CEMs for DOE mixed waste, Dr. French noticed that many people were making "off the cuff remarks" about mercury CEMs based on a 1997 DOE/EPA test. Due to the poor results of the test, the report was neither published nor peer reviewed; that is, the developers often did not see the data or results. In 1998, another test was conducted by the DOE/TSCA on an incinerator in Tennessee. In her presentation, Dr. French discussed results from both tests.

1997 EPA/DOE Test

Three CEMs were tested during the 1997 EPA/DOE test. The CEMs were tested: 1) for suitability for the upcoming OSW-MACT rule; 2) to evaluate and revise the draft performance specification (i.e., PS 12); 3) to specify calibration techniques and refine experimental test procedures; and 4) to define the best performance under worst-case conditions.

The Holnam, Inc., cement kiln in Holly Hill, SC was chosen as one of the test sites. OSW was regulating three industry types and this site was determined to be the "worst case." It was chosen because:

- The EPA database showed mercury emissions at 17 µg/dscm without spiking.
- The facility was willing to be the host and duct access was good.
- Cement kilns do not control sulfur dioxide and nitrogen dioxide.
- There were no wet scrubbers located at the facility; therefore, both elemental and ionic mercury were present

The mercury reference method measurements used during the test indicated that mercury exists almost entirely in the gaseous form, with less than 1% in the particle-bound form. This finding indicated that it is not critical to draw isokinetic samples. Also, both elemental and ionic mercury (important for the test) were present.

The three tested CEMs were manufactured by Verewa, now owned by Durag; Seefelder Messtechnik; and Perkin-Elmer (Bodenseewerk), now owned by Sick Instruments. Descriptions of each of the CEMs tested are presented below:

- Perkin-Elmer (Bodenseewerk) – The Perkin-Elmer CEM uses a chemical reactor to convert speciated mercury to elemental mercury. Following vapor separation, the material is cooled and dried before being collected for about 15 seconds on a cool, gold/platinum trap. A heated trap is used to thermally desorb the mercury with nitrogen (which minimizes interferences). Calibrations are checked with a mercury permeation tube, but no adjustments can be made in response to the check.
- Verewa – The Verewa CEM uses heat and chemical reactions to convert speciated mercury to elemental mercury. An UV photometer (at 253.7 nanometers) and a double-beam configuration (to reduce interferences) are employed. The unit is also not equipped with an automatic calibration check, in part because this is not required by German regulations.
- Seefelder Messtechnik – The Seefelder Messtechnik CEM uses chemical reactions to convert speciated mercury to elemental mercury. An UV photometer (at 253.7 nanometers) is used. Also, Ecochem Technologies added a 2 micrometer, heated, sintered metal filter to the unit to prevent sample lines from clogging.

1997 EPA/DOE Test Results

The EPA/DOE study found that the high levels of sulfur dioxide caused extreme interferences. High maintenance was required, but due to miscommunication, no daily spot checks were performed. Also, the monitors were susceptible to clogging from moisture and particles in the stack. None of the CEMs met EPA draft performance specification requirements for either availability or for a comparison against a reference method.

Obtaining certified calibration material to dynamically spike CEMs with known amounts of elemental and ionic mercury during the daily calibration checks was problematic. The Perkin-Elmer and Seefeldler Messtechnik instruments both used mercury permeation tubes [not National Institute of Standards and Technology (NIST) certified] which are only available for elemental mercury, not ionic mercury (such as mercuric chloride). This resulted in a problem because the test called for a calibration that was not even possible. Also, the CEMs were not designed to conduct system calibrations for linearity and response checks.

The high concentration sulfur dioxide, particulate matter, and moisture at the Holnam kiln also caused a number of problems. It was a huge challenge for these dry, extractive CEM sampling systems to measure reactive, water-soluble species. The kiln did not have a scrubber in the air pollution control equipment, resulting in emissions that contained high sulfur dioxide concentrations (150 to 500 ppm), 94 to 97% relative humidity, and high particulate matter in the process dust (particulate matter-bound mercury was not measured).

A site-specific calibration factor was measured for each CEM. According to Dr. French, it is important to use an onsite calibration factor, which is based on a comparison with a reference method. These calibration factors need to be calculated for each CEM using nine reference method measurements. The calibration factor is the ratio of the average reference method response to the average CEM response.

Some of the issues associated with the draft performance specifications include:

- PS 12 has no guidelines for specific reference materials
- Need to evaluate the entire CEM sampling system
- Permeation tubes with custom dilution devices are the most viable option, preferably NIST traceable for mercury
- Not exact or calculated; systematic bias is also a problem
- Use Method 101A to measure calibration concentrations.

The door is open for new performance specifications beginning with PS 12, which can then be added to with experience.

Other test results based on the 1997 EPA/DOE test showed that high moisture by itself was not a problem for the Seefeldler Messtechnik; however, when it was combined with sulfur dioxide an acid was created, which, when combined with particulate matter, resulted in plugging. Both of these scenarios required maintenance. The calibration requirements were also fundamentally different for the European applications.

The bottom line is that this test facility was not a reasonable worst case for HWC applications; it still leaves questions as to whether CEMs would perform well on a cement kiln.

1998 DOE/TSCA Test Results

The 1998 DOE/TSCA wet stack test was a 2-month evaluation of the Perkin Elmer MERCEM. During this test, CEM data were compared to Method 101A data. Mercury concentrations were fairly low (5 to 60 $\mu\text{g}/\text{dscm}$). The relative accuracies varied (from greater than 300% to 20%) based on the feed; good accuracies were obtained for liquids, but as the number of particles in the effluent increased, the accuracies decreased. This test raised questions about the reference method and calibration standards.

General Comments

It is important to note that dedicated mercury CEMs are widely used throughout Europe, where the MWC and HWC emission limit for total mercury (elemental mercury and mercuric chloride) is 50 $\mu\text{g}/\text{dscm}$. There are a lot of TUV data on their use. Furthermore, in the absence of high sulfur dioxide and particulate matter, the CEMs described in this presentation will perform quite well.

For PS 12 and using all of the test data, the information can be summarized in three areas: interference gas, absolute calibration, and calibration standards. At the current performance specification limit of 500 ppm, the sulfur dioxide level may need to be lowered to 100 ppm to be representative of HWCs. Absolute calibration (with mercury and mercuric chloride) is currently being done daily; although Europe requires absolute calibration only every 3 months. There needs to be a way to do a daily qualitative check with elemental mercury, which is more realistic with these instruments. Also, calibration standard availability, specifically for mercuric chloride and elemental mercury, needs to be improved.

Mercury CEM performance is not at the required standard and these instruments are large, complex, and expensive. Ideally, there is a need for simpler, cheaper alternatives (e.g., using dry chemistry) and a need for realistic performance specifications and validation tests.

Evaluation of CEMs for Mercury Speciation

Presented on September 14, 1999 by Dennis Laudal, University of North Dakota EERC

Advantages and Limitations of Mercury CEMs

EERC has been performing bench-, pilot-, and field-scale mercury CEM tests for the last 5 years. In addition to providing real- or near-real-time results, mercury CEMs may potentially be less costly than current monitoring approaches and can be used as a feedback for mercury control strategies. At this time, however, available CEMs can only be used to measure total mercury (or elemental mercury) and are largely unproven for fossil fuel combustion systems. Further, in addition to reliability concerns (e.g., maintenance schedules), the precision and bias have still not been established for mercury CEMs. Finally, operation is complicated by the fact these systems often need to use a pretreatment/conversion system prior to the detection portion of the instrument.

Mercury CEMs Tested

EERC has tested three CEMs: the Perkin Elmer MERCEM, the PS Analytical Sir Galahad, and the Semtech Hg 2000. The Perkin Elmer unit was tested with good results at the pilot-scale level and PS Analytical's unit was successfully tested at both the bench and laboratory levels and is scheduled to be field-tested shortly. Each of these CEMs is discussed in more detail below:

- Perkin Elmer MERCEM - The Perkin Elmer CEM (MERCEM) measures TGM using a batch process (3 to 5 minutes long) and a gold trap to capture the mercury. This large and expensive unit also uses stannous chloride to reduce mercury(II) to elemental mercury and a CVAAS to analyze the elemental mercury. The Perkin Elmer CEM has been certified by TUV and is in use at five incineration plants in Europe. Although the unit is not currently being used at a US facility, demonstration and pilot-scale tests were conducted at a cement kiln in Holly Hills, North Carolina and at EERC, respectively. The unit has also been successfully tested on a mixed-waste incinerator using the RATA protocols at the Oak Ridge National Laboratory.
- Semtech Hg 2000 - The lightweight and portable Semtech CEM (Semtech Hg 2000) is essentially a Zeeman-modulated CVAAS that continuously monitors elemental mercury. As such, this unit can effectively measure elemental mercury in streams with sulfur dioxide concentrations from 250 to 500 ppm. Unfortunately the unit tends to develop excess noise in the signal (1 to 3 micrograms per normal cubic meter) and has some problems with zero drift. Furthermore, the company, which is located in Sweden, is not very responsive to customer inquiries. On the positive side, Semtech CEM has been certified by TUV and is used at several incinerators in Sweden. The unit has also been successfully pilot-scale tested by EERC and is currently being used at three US power plants.
- PS Analytical Sir Galahad - The PS Analytical CEM (Sir Galahad) also measures TGM using a batch process (every 5 to 10 minutes) and a specialized gold trap to capture the mercury. The unit uses atomic fluorescence (AF) spectrometry as a measurement technique and has a wide measurement range (3 to 7 orders of magnitude). Unfortunately the unit has problems with signal attenuation due to hydrogen chloride and nitrogen dioxide reactions with the gold trap and either the hydrogen chloride or nitrogen dioxide must be removed from the gas stream prior to the instrument. (Note: All AF systems which use gold traps have problems with hydrogen chloride and nitrogen dioxide reactions. To improve effectiveness, these units need to remove either the hydrogen chloride or nitrogen dioxide.)

As noted previously, in order to measure total mercury, some monitors (e.g., the Semtech and Perkin Elmer CEMs) need to pretreat the flue gas to convert the mercury to elemental mercury to measure total mercury. Generally stannous chloride is used to convert mercury(II) to elemental mercury. Since the efficiency of this conversion is greatly impacted by the presence of sulfur dioxide, it may also be necessary to pretreat the flue gas to remove the sulfur dioxide. It may also be beneficial to remove other acid gases (hydrogen chloride, and NO_x) to reduce corrosion problems with the instruments. The EERC mercury pretreatment/conversion system was then discussed.

Pilot-Scale and Field Test Results

A pilot-scale comparison of the Perkin Elmer and PS analytical CEMs to three impinger-based mercury sampling methods (i.e., EPA Method 101, Tris-Buffer Method, and the Ontario Hydro Method) showed that both analyzers work well with no pretreatment at the pilot-scale level. However, these tests were of short duration. The Ontario Hydro results were low since it was not known at the time that the mercury in the potassium chloride solution needs to be stabilized with potassium permanganate prior to analysis. Both mercuric chloride and elemental mercury were spiked into the flue gas during these tests. Furthermore, since hydrogen chloride and sulfur dioxide levels in flue gases from Blacksville coal combustion are relatively high (e.g., 50 ppm hydrogen chloride and 1700 ppm sulfur dioxide), these were relatively challenging

A pilot-scale comparison between the Semtech CEM and the Ontario Hydro Method also achieved good performance (at measuring elemental mercury and total mercury). These results illustrate how users can speciate the mercury by difference using a pretreatment/conversion system. This was also a very challenging test, since hydrogen chloride and sulfur dioxide concentrations in the flue gas were near 200 and 3,000 ppm, respectively.

Field tests designed to support mercury research, rather than to verify instrument performance, were also performed using the Semtech and PS Analytical CEMs at two lignite plants located in North Dakota (the Great River Energy Coal Creek Station and the Minekota Power Cooperative Milton R. Young Station). A comparison of Semtech Hg 200 CEM and the Ontario Hydro Method showed good results (within 20%) for total mercury. Again, these were relatively challenging tests, since the moisture content of North Dakota lignites is very high.

Direct comparisons between the Semtech CEM and the Ontario Hydro Method following the firing of a bituminous coal at a Midwestern plant also yielded reasonable speciation results in the flue gas over time (total mercury and elemental mercury), especially considering the relatively high sulfur dioxide and hydrogen chloride concentrations in the flue gas.

Conclusions and Recommendations

Mr. Laudal closed with the following conclusions and recommendations:

- The Perkin Elmer MERCER, Semtech Hg 2000, and PS Analytical Sir Galahad have shown the ability to measure total vapor-phase mercury with $\pm 20\%$ of the wet chemistry methods.
- For all the analyzers to work well, a pretreatment system is needed to remove the majority of the acid gases (sulfur dioxide and hydrogen chloride) produced when burning coals with high chlorine and sulfur.
- Although mercury CEMs have real potential to accurately measure total mercury, there are no commercially available CEMs capable of measuring speciated mercury (e.g., both oxidized and elemental). A CEM capable of measuring speciated mercury may be particularly useful for coal-fired power plants, since different coal types generate different

ratios between elemental mercury and mercury(II). These data could eventually be used to adjust mercury controls (e.g., adsorbent, etc.) and save money at those facilities.

- Mercury CEMs must be rigorously tested at the pilot-scale and in longer-term field tests to resolve questions regarding accuracy, precision, reliability, and maintainability before they can be routinely used for mercury measurement in utility flue gas applications.

International Monitoring/Measurement Activities for Atmospheric Mercury

Presented on September 14, 1999 by John Munthe, Swedish Environmental Research Institute (IVL)

Most ambient air or stack gas mercury speciation methods are operationally defined and based on the physical and chemical properties of the compounds. Exceptions include direct spectroscopic methods, specifically DOAS and Laser Radar (LIDAR). Uncertainties regarding which compounds should be measured need to be considered when comparing different sampling and analytical methods.

Examples of operationally defined methods include:

- TGM - Sample passes through a filter and is then collected on gold.
- RGM - Material is collected by using a potassium chloride denuder or a mist chamber with a hydrochloric acid solution.
- Particulate mercury - This method is dependent on the collection device.

United Nations Economic Commission for Europe Convention on Long-range Transboundary Air Pollution

The United Nations Economic Commission for Europe (UN-ECE) Convention on Long-range Transboundary Air Pollution (CLRTAP) convention produced the first internationally legally binding protocols to address air pollution problems on a broad regional basis. It was initiated after the long-range transport of sulphur from Europe to Scandinavia was first discovered.

UN-ECE operates under the European Monitoring and Evaluation Program (EMEP), which addresses atmospheric transboundary air pollution. There are two meteorological synthesizing centers (MSC) within EMEP responsible for modeling; MSC-E in Moscow and MSC-W in Oslo. MSC-E models metals and persistent organic pollutant (POP), and MSC-W models sulfur and nitrogen. There is also a chemical coordination center (CCC) in Oslo, which is responsible for collecting data from all the countries that have signed the CLRTAP protocols.

Under the CLRTAP protocols, approximately 35 countries have agreed to reduce emissions using best available technologies (BATs). The first CLRTAP protocol (for sulfur) was developed in 1980. Since then protocols for VOCs, nitrogen, metals (including mercury), and POPs have been developed. The first protocol for POPs and heavy metals (for mercury, cadmium, and lead) was just recently signed in 1998. Data reporting for metals and POPs is voluntary.

The following mercury data are publically available in Europe:

- Ambient air measurements reported to EMEP CCC
 - TGM concentrations from Sweden, Norway, Finland, and Ireland
 - Wet deposition total mercury data from Sweden, Finland, Norway, Germany, and Ireland
- Unfortunately, no data are routinely being collected for methyl mercury or any other mercury species.

Rorvik, Sweden, TGM data show the differences in mercury concentrations over the last 20 years. In the 1980s, there were significant episodes of high concentrations from regional sources in central Europe. During the last 4 to 5 years, these concentrations have completely disappeared. The

baseline for the 1990s is below 2 nanograms per cubic meter. In addition, wet deposition of total mercury at Swedish monitoring sites decreased from 1995 through 1997.

Research on Atmospheric Mercury in Europe

The following two European Union (EU)-funded projects are currently operating in Europe: Mercury Over Europe (MOE) and Mediterranean Atmospheric Mercury Cycle System (MAMCS). The main goal of MOE is to determine sources of methyl mercury and other mercury species in wet deposition in Europe. MOE is responsible for collecting data on mercury emissions data (including speciation) and the chemistry of mercury in flue gases and ambient air. MOE also develops process and long-range transport models. MAMCS maintains an emission inventory, performs field measurements, and performs process and long-range transport modeling.

A number of different measurement techniques have been used by MOE and MAMCS to obtain the following speciated atmospheric mercury measurements: TGM, RGM, gaseous monomethylmercury, gaseous dimethylmercury, particulate mercury, and total mercury and methyl mercury in precipitation. For TGM, Tekran, Gardis, and manual gold trap methods have been used. A mist chamber, annular denuders, and tubular denuders (both automatic and manual) have been used to measure RGM. For particulate matter, AES mini traps are mainly being used, as well as Teflon filters. Modified mist chambers are being used to measure gaseous monomethylmercury. TGM, RGM, and particulate matter measurements have been obtained from 10 sites and gaseous monomethylmercury measurements have been obtained from two sites. Both organizations have also attempted size fractionation for particulate mercury but have not been very successful.

A comparison of TGM results shows that there is some scattering in the data, indicating that the site location for the measurements could be improved. Using four different techniques for RGM, preliminary results show a general trend for each technique and fair scattering.

Local and regional sources have a relatively small impact on ambient atmospheric TGM concentrations. Regional sources, however, have a relatively large impact on particulate mercury, and local sources have a moderate influence on RGM, although the reasons for this impact are not very well understood. Speciated mercury data are needed to better understand mercury impacts. Also, a hemispheric or global perspective needs to be developed using TGM data.

Source-Receptor Relationships for Mercury: Monitoring and Modeling

Presented on September 14, 1999 by Gerald Keeler, University of Michigan, Air Quality Laboratory

Dr. Keeler opened his presentation by noting that he intended to address receptor versus deterministic approaches for defining source-receptor relationships for atmospheric mercury, as well as some of the difficulties and uncertainties associated with these approaches. He then credited the research performed by the University of Michigan and US EPA NERL over the last 7 years. This research was funded by US EPA, the State of Florida, the Great Lakes Protection Fund, and NOAA.

Ultimately mercury researchers are interested in understanding "what is driving the loading in fish," in part due to consumption advisories in effect for fish caught in US waterways. Since source-receptor relationships are very complex and involve numerous interactions between multiple factors, Dr. Keeler noted he would limit his presentation to "source-receptor relationships to the atmosphere" (i.e., the impact atmospheric deposition has on the cycling of mercury in the environment) and not address uptake by the fish.

Understanding source emissions, particularly mercury speciation and co-emitted tracer species, is essential to understanding source-receptor relationships. This can be approached by applying source data to a mathematic model to define what happens with these emissions. It is also necessary to be able to describe and account for the processes that remove these different compounds, including elemental mercury and mercury(II) atmospheric chemistry relationships. As mentioned during previous discussions, removal from the atmosphere is largely dependent upon the form of the mercury (elemental, reactive, or particulate). Finally, atmosphere-surface processes, including dry deposition and surface re-emission, need to be understood. Unfortunately, most atmospheric models only provide loadings to a water body and do not address air/water exchanges or the processing of pollutants at the surface of a water body or as they come into contact with biota.

Conclusions

Dr. Keeler then presented the following conclusions:

- The importance of local versus regional sources varies dramatically as a function of location - For example, approximately 70% of the mercury deposited in Southern Florida (the Everglades) comes from local sources, as compared to only 40% for the Great Lakes. Furthermore, these proportions are expected to change from year to year depending upon meteorology and source activities.
- Incomplete characterization of mercury emissions limits mercury modeling and risk assessment activities.
- Atmospheric mercury chemistry further complicates mercury speciation considerations - The reduction/oxidation chemistry of mercury emitted from sources (i.e., the rate at which it transforms from the reactive to elemental form as it is transported) complicates speciation efforts.
- Dry deposition equals wet deposition - Dry deposition is poorly understood, in part because of difficulties measuring and modeling this factor. In general, however, dry deposition can be assumed to be approximately equal to wet deposition in most of North America.

- Lack of ambient measurements of mercury forms (species) limits improvement of model parameterizations and ground-truth for models - More data are needed to refine models so that they correlate well with actual conditions.

Two approaches can be used to define source-receptor relationships: a source-receptor approach and a meteorological approach.

Source-Receptor Approach

The University of Michigan often uses a receptor-oriented approach (that does not rely on emission data) to define source-receptor relationships. When this approach is employed, monitoring stations are set up at the receptors of interest (e.g., the Great Lakes). This approach depends on the researcher's ability to measure the species for which he/she wants to define the source-receptor relationship.

The receptor-orientated approach was applied during the Great Lakes Atmospheric Mercury Project. During this 2-year-long project (from 1995 through 1996) the University of Michigan measured gas- and particle-phase mercury every sixth day for a 24-hour period. Seasonal particle-phase mercury averages based on 120 samples per site and statistically different concentrations for the northern and western sites were slightly lower than the average concentrations for the southern and eastern sites.

When individual mercury measurements are compared to other parameters collected on the same frequency, the structure in the data can be used to identify what factors are influencing the results (e.g., meteorological). The database obtained from this Great Lakes Study is one of the largest of its kind and includes trace element data as well as TGM concentration (via gold traps). When particulate-phase mercury results are coupled with other parameters (zinc, lead, iron, manganese, copper, bromine, sulfur, and selenium) site-by-site associations (120 samples for each site) can be made between the various trace metals and particulate-phase mercury. These comparisons can be used to help determine what is "driving the source of the mercury and the other trace elements."

Dr. Keeler then discussed the variation obtained between two sites, 30 miles apart. Based on the results presented, Dr. Keeler was able to determine that very little of the deposition at the northern site was due to coal combustion or iron/steel manufacturing, and that the southern site was impacted more by incineration and iron/steel manufacturing activities. These data show that by coupling mercury with other elements, "the signature of the coupled element can tell where the mercury is coming from."

Meteorological Approach

The second approach used to define the source-receptor relationship involves using meteorological information to calculate back trajectories that coincide with the sampling events. During a March 10, 1995 monitoring event, high particulate mercury concentrations were obtained across the entire network, particularly at the Lake Ontario Point Petrie site [71 picograms per cubic meter (pg/m^3)]. It is possible, once this information is combined with a hybrid monitoring approach and the removal processes are accounted for, to assess the contribution of particulate mercury from the Great Lakes Basin to the Great Lakes. This analysis has been used to develop a map which shows mercury contributions to the Great Lakes on a pg/m^3 basis.

After noting that particulate-mercury results showed a pronounced source-receptor relationship, Dr. Keeler noted that the source-receptor relationships obtained for the gas-phase mercury results were not as pronounced. This was attributed to the fact that the study was measuring TGM only, since

RGM could not be measured in 1995. Additional data were then presented which indicated that sources in the south were responsible for elevated elemental mercury concentrations. Unfortunately, "there were no strong signatures in the data."

Recent RGM data (from the last 1.5 years) clearly indicate that elemental mercury and RGM do not correlate well. As a result, none of the TGM data collected during the Great Lakes Study will provide the "signal mercury researchers are interested in." These data also show that RGM can be measured in the ambient environment, as demonstrated by the fact that RGM concentrations rose when the wind shifted in the direction of an incinerator located approximately 4 kilometers from the monitoring site.

RGM was also measured during a dry deposition study in Florida during the winter of 1998/1999. The purpose of this study, which was funded by the Florida DEP and EPA, was to determine the impact of dry deposition to the Florida Everglades in the winter. During this study, researchers noted that RGM levels tend to follow a diurnal pattern. Researchers also observed that when dew was present at the sampling site, most of the RGM was removed from the atmosphere to the dew.

After noting that RGM is very important to modeling deposition to bodies of water, Dr. Keeler presented wet, RGM, and particulate mercury deposition to Lake Michigan model results. These results, which were obtained from the LLMBBS project, showed that wet deposition was responsible for introducing the majority of the mercury to Lake Michigan (over 600 kilograms per year), but that combined RGM and particulate mercury deposition rates almost equaled wet deposition rates.

The University of Michigan has also been developing source-based models which combine emissions data with high resolution meteorological data to model mercury deposition to specific water bodies on a small-scale basis (i.e., 1 to 5 kilometer grid spacing). Dr. Keeler then presented modeling results obtained by applying data accumulated over a 24-hour period (when a front passed across the Great Lakes) to a wet deposition model. In the first scenario modeled with these data, the modelers assumed that only RGM was emitted during this 24-hour period. To support this assumption, the modelers had to appropriately convert the emissions data from the EPA Report to Congress database. In the second scenario modeled with these data, modelers assumed that only elemental mercury was emitted during the 24-hour period. The model results obtained for the different scenarios differed by approximately 2 orders of magnitude; the second scenario yielded results that indicate that almost no deposition to Lake Superior. These data support the need for speciated emission data from the stacks.

After noting that the results obtained during a similar analysis (elemental mercury only and RGM only) for a dry deposition source differed by approximately 2.5 orders of magnitude, Dr. Keeler then noted that techniques have been developed to measure dry deposition. As a result, it is now possible to use dry deposition measurements to "ground truth" the deposition calculations in the models.

Dr. Keeler closed by responding to the question "Which do you need more, monitoring or modeling?" According to Dr. Keeler, both types of data are needed. In particular, speciated emissions data (to be used for modeling) and speciated ambient data (to enable modelers to verify the models) are needed.

Manual Speciation Methods for Measuring Atmospheric Mercury: Applications/Implementation

Presented on September 14, 1999 by Matthew S. Landis, US EPA, NERL

Elemental, reactive, and particulate mercury behave very differently in the atmosphere. As a result, speciated mercury data are needed to support atmospheric transport and deposition modeling efforts and to evaluate bioaccumulation, exposure, and risk assessment. Fortunately, methods to measure ambient ionic or RGM and particulate mercury are improving.

Challenges To Measuring RGM

There are a number of challenges associated with measuring RGM in the ambient atmosphere, many of which may be attributed to the need to measure the compounds at trace levels. Not only does the methodology used to measure RGM need to completely reject the much larger elemental mercury component, it also needs to be one to two orders of magnitude more sensitive than total mercury methods. Since RGM is relatively "sticky," the methodology must also be able to quantitatively "pass" RGM to the collector. Finally, the RGM method must also exclude particulate-phase mercury while avoiding filter artifact.

Ambient Speciation Methods

Examples of currently available ambient speciation methods include: impregnated (ion exchange) filters; refluxing mist chambers; and annular thermal denuders. Annular thermal denuders are the most promising methodology for avoiding artifact formation.

Annular Thermal Denuders

Denuders are not a new technology. Tubular denuders were previously used in Europe to speciate mercury in stacks and annular denuders have been used for decades for sulfur dioxide and ammonia determinations. In order to use denuders for ambient mercury speciation, however, two key modifications were made from the previous designs. A single annulus quartz denuder was constructed and coated with potassium chloride to efficiently capture RGM at a flow rate of 10 liters per minute, and rather than perform a wet chemical extraction and subsequent analysis, the quartz denuders are thermally desorbed. At approximately 500°C, RGM is quantitatively converted to elemental mercury vapor and purged directly into a CVAFS. Once desorbed the denuder is regenerated and ready for reuse.

In addition to being relatively easy to use, annular thermal denuders are capable of obtaining high collection efficiencies even at relatively high mass loadings, as demonstrated during laboratory testing at Frontier Geosciences, Seattle, WA. During this laboratory study, the collection efficiency obtained for mercury chloride was 97.8% for a total mass loading of 5 nanograms and 97.2% for a 12 nanogram loading.

Denuders can also be used to perform high-resolution sampling at relatively low MDLs. The mean field blank for the potassium chloride annular denuder was determined to be 2.21 ± 2.26 picograms; this translates to MDLs from 0.3 pg/m^3 for a 12 hour sample to 3.8 pg/m^3 for a 1 hour sample at a flow rate of 10 liters per minute. In fact, during tests in Baltimore, Maryland; Research Triangle Park, North Carolina; and the Florida Everglades, the minimum RGM concentrations (5.4; 3.5; and 2.5 pg/m^3 , respectively) were never below the detection limit of the method.

This method is highly accurate; precision has been demonstrated to be excellent (approximately 10% RSD) even at concentrations as low as 4 pg/m³.

Role of Manual Sampling

In light of the availability of the Tekran, Inc. automated speciation sampler, which utilizes the thermal denuder methodology, Dr. Landis pointed out that there is still a substantive role for manual speciation methodologies. Manual sampling can be used in routine projects (to support monitoring networks), exploratory projects (for fugitive emission monitoring), special projects (for aircraft measurements and chlor-alkali facilities), and to support QA/QC efforts (via collocated precision efforts). Although there are a number of factors that can limit these efforts (cost, expertise, etc.), these can be partly overcome through more collaborative approaches. For example, the cost and expertise needed to perform routine projects could be overcome by setting up a monitoring network in which the samples are sent back to a central laboratory for analysis. In addition to reducing costs, quality assurance is improved by this centralized approach (by using one person and one lab to analyze the sample).

EPA NERL Research Initiatives

Future EPA NERL research initiatives will focus on speciation method evaluation (both in the lab and in the field) and applied research (including aircraft measurements, arctic depletion events, and fugitive emissions). It is anticipated that the laboratory method evaluation efforts will concentrate on evaluating method accuracy, comparability, and interferences, while the field evaluation efforts will focus on two sites in Florida and Ohio.

Conclusions

The annular denuder methodology provides ambient speciation of elemental, reactive, and particulate mercury without known interconversion problems. Dr. Landis also noted that low denuder MDLs allows for high resolution, low concentration sampling. Furthermore, the manual sampling configuration is relatively inexpensive, simple, and mobile.

Automated Mercury Speciation Methods and Demonstrations

Presented on September 14, 1999 by Robert Stevens, Florida DEP

Background

Mercury in the atmosphere exists primarily in three distinct forms. They are elemental mercury, RGM, and particle bound mercury. Most researchers believe the atmospheric RGM is in the form of mercuric chloride. The rationale for this assumption is that mercuric chloride would be formed during the high temperature combustion processes in such sources as incinerators and fossil-fueled power generating facilities. These sources use fuels that contain mercury and chlorine in ratios that favor the formation of mercuric chloride. These three forms of mercury have very different chemical and physical properties. Particle bound mercury and mercuric chloride have much higher deposition rates than the relatively unreactive elemental mercury. For example mercuric chloride has a half life of hours due to its high deposition and water solubility. Elemental mercury, on the other hand, has a half-life in the atmosphere of 6 months to a year. The forms may be interconverted in the atmosphere and in various reservoirs. Particle bound mercury half-life is dependent on the size of the particle. For particles less than 2.5 micrometers in diameter, the half-life is days. For particles greater than 2.5 micrometers, the half-life is hours.

In source characterization studies conducted in South Florida in 1995, Method 29 and a DOAS system were used to speciate the forms of mercury emitted from a resource recovery incinerator. In this study elemental mercury represented 87% of the mercury emissions. The balance was in the form of RGM. A few percent of the mercury emissions were in the form of particle bound mercury. Similar results were also observed in the stack emissions from a medical waste incinerator in South Florida. These mercury source studies revealed that RGM emissions could potentially be responsible for contaminating nearby sensitive ecosystems. At that time a reliable method to measure atmospheric levels of RGM did not exist.

Difficulties Measuring RGM

In order to measure expected atmospheric concentrations (1 to 100 pg/m^3), the measurement method must be one to two orders of magnitude more sensitive than methods currently used to measure total mercury. In order to accomplish this, EPA considered and assisted in the development of a unique automated annular denuder system that concentrates atmospheric aliquots of RGM on an annular denuder for subsequent thermal release into a Tekran 2537 mercury AF analyzer. The analyzer consists of a Teflon-coated impaction inlet to remove coarse particles, coupled to a potassium chloride-coated quartz annular denuder inside a thermally regulated oven/housing. This in turn is coupled to a Tekran 2537A mercury AF analyzer.

RGM Sampling Phase

The denuder and inlet during the 1 to 2 hour sampling phase are maintained at 50°C. The denuder captures all RGM while passing elemental mercury. The sampling flow rate is 10 liters per minute. At this flow rate and with the unique potassium chloride-coated annular denuder, the RGM (mercuric chloride) diffuses to the walls of the denuder and is quantitatively removed from the sample stream, while allowing the elemental mercury to pass to the Tekran 2537 for analysis. After a 2 hour collection time the denuder is heated to 500°C. The RGM is converted to elemental mercury. The elemental mercury flows to the Tekran 2537 and is measured and reported as RGM. This instrument has been used in several field studies. Elemental and RGM measurements from Dexter, Michigan indicated that RGM concentrations increased throughout the day, reaching as high as 28 pg/m^3 . The

RGM then began to disappear as the humidity increased as expected, due to RGM's (as mercuric chloride) high water solubility.

Ambient measurements from a test in Baltimore, Maryland indicated that RGM was present at about 20 to 40 pg/m³ for a number of hours before the wind shifted to a southerly flow. At that point, for approximately 10 hours, levels of RGM were well above the background values. In both cases the concentrations of elemental mercury remained relatively constant. This indicates that mercury emissions from the source, an incinerator about 7 kilometers south of the monitoring site, were largely in the form of RGM.

In summary, the potassium chloride-coated quartz annular denuders have proven quantitatively effective in collecting RGM. RGM is thermally (at approximately 500°C) converted to elemental mercury. The Tekran 1130 has demonstrated its utility in several ambient mercury studies.

For future research, Tekran has incorporated continuous particulate collection abilities (in addition to RGM) into mercury speciation instrumentation. It appears that this technology will be effective in quantifying mercury emissions on a routine basis rather than relying solely on research from power plants and incinerators.

Wet Deposition Sampling - Applications/Implementation

Presented on September 14, 1999 by Timothy Dvonch, University of Michigan

Several groups around the globe have measured wet deposition using a variety of wet deposition collectors and frequencies (daily, weekly, monthly). In general, most of these approaches have been relatively successful at quantifying seasonal mercury deposition. The next step in addressing mercury deposition is to determine its origin, particularly when it is being deposited from the atmosphere to sensitive ecosystems. Accordingly, Dr. Dvonch's presentation addressed a framework collection system developed by the University of Michigan to both quantify annual deposition and to investigate source-receptor relationships and source apportionment approaches. Because of the time-scales and distances associated with the transport and deposition of mercury [mercury(II) and particulate], measurements need to be taken daily to ensure accurate source-receptor relationships. Other air quality pollutants/parameters should be measured concurrently, to provide a comparison which can help explain some of the observed mercury processes. It is also important to: 1) incorporate clean techniques; 2) insure sample stability; 3) minimize sample artifacts and losses; and 4) minimize the potential for dry deposition (using a wet only approach)

UM-B Wet-Only Automatic Precipitation Collector

The UM-B wet-only automatic precipitation collector was modified from the MICB collector by replacing the large Teflon-coated funnel with an acrylic insert so that two separate sampling trains could be independently quantified. The mercury sampling portion of the collector uses a borosilicate glass funnel with a Teflon bottle and a glass "p trap" which serves as a vapor lock. The trace element sampling portion of the system uses a polypropylene funnel. In order to measure to pg/m^3 levels in the atmosphere, the whole sampling system is acid cleaned to ensure that valid data can be collected.

The UM-B collector was evaluated using collocated measurements collected during field sampling. Losses to the funnel surfaces were also evaluated, among other factors. The evaluation indicated that in addition to being accurate and precise, the collector minimizes the potential for dry deposition and sample artifacts and losses. Over the last 5 years a number of UM-B collectors have been set up at multiple sites in the Eastern US.

UM-B collectors were used in the Everglades and Davie, Florida during the South Florida Atmospheric Monitoring Study (SoFAMMS), and in Chicago during the Lake Michigan Mass Balance Study (LMMBS). During the SoFAMMS study, data were collected from five Everglades sites during summer of 1995 and from the Davie site for a full year (from the summer of 1995 to the summer of 1996). Data from these tests were applied to the receptor model, which uses a "principal component analysis (PCA) followed by a multiple linear regression of absolute factor scores against mercury to perform a source apportionment of the mercury measured during the deposition." With this approach, "PCA is used to reduce the dimensionality of a data set of interrelated variables so that a minimum number of factors can explain the maximum amount of variance in that data." This is accomplished by referencing the trace element data collected with the mercury results.

When PCA is applied to air quality data, the factors identified often represent specific source types (e.g, waste incinerators, marine sources, oil combustion sources, and crustal sources). The results obtained from the Everglade samples collected during the SoFAMMS test indicated that the output for Factor 1 (waste incinerators) had high loadings for lead and antimony. Significant factors were

also established for the marine, crustal, and oil combustion components. Using this approach, researchers were able to account for 71% of mercury measured using wet deposition. Following analysis, the researchers were also able to apportion 77% of mercury deposition at that site over the 1-year period. Factors such as crustal sources, incineration, oil combustion, marine sources, arsenic, copper, and zinc were identified.

Dr. Dvonch then emphasized the importance of performing event measurements of precipitation. Not only can trace element data be used for receptor-modeling, but more meteorological approaches can also be used. This approach was used in Southern Florida during the SoFAMMS study. Radar images and data obtained every 6 minutes from National Climatic Data Center were used to track the path of individual storm cells by known source types to the precipitation sampling sites. This independent receptor-oriented approach was used to confirm and provide a more robust analysis of the source apportionment using trace element data.

The LMMBS project also used the same PCA, multiple linear regression approach to source apportioning the mercury collected via wet deposition during the 16-month study in Chicago. Up to 83% of the mercury was explained using this approach. A meteorological-based analysis was also used to independently confirm the relationships established with the trace element data. Researchers were also able to identify significant differences according to the transport pattern (i.e., the path the air followed to the receptor site).

Dr. Dvonch then noted that daily event sampling does not provide a small enough time resolution. A lot of variability exists from one event to the next. Sequential sampler data obtained manually during a single rain storm illustrated the changes (e.g., spiking) in concentrations that occurred during a single rain storm as conditions changed. A automated sequential sampler was developed using the UM-B framework. This event sampler is designed so that one bottle is collected per day over a 7-day period. Using this approach, bottles are changed based on the volume received or other programmable parameters such as time.

Dr. Dvonch closed by noting that in order to examine source-receptor relationships and determine source apportionment, discrete precipitation events need to be sampled and trace elements need to be quantified (in addition to mercury). Also, dispersion/deposition models need to be compared to event data to "ground truth" the models.

Atmospheric Wet Deposition of Mercury in North America

Presented on September 14, 1999 by Clyde Sweet, Illinois State Water Survey

The MDN is part of the NADP. The NADP Program is designed to make long-term measurements of the chemistry of wet deposition. The program is organized as a cooperative effort among Federal, State, and some private and local organizations. Each "partner" in this program is responsible for the collection and analysis of samples from its site.

Mercury cycling and transformation in the atmosphere and water is a very complicated process. Current efforts focus on wet deposition testing because dry deposition testing is very difficult to perform over the long-term at remote, rural sites using inexpensive equipment and procedures. Also, wet deposition contributes approximately 50% of the total mercury input to surface water from the atmosphere. Furthermore, RGM and particulate mercury are (preferentially) scrubbed from the atmosphere by precipitation and wet deposition more efficiently than elemental mercury.

The majority of the MDN sites are currently located in the Eastern States along the northern tier and the Gulf Coast. (Note: Four sites are also located in Canada and some MDN sites are monitoring methyl mercury.) The results obtained from MDN are fairly uniform except in Southern Florida.

Mercury wet deposition measurements (from 1997-1998 MDN results) were compared to RELMAP and TEAM simulation results for the following five areas: Minnesota, Central Pennsylvania, Southern Florida, Northeast Texas, and Northern Maine/New Brunswick. The MDN results presented generally agree with the simulation estimates, except for Central Pennsylvania where higher levels of mercury wet deposition were predicted by the models [greater than 20 $\mu\text{g}/\text{m}^2/\text{yr}$ from RELMAP and 15 to 30 $\mu\text{g}/\text{m}^2/\text{yr}$ from TEAM, as compared to 7 to 10 $\mu\text{g}/\text{m}^2/\text{yr}$ measured by MDN]. This may indicate a problem with the model for that region.

Goals and Future Directions

A good goal for the future is to expand the network to cover the United States and Canada, like the acid rain network. The NADP would also like to target the evaluation of long-term trends. To accomplish this, sites within the network will need to commit for a minimum of 5 years. Data could also be used to support a database for research and modeling studies, and to develop a baseline to evaluate the effectiveness of future controls on mercury. In the future, the NADP would also like to add other toxics such as trace metals, pesticides, and industrial organics, to its monitoring network.

Summary and Concluding Remarks

Presented on September 14, 1999 by Scott Hedges, US EPA, ORD, NRMRL

Mr. Hedges closed the conference by summarizing future mercury related activities for EPA ORD and follow-on actions to the conference.

Future EPA ORD Activities:

Based on pre- and post-conference activities, EPA ORD needs to:

- Provide assistance and encourage manufacturers to develop mercury monitoring/sampling systems and for industrial sources to install these systems; EPA's ETV Program and the EPA and DOE SBIR programs are vehicles for this assistance.
- Provide assistance and encouragement to the academic community through research grants; EPA's environmental research grant and fellowship (STAR) programs are additional types of vehicles to provide this assistance.
- Provide assistance and encouragement to the military through Interagency Agreements.
- Continue collaboration with DOE.
- Make the EPA Program Offices and Regions, State and local permitting authorities, industry, and the international community aware of the developments in manual and continuous systems to measure mercury.

Panel Discussion Summaries

A.1 Introduction

Two panel discussions were held during the workshop; the first addressed source monitoring/testing needs and the second addressed ambient monitoring needs. Each panel discussion opened with an overview emphasizing key findings and issues presented during the workshop. After each source panelist briefly discussed what he or she thought were the most critical and controversial issues, an open discussion period was initiated. It was assumed that the issues discussed by the panelists and audience would be based on the list of questions and topics provided to workshop attendees prior to the workshop. The goal of the panel discussions was to work toward consensus on these critical issues.

Each panel session contained two co-chairs and seven to nine panelists. Each panel session also had a facilitator (one of the co-chairs) as well as a note-taker to help discussions proceed. The focus of each panel and copies of the questions provided to workshop attendees are included in the written summary generated for each panel session.

B.1 Focus/Emphasis of Panel Discussion of Source Monitoring/Testing Needs

The Panel Discussion of Source Monitoring/Testing Needs (otherwise known as the "source panel") concentrated on the needs and barriers ("Catch 22") to developing and implementing mercury CEMs and associated performance specification protocols for use in regulatory compliance. For discussion purposes, it was hypothetically assumed that mercury emissions from the major combustion sources (e.g., utility boilers and waste incinerators) will be regulated. Research CEMs are also needed to fill in fate and transport and source-receptor research gaps. (Filling these gaps will provide valuable information to be used in the regulatory decision process.)

B.2 Source Panel Members

Jeffrey Ryan and Nina Bergan French were the source panel chairs and Russell Bullock, Scott Rauenzahn, Stephen Priebe, Thomas Brown, Ronald Baker, John Bosch, and Catherine Massimino served as panelists.

B.3 Questions/Topics for Source Panel Discussion

- 1) Do you believe total mercury CEMs are capable of cost-effectively monitoring emissions for compliance assurance?

Why or why not?

Which technologies are forerunners, and why?

Which technologies are you less sure of and why?

- 2) What are the greatest concerns associated with CEM operation?

What are the risks?

What are the technical obstacles (e.g., interferences, filter artifacts, durability, biases)?

- 3) How should CEM performance be evaluated?

What are the most important considerations with respect to CEM performance (e.g., drift, calibration technique, sensitivity, precision, durability, etc)?

Is PS 12 still considered to be the appropriate method for evaluating total mercury CEM performance?

Why or why not?

Should PS 12 be revised? Who will do it? When?

What tools (e.g., gas standards, reference materials, comparison methods, techniques) are needed to fully evaluate CEMs?

Are existing reference methods (i.e., Methods 101A and 29) satisfactory as an accuracy check or reference point for total mercury CEM (averaged) data?

- 4) What type of field demonstrations and/or technology improvements/cost reductions are necessary to reduce the risk of implementing total mercury CEMs?

What type and how many field demonstrations will be required to fully demonstrate CEMs?

What are the types of sources that must be considered?

Can nominal and/or worse case monitoring conditions be defined?

- 5) Where are speciating CEMs needed?

Is speciation by difference adequate or are direct speciating techniques needed?

Are performance specifications needed for speciating CEMs?

- 6) Does the CEM technology available today provide an accurate description of the chemical and physical forms of mercury introduced into the ambient air after the stack emissions have diluted and cooled to ambient temperatures?

- 7) What is EPA's role in the development of mercury CEMs? What are the roles of others (e.g., DOE, vendors, State, and local)?

- 8) What actions or outcomes are required to move towards implementing mercury CEMs for compliance assurance?

B.4 Summary of the Source Monitoring/testing Needs Panel

B.4.1 Chair Comments

Jeffrey Ryan, US EPA NRMRL

Mr. Ryan opened by summarizing the following applications/ideas for mercury CEMs presented during the first day of the workshop:

Compliance: CEMs are needed for compliance monitoring; however, efforts to use CEMs for compliance are hampered by the following "Catch 22:" 1) as a market driven technology, CEM developments/advances occur in response to regulatory actions/mandates; however, 2) before regulatory requirements mandating CEM use can be set, technology performance needs to be demonstrated.

Control Technology Research: CEMs capable of measuring both total and speciated mercury are needed to advance control technology research. In addition to methods/technologies which calculate oxidized mercury by subtracting elemental from total mercury measurements (and assuming that the oxidized portion is mercuric chloride). Technologies are also needed which can directly measure different oxidized forms of mercury.

Process Control: CEMs are needed for measuring total and speciated mercury during process control applications. Again, a method/technology which calculates speciation by difference can be used for these applications. It may also be possible to tie CEMs into the process control systems as part of neural networks.

Source-receptor and Fate and Transfer Modeling: CEMs can also be used to support source-receptor and fate and transfer modeling research. There is a clear need to relate stack, plume, and ambient measurements. Based on presentations made earlier in the workshop, current dilution techniques can be used to effectively simulate mercury transformation as emissions exit the plume. In addition to advancing the scientific community's understanding of mercury emissions, source-receptor and fate and transport data are needed to support the regulatory determination process.

In general, however, the workshop focused primarily on using CEMs for compliance monitoring. Based on presentations during the workshop, not only do there appear to be many viable CEMs currently in existence, but less complicated models/techniques are being continually developed (e.g., wet conversion techniques are being replaced with dry chemistry techniques). Although current regulations do not require CEM use, they do provide for and encourage their application. According to Mr. Ryan, the panel/workshop participants need to define what factors encourage CEM use.

Finally, the following points were made:

Performance Specs: The current performance specifications are still in draft form and should be used as guidance. They are open to modification, as long as the changes are scientifically justified.

Emission Ranges: mercury emission levels differ based on their origin (e.g., utility boilers, HWC, or cement kilns). As a result, we need to define the concentration ranges that CEMs need to measure and the conditions they operate under.

Mr. Ryan closed by noting that the purpose of the panel is to define/address obstacles and issues associated with using mercury CEMs for compliance assurance and to develop a list of actions, outcomes, responsible parties, etc., to further CEM use.

Nina Bergan French, Sky+ Inc.

After noting that Mr. Ryan had already summarized many of the points she believed needed to be made, Dr. French stressed that for mercury CEM implementation to occur, users need reliable ("strong") operation data which allow users to confidently assess how CEMs will perform during facility applications. As a result, scientists, facilities, and EPA need to work together to collect these

data (e.g., data which support and define claims that "gold traps can handle sulfur dioxide). Dr. French then asked each of the panel members to briefly respond to the issues raised by the questions distributed before the workshop.

B.4.2 Panel Member Comments

Stephen Priebe, Bechtel B&W Idaho

From a user perspective, Dr. Priebe asked "Why should I (use CEMs) unless I absolutely have to?" Not only are CEMs data viewed as fairly unreliable, many potential users are concerned about maintenance difficulties (e.g., obtaining parts from Europe), unit life-span, reliability, cost, and the possibility that voluntary CEM use could eventually result in CEMs being written into their permits. Furthermore, many potential users may not want to voluntarily use CEMs since they do not really want to know what is happening.

Scott Rauenzahn, US EPA OSW

EPA cannot require facilities to install CEMs unless sufficient data are available to justify the promulgation of a CEM-based standard. Since facilities are not required to install CEMs, EPA is not able to obtain data on the application of CEMs. This "chicken and egg" scenario has hindered the application of CEMs for compliance purposes.

While EPA was able to overcome this obstacle for particulate CEMs (by collecting data as part of an EPA effort), its preference is to use facility-provided data to justify further CEM-based performance specifications and standards. This can be best accomplished by collecting quality data from the largest segment (i.e., industry) where CEMs can be used.

Since thus far EPA has only specified total mercury CEM standards; future compliance requirements will probably be developed for total mercury CEMs rather than elemental mercury CEMs. Since there are not enough elemental mercury "numbers" available to set a standard, it will be difficult to develop elemental mercury CEM requirements in the near future. Additionally, since the speciated fraction is more likely to end up in water bodies, total mercury CEMs are more likely to be used as an ambient tool and speciated CEMs are more likely to be used as a research and risk/fate assessment tool (although manual methods may be more appropriately used to characterize a source).

Catherine Massimino, US EPA Region X

From the perspective of a hazardous waste combustion permitter, Ms. Massimino is concerned about the day-to-day performance of mercury CEMs after they are implemented at actual, operating combustion facilities. This information is essential, since it has to be incorporated in an enforceable fashion into a permit. To reach this goal, an acceptable performance specification (e.g., PS 12) and good field calibration techniques are needed:

The final acceptance criteria for the performance specification also need to be resolved. When developing these criteria, the following questions need to be addressed:

- Can currently available monitors meet the final acceptance standards?
- What level of monitor performance can we live with?
- Can the performance specifications, the monitor capabilities, and the standards for combustion facilities be "matched up"?

Another issue that needs to be addressed is whether CEM data can also be used to assess risk. This is largely dependent on the capabilities of the monitors and the permitter's ability to "tie back

to the risk numbers" (e.g., if the mercury risk standard is a tenth of the mercury standard, it may be difficult to use CEM data to assess risk). This will probably become a larger issue in the future.

Additionally, the CEM monitors specified in the performance specifications need to be commercially available; maintainable (via a local vendor or, at a minimum, from a company with a US presence); economical (since duplicate systems will probably need to be installed at most HWCs which use CEMs as their primary control); and reliable (i.e., operable/online for periods greater than a week).

A phased-in approach to CEM use was suggested to address concerns whether current CEMs are able to meet the acceptance criteria in the current performance specification (PS 12). During the phase-in period, monitor performance needs to be correlated to waste characteristics, operating limits, and the manual method.

Ms. Massimino concluded by listing the following benefits that facilities may experience if they use CEMs:

- Potentially larger operating windows and less conservative limits
- Public assurance
- Improved ability to characterize legacy waste.

Ronald Baker, Aldora Technologies

Mr. Baker opened by noting that his presentation was designed to address what can be demonstrated using PS 12 from a vendor's perspective (i.e., how the 130 µg/dscm standard cascades down through the performance specification).

There are four tests within PS 12: the interference test, the calibration drift test, the calibration error test, and the relative accuracy test. Mr. Baker commented on each of these tests:

Interference Test: Mr. Baker noted that: 1) there are minor differences in how technologies deal with interferences (e.g., sulfur dioxide and/or particulate); and 2) that TUV uses acceptance criteria that are similar to PS 12 and have been fully demonstrated for certain mercury analyzers, and they therefore should not be an issue.

Calibration Drift Test: During a calibration drift test, an analyzer has to achieve a repeatability goal in comparison to a standard over seven consecutive 24-hour periods. In support of this test, Mr. Baker noted recent successes over the last year calibrating against compressed gas cylinders of elemental mercury (similar to how a NOx analyzer is calibrated against nitrogen oxide rather than nitrogen dioxide). He proposed, based on these results, that total mercury analyzers could be calibrated daily against elemental mercury. In locations where the standard is 130 µg/dscm, Aldora is "comfortable" with concentrations of 20 to 150 µg/dscm, although calibration gas vendors need to make more developments and gain more experience in developing products to address these concentrations.

Calibration Error Test: Three concentrations are tested during the calibration error portion of the certification and performance specification process. In locations where the standard is 130 µg/dscm and concentrations of 50 or 100 µg/dscm are expected, errors within 10% of the reference concentration (at 5 or 10 µg/dscm) can be accomplished.

Relative Accuracy Test: After stating that the relative accuracy test receives the most attention of the four tests mentioned under the PS 12, Mr. Baker noted that the "bottom line

yardstick" is 20% relative accuracy or 10% of the standard. Many CEMs (carbon monoxide or sulfur dioxide) are passing on 10% of the standard at lower concentrations. In locations where the standard is 130 µg/dscm, 13 µg/dscm can usually be accomplished downstream of a wet scrubber.

In response to complaints regarding monitor complexity, Mr. Baker noted that vendors are asked to develop "generic" analyzers to address a variety of industries (e.g., utilities, hazardous waste, etc.) and concentrations. Monitor complexity can be reduced to optimize instrument application after specific applications are identified. Additionally, issues regarding service, parts availability, and local representation are a function of the market and the number of installations.

Thomas Brown, DOE NETL (formerly FETC)

CEMs are not ready to be installed in any facility in the US, particularly the utility industry where the nominal mercury concentration is 10 µg/dscm. In addition to producing a variety of flue gas conditions, associated in part with burning three different ranks of coal at over 1,100 facilities in the US, the emissions from the utility industry commonly contain compounds that interfere with measurement accuracy [sulfur dioxide (300 to 3,500 ppm); hydrogen chloride; and nitrogen dioxide (typically 5% of NO_x)].

Although monitors are currently available which can measure mercury concentrations ranging from 20 to 130 µg/dscm, none of these CEMs are capable of routinely and reliably measuring mercury concentrations at coal-fired utilities. Impacts from fine particulate, mercury adsorption, mercury conversion, etc., still need to be addressed, perhaps through the application of up front conditioning systems (to remove hydrogen chloride, sulfur dioxide, and nitrogen dioxide, although the last is more difficult).

Furthermore, vendors need to be worked with to test CEM performance under controlled, pilot scale tests in which one or more types of coal are fired. These tests should be long-term and designed to assess particulate impacts. They should also be designed so that different concentrations of sulfur dioxide and hydrogen chloride can be injected into the flue gas.

In conclusion, the effective application of CEMs across the entire utility industry is complicated by variations between facilities (due to the different types of coal, controls, etc.) and may eventually prove to be impossible. CEM application will also be impacted by the limits set for coal-fired utilities (e.g., if the limit for coal-fired utilities is set between 5 to 10 µg/dscm rather than 10 µg/dscm or above, this will have a big impact on CEM use). Finally, field testing has to be done and calibration systems (with elemental and oxidized mercury) have to be developed so they can be run through the conditioning systems into the analyzers.

John Bosch, US EPA OAQPS

EPA OAQPS is currently involved in a study, scheduled to be completed by the end of next summer, which will be used to help determine whether coal-fired utilities will be regulated. If EPA decides to regulate this industry, periodic and continuous compliance monitoring will be required, probably using CEMs. If CEMs have not been demonstrated to be useful when the regulations are developed, monitoring alternatives will be specified in the regulations.

After stating that permitting and air toxic issues may also have an influence on future mercury CEM use, Mr. Bosch noted the recent advances in CEM technologies and possible improvements to PS

12. Mr. Bosch then suggested that EPA field test a number of CEM technologies to assess optimum performance and to obtain data to revise PS 12.

After revising the PS 12 standard, OAQPS is considering using the EPA ETV Program to expand the number of technologies/vendors known to be capable of meeting the PS 12 standards. Ultimately OAQPS and ETV data could be used by the emission standard division director to justify including CEMs in the regulations.

Russell Bullock, US EPA NERL

Mr. Bullock stated his need, as a modeler, to be able to explain the differences between source and ambient monitoring data (post-stack reactions and their impact on ambient concentrations). Contrary to the expectations of some ("We need you to model the emissions and ambient conditions because we cannot afford to measure them"), ambient and source data are needed in order to develop good models. Although a draft model can be developed based on the first principles of science (e.g., chemical and physical reactions), emissions data (especially source data) and ambient data are both needed to test whether the most important parameters and reactions in the atmospheric processes are adequately addressed by the model. Only after the models are fully developed and tested in this manner can they then be used as a substitute for ambient monitoring. Source data will always be required, even by fully developed and tested models, to assure that the emissions rates simulated by the model are accurate.

After noting the difference between research and compliance mode monitoring, Mr. Bullock emphasized the importance of obtaining speciation data (the difference between oxidized and elemental mercury in emissions) for research and model development. After the models have developed the level of complexity needed to account for conditions in the atmosphere, it may be possible at that point to reduce/simplify monitoring requirements to TGM measurements.

Mr. Bullock concluded by noting that although source sampling at the stack provides important information, air quality simulation models need to be developed which address plume reactions immediately after emission. In order to better understand the condensation and sorption of oxidized mercury gases on particulate in the atmosphere, reactions within the first 10 to 30 seconds after emission need to be better understood. This may be accomplished through dilution sampling.

B.4.3 Open Discussion

James Kilgroe, US EPA ORD

EPA ORD has a substantial budget for control technology projects, including measurement technologies. If it is assumed the Agency decides to regulate mercury from utility boilers, a 2 to 4 year test program will need to be developed which uses CEMs to evaluate different control technologies so that real-time, parametric data can be obtained. Assuming a number of CEM vendors participate in this study, this program may provide a good opportunity to promote the development of CEMs by obtaining data which could later be used to assess whether CEM monitors have the potential to be used as compliance assessment tools. Mr. Kilgroe closed by noting his intention to encourage EPA to work more closely with dilution samplers to understand speciation out of the stack.

In response to Mr. Kilgroe's comments, Mr. Brown noted that DOE is planning to release a solicitation in December 1999 or January 2000 regarding demonstrating/evaluating mercury control technologies. He believes CEMs will play an important role in this study, allowing DOE to collect

data within a couple of days or weeks which would normally take months to a year to collect manually. He encouraged CEM vendors interested in becoming involved with DOE and EPA studies to contact him and Mr. Kilgroe.

Fredric Chanania, US EPA OSW

Mr. Chanania cautioned that many of the points made thus far were made from a research perspective and do not reflect regulatory ("real world") conditions or events. Although the challenges for coal-fired power plants are very different from the challenges faced by HWCs, this is a reflection of differences associated with the level of scrutiny, regulatory history, and nature of the emissions (e.g., sulfur dioxide) from these facilities.

Additionally, there are currently a number of tools ("hammers and carrots") available to the HWC industry which are not currently available for the electric utility industry. To address this need, EPA OSW is about to begin a program which encourages facilities to use CEMs not for compliance purposes, but to generate data on CEM performance and to obtain data to improve a facility's ability to understand variability within their system and how they can meet the standards. As an incentive to enter this program, EPA is allowing these facilities to use very long averaging times (to account for spikes) and (potentially) allowing these facilities an extra year to install APCDs to meet MACT standards.

Although EPA is emphasizing the use of incentives ("carrots"), OSW is taking a broad-based look at mercury treatment standards in the ANPRM for Mercury. Although thus far EPA has not directed specific waste types towards specific types of units (i.e., specific types of incinerators or systems with specific air pollution control or monitoring devices), this may be a possibility in the future. OSW is aware that many facilities have anxieties about compliance issues and is interested in defining what steps need to be taken to get facilities to install CEMs. OSW's focus, however, is not research, but protecting the public and meeting its demand for real-time monitoring.

Mr. Chanania then noted that EPA is not currently targeting the development of nationally codified specifications or a national PS 12 capable of fitting every type of machine/situation; instead EPA is encouraging the development of site-specific approvals/permits developed under the current guidance. From a policy perspective, Mr. Chanania then noted that participants need to remember that science informs but science does not control. As a result, policy makers can not always wait until they have "perfect data" before proceeding with some level of regulation/policy development and that sometimes informed assumptions or "best guesses" need to be used to get policy started.

John Jenks, New Jersey DEP

Although mercury may be the single most toxic air pollutant, a large amount of circular logic ("chicken and egg", etc.) is interfering with the development of approaches to deal with this pollutant. It is necessary to stop "researching (the issue) to death" and start employing a phased-in approach to address mercury monitoring needs. Furthermore, the "flaws" in PS 12 should not be used as a justification to stall CEM use, since a more stringent standard can be phased-in at a later date as more information becomes available. This can be done either using regulations or incentives (preferably).

Dr. French and Mr. Rauenzahn responded that this would be best accomplished by providing incentives to facilities to install CEMs and not focusing on compliance and/or the revision/implementation of the PS 12 procedure. Additionally, Mr. Rauenzahn believes that the processes and procedures defined in PS 12 were essentially "final," but that data are needed to set

the acceptance criteria and that hopefully over the next couple of years these data can be obtained (potentially by category).

Catherine Massimino, US EPA Region X

When justifying alternate monitoring to the public, there is a need to justify why alternate monitoring is not being used for compliance. When developing a permit, phasing-in these data for use in compliance with time should be considered. Furthermore, this intent should be clearly stated up front.

Evan Granite, DOE

The workshop emphasized the use of UV-based CEMs. In response to Mr. Granite's question whether mass spectrometer or atomic emissions spectrometers could potentially replace UV-based CEMs, Dr. French responded that this is possible (and a promising simplification), but since CVAA systems can be made to work, she could not predict that atomic mass spectrometry will replace these methods.

Dana Oliver, Pioneer Chlor Alkali Company, Inc.

When a new regulation/standard is anticipated which is expected to use instrumentation that still needs to be developed, industry wonders whether it can meet the specification/regulation when it comes out and whether the data collected using these new monitors can be used against them if the monitors indicate the facility is not complying with the regulation. Not only does industry want to work with EPA to help develop technologies for monitoring, but it also wants to develop real standards that can be both met and monitored. In the long run, a collaborative, long-term approach to implementing CEMs will result in a standard EPA, industry, and the public can live with.

Scott Rauenzahn, US EPA OSW

Mr. Rauenzahn questioned whether mercury CEMs could be used if the mercury emissions standards for boilers were raised from 10 µg/dscm to 150 µg/dscm. Mr. Brown responded that because the majority of coal-fired units produce levels of 10 µg/dscm, the monitor has to work at these lower limits with higher concentrations of other interfering gases.

Dennis Laudal, University of North Dakota

Mr. Laudal then stated that although mercury CEMs are available to monitor concentrations near 10 µg/dscm, their reliability and consistency needs to be proven over time, through real world applications. In response, Mr. Baker noted that some mercury CEMs are currently capable of monitoring sources with higher emissions and, similar to sulfur dioxide monitors, these CEMs will eventually evolve to the point where they can be used to reliably monitor low concentrations sources (e.g., achieve single digit detectabilities).

Nina Bergan French, Sky+ Inc.

Dr. French questioned whether utility lobbies would effectively block mercury CEM implementation since the technologies could be easily improved by orders of magnitude. Mr. Brown responded that there are significant technical obstacles that need to be overcome, which is the focus of the workshop.

John Bosch, US EPA NRMRL

The Enhanced Monitoring Rule (EMR), which was later replaced by the Compliance Assurance Monitoring (CAM) Rule, potentially affected a large number of sources and could have resulted in the installation of 100,000 CEMs. Although this is not the case with coal-fired utility boilers, once EPA demonstrates CEMs for these applications, EPA also hopes to use the data to encourage the broader application and expanded use of these technologies.

William Haas, Ames Laboratory

(The chair restated the goal of this panel: to identify what needs to be done to begin implementation of mercury CEMs.) Mr. Haas proposed that EPA ETV and TUV collaborate to demonstrate CEM suitability for compliance monitoring. Mr. Kilgroe responded that EPA OAQPS intends to use the ETV Program, which can only test commercial-ready technologies, to the maximum extent possible to support its efforts.

James Kilgroe, US EPA NRMRL

The inlet loadings used to develop MWC regulations for incinerators (200 to 1,500 $\mu\text{g}/\text{dscm}$) were significantly higher than the inlet loadings experienced by utility boilers (approximately 10 $\mu\text{g}/\text{dscm}$). If the Agency decides to target 90% control in this industry, CEMs with an operating range of 1 $\mu\text{g}/\text{dscm}$ will be needed. Based on Mr. Kilgroe's experience, this will be a significant technical challenge.

Lee Alter, Northeast States for Coordinated Air Use Management

In response to Dr. French's question regarding what needs to be done to begin implementing mercury CEMs, Mr. Alter noted that in order to implement CEMs at utilities, it is necessary to be able to distinguish total from speciated forms in order to facilitate trading. Since total CEMs will most likely be proposed for use, this may impede the development of an effective utility program (since these CEMs do not distinguish between elemental and ionized mercury). This comment was echoed by some members of the panel.

Ronald Baker, Aldora Technologies

Mr. Baker tied Mr. Alter's discussion to the redundancy issue by suggesting the use of two monitors, one to measure total mercury and one to measure elemental mercury. In addition to obtaining ongoing, real-time total and elemental mercury concentration data for trading purposes, facilities would be equipped with a backup monitor in the event one monitor goes offline.

Warren Corns, PS Analytical

As a clarification, Mr. Corns noted that AF-based technologies can achieve sensitivities near nanograms per cubic meter levels, even in flue gas matrices, making these technologies almost 500 times more sensitive than needed to support their application at coal-fired utilities.

Jeffrey Ryan, US EPA NRMRL

Based on implementation-related discussions thus far, Mr. Ryan noted that there are opportunities to implement CEMs but that first EPA needs to identify and prioritize which types of sources they need to be implemented at first. This will be partially driven by the incentives used to encourage facilities to use CEMs (e.g., opportunities to expand operating envelopes or delay implementation of the regulations). It also appears that hazardous waste facilities, particularly facilities with wet scrubbers, will be the most amenable to implementing CEMs. There is still a need to determine how to develop the performance specifications for individual sites using the current guidelines. For these first applications, the acceptance criteria will need to remain somewhat open-ended or "to-be-

determined" at a later date. Ultimately, however, EPA needs to define which sources find the incentives to test CEMs the most appealing.

Stephen Priebe, Bechtel B&W Idaho

Dr. Priebe pointed out that there is a need to determine how to initiate interaction between the regulator/permittee and facility to encourage voluntary CEM use. Who is responsible for initiating interactions between the facility, permittee/regulator, or an independent group (e.g., an industry group) needs also to be determined.

According to Mr. Brown, this needs to be done at the local level (not through Washington). Also, based on his personal experiences, many trade associations contain members who are opposed to moving ahead with environmental regulation. Since these organizations are run by consensus, they tend to be more conservative when facing environmental change. Also, Mr. Brown has had better success with voluntary incentive programs when approaching individual companies rather than trade organizations or industry groups.

William Haas, Ames Laboratory

If TUV and ETV collaborate to evaluate the suitability of these monitors, this will most likely be done using the TUV model. As a result, these tests will be performed at specific sites, which can be viewed as a 50,000 dollar incentive for those facilities. Furthermore, TUV also has significant testing competence, which can be used to ensure that appropriate test plans are developed under the technical guidance of the developer.

Scott Rauenzahn, US EPA OSW

As a private company, TUV would need to be paid to participate in this effort. Also, TUV-generated data belong to whoever paid for testing (although many vendors are willing to release these data), and thus are not always publicly available. This fact will need to be overcome in order for data reciprocity to occur. Additionally, there are huge differences in the methods and approaches used in the two programs which would also need to be addressed.

Thomas Kelly, Battelle

Although the ETV Program initially considered using data obtained elsewhere to verify technologies, this is no longer an option.

Dennis Laudal, University of North Dakota

From the vendor's perspective, the fact that the ETV Program is not a certification process is a definite drawback.

James Kilgroe, US EPA NRMRL

It is not necessary to spend too much time debating ETV, since ETV has committed to testing commercially-ready mercury monitors (although the specific details of these tests still need to be worked out) and EPA plans to use this approach to support the implementation of these monitors.

Jeffrey Ryan, US EPA NRMRL

What do EPA and DOE need to do to obtain the information needed to move these technologies forward? Does EPA need to develop the conditioning systems?

Ronald Baker, Aldora Technologies

In order to move forward, a cylinder of gas needs to be certified against Method 29. This will provide a reference from which acceptable tolerances can be developed. Incentives can also be given to encourage calibration gas vendors to develop gases at given concentrations.

PS Analytical

Why should an absolute standard be calibrated against Method 29 if there is an absolute method for measuring how much mercury is in a cylinder of gas? This saturation method, which uses volume measurements from a pool of mercury at a fixed temperature, was published in 1985. As mentioned by another participant, the technique, however, does not work for UV light sources.

Comment (Unknown Participant)

ASTM should be approached about defining/developing terminology and procedures for testing CEM suitability, including checks for automatic zero, span drift, calibration error, etc.

Eric Prestbo, Frontier Geosciences

EPA is currently considering regulating coal-fired utility boilers; however, the resulting monitoring requirements are still unknown (i.e., whether CEMs will be required or whether quarterly testing will be sufficient). Also the concentrations in the coal-fired utility industry do not vary as much as concentrations within the HWC industry, due to the fact that mercury concentrations in different coals only vary by a factor of three. Also, the upcoming ICR data will most likely show that concentrations in coal and flue gases are dramatically lower than expected (up to a factor of 2) due to coal switching in response to the sulfur dioxide regulations. These data will probably have a significant impact on whether a regulation is put in place. Furthermore, if mercury concentrations in coal flue gas are regulated, a standard of approximately 1 µg/dscm will have to be targeted to observe a visible emission impact (more than a 10% reduction). Finally, since it will probably take billions of dollars to develop, research, and implement/install CEMs in coal-fired utility power plants, as a taxpayer Dr. Prestbo believes that society would benefit from using these resources to learn more about mercury fate, instead of learning how to calibrate CEMs for these utility applications. Perhaps a better approach would be to obtain the aid of the utility industry (both monetary and technical) to study the fate and effect of mercury in coal instead of focusing our efforts toward developing regulations requiring CEM use.

Jeffrey Ryan, US EPA NRMRL

In response to these comments, Mr. Ryan noted that the panel is seeking to identify technological improvements to CEMs given potential applications and did not plan to discuss whether utilities should be regulated.

Fredric Chanania, US EPA OSW

Based on experiences with public's response to EPA's plan to better understand HWC emissions, the public will not care what EPA finds out about mercury emissions; they just want EPA to make sure the emissions are as low as possible.

Eric Prestbo, Frontier Geosciences

As an alternative, Dr. Prestbo suggested using this funding to educate the public about mercury.

Jeffrey Ryan, US EPA NRMRL

Based on today's discussion, some of the information needed to move forward on certain fronts is currently available. However, a phased-in approach to address the steps required to define information needs, to identify and provide incentives to sources, etc., will need to be employed.

C.1 Focus/Emphasis of the Panel Discussion of Ambient Monitoring Needs

The Panel Discussion of Ambient Monitoring Needs (otherwise known as the "ambient panel") concentrated on the status and role of ambient mercury speciation methods and models to quantify source-receptor relationships. It was designed to address the needs and requirements to set up ambient and wet deposition measurement stations/networks at several urban locations. It also discussed what source, ambient and meteorological data are needed to support regulatory decisions as well as what mercury exposure/bioaccumulation/TMDL modeling are needed.

C.2 Ambient Panel Members

Robert Stevens and Matthew Landis were the ambient panel chairs and Gerald Keeler, Eric Prestbo, John Munthe, Thomas Atkeson, Matthew Landis, Carl Kamme, and Russell Bullock served as panelists.

C.3 Question/Topics for the Panel Discussion of Ambient Monitoring Needs

- 1) What is the state-of-the-science in measurement methods?
- 2) What are the needs for representative and comparable data?
- 3) Do we need to expand the wet deposition and aerosol mercury monitoring network and add additional atmospheric mercury measurements?
- 4) What are the needs for method standardization and ambient reference method(s)?
- 5) Use of manual versus automated sampling techniques.
- 6) What are the needs for speciation?
- 7) What ambient and source inputs are needed for dispersion modeling?
- 8) What is EPA's role in the development of ambient monitoring techniques? What is the role of other groups?
- 9) What does EPA need to do and when?

C.4 Summary of the Panel Discussion of Ambient Monitoring Needs

C.4.1 Chair Comments

Robert Stevens, Florida DEP

Mr. Stevens opened by summarizing the principal focus for the panel as follows:

"The panel will concentrate on the status and role of ambient mercury speciation and the methods and models used to quantify source-receptor relationships. It will address the needs and requirements to set up ambient and wet deposition measurement stations and networks at several urban locations. The panel will also discuss what source, ambient, and meteorological data are needed to support regulatory decisions, as well as what mercury exposure, bioaccumulation, and TMDLs are needed."

After noting that ambient measurements are often used to develop TMDLs, bioaccumulation estimates, and source-receptor relationships, Mr. Stevens mentioned that the panel was at a disadvantage since there is only a handful of source profiles in the US. According to Mr. Stevens, the last major effort to generate a complete set of source profiles was performed in 1982 in Philadelphia (using receptor modeling for fine and coarse particulate for three major sources – an incinerator, a coal-fired power plant, and a smelter). Furthermore, only limited work is currently being done in the US (e.g., in Glenn Cass and John Watson's laboratories).

Mr. Stevens closed by suggesting that source, ambient, and modeling efforts need to be "brought together" (collaborative efforts, with similar agendas). Mr. Stevens then asked each of the panel members to briefly discuss ambient monitoring issues identified as the focus of the panel.

C.4.2 Panel Member Comments

Thomas Atkeson, Florida DEP

Dr. Thomas Atkeson, Florida DEP, outlined mercury research needs in relation to EPA's application of the TMDL approach. He noted that many of the topics of concern had already been discussed, and that the EPA Office of Water and Office of Air are currently collaborating with Florida and Wisconsin on two TMDL pilot projects to study the effects of atmospheric mercury on water bodies. In the past, water and air programs at both the national and State level have been criticized for being "separate"; however, more collaborative efforts have been taking place in recent years, as demonstrated by projects examining air-water interactions in the Great Lakes and Chesapeake Bay.

When the CWA was first developed, a cycle of monitoring, assessment, and remediation activities was established. Although monitoring and assessment efforts are commonplace, remediation efforts (e.g., feedback into watershed management) have not progressed to the same degree.

Initially, TMDLs were developed to assess relatively straightforward source/effect relationships/impacts [e.g., determining how much biological oxygen demand can be introduced to a water body by a sewage treatment plant without causing a dissolved oxygen (DO) violation]. With time, EPA's approach to assessing impacts broadened, such that once a water body is classified as impaired, EPA has to identify and control the source of the impairment. (Note: A water body can be determined to be impaired if does not conform to all the criteria associated with its classification type. For example, if someone determines that the fish from a Class III lake cannot be eaten, the lake will be classified as impaired and EPA will need to begin investigating and controlling the pollutant source(s) responsible for the problem).

EPA is currently considering expanding its approach to address impairments to water bodies attributed to contaminants from the atmosphere. If this approach is employed, the CWA and CAA will be "married" so that air sources may be regulated based on water problems. Furthermore, the resulting TMDL's for mercury will be driven by EPA's risk assessment for mercury and forthcoming water quality criteria (due in 2000).

In response to these changes, ambient, source, and modeling representatives need to be ready to answer questions about source-receptor relationships, specifically what proportion of the mercury deposited in an area is coming from within the different States and the US (which the States or Federal governments may be able to control in some fashion) and what proportion is coming from farther afield. This is particularly important for Florida, since 95 to 98% of mercury present in the Florida Everglades came out of the atmosphere.

Therefore, to better estimate the amount and form of mercury, emissions data need to be obtained and provided to modelers and regulators responsible for recommending regulatory strategies to reduce exposure to mercury.

Clyde Sweet, Illinois Water Survey

Clyde Sweet, Illinois Water Survey, discussed the development of the North American Mercury Deposition Network. The approach used to develop the network is to set up a number of sites across the region (similar to the National Atmospheric Deposition Program) coupled with a smaller number of research sites where source-receptor modeling, dry deposition testing, and other mercury-related research could occur.

Since this proposal was developed, approximately 40 MDN sites have been added to the network, which, when coupled with some of the smaller wet deposition networks already in existence, can be used to form a NADP acid rain-style network, at least for the Eastern US. Dr. Sweet emphasized the need to maintain these sites over a long enough time period to establish the effectiveness of mercury emission controls.

Finally, two research sites are being set up in Ohio and Florida with funds provided by EPA NERL. Hopefully these sites will also help answer questions which cannot be answered based on work done at wet deposition-only sites (e.g., sources of mercury, dry deposition, etc.).

John Munthe, IVL Swedish Water and Air Pollution Research Laboratory

Dr. John Munthe, IVL Swedish Water and Air Pollution Research Laboratory, Göteborg, Sweden, explained that when speciating mercury, both in emissions and ambient air, it is important that research goals be understood. These goals then help in establishing and prioritizing EPA Agency needs. Since mercury is known to be a toxic element, society may benefit more from using current research funding to control emissions. However, EPA must first identify the form of mercury that is being emitted to better design the most effective controls. For example, the control used for elemental mercury would be very different from the control technology used for mercuric chloride.

Source-receptor relationships for mercury are being investigated so that the regulatory and scientific community can determine where the mercury is originating and determine how to control its impact. In Europe, the UNEC has focused its control efforts on apportioning mercury emissions and deposition to different countries. In many cases, emission limits and reductions are used to reduce depositions to sensitive areas. This is accomplished by apportioning the emissions to different sources (or source categories) and relying on atmospheric modeling results.

To ensure that sound atmospheric modeling results are obtained, however, the regulatory and scientific community needs: 1) good total and speciated mercury emission measurements; 2) a thorough understanding of mercury reactions in the atmosphere; and 3) atmospheric data which can be used to modify/validate model results. Although it may not be practical to measure the speciated emissions from all major sources, research efforts need to be focused on measuring speciated

emissions from all the major source categories, so that this information can be used to update emission inventories.

Eric Prestbo, Frontier GeoSciences

Dr. Prestbo, Frontier GeoSciences, suggested that the following three items are needed to support mercury efforts: 1) a national deposition network; 2) data obtained close to sources; and 3) the capability to do mercury field calibrations for CEMs.

In order to develop the deposition network, methods for validating the available models need to be developed. After noting that results from the NADP sites have shown that the US sulfur dioxide controls have had a dramatic effect on sulfur dioxide/nitrogen dioxide deposition in the Northeast, Dr. Prestbo noted that similar comparisons and effects of control regulations may be possible for mercury deposition if US monitoring efforts begin coordinating with each other (before the mercury controls are put in place) in support of this goal. Dr. Prestbo then suggested that EPA may want to actively ensure that the different testing groups cooperate with each other and use similar mercury measurement methods. Additionally, "super sites" are also needed for speciation testing, event sampling, and other mercury-related research.

The availability of mercury deposition data close to sources is limited. Although a similar, but more complex, study was done in Florida, there are currently no data in the US documenting mercury rainwater deposition underneath a plume from an isolated single source during a rain event. Accordingly, new studies need to be performed in which event sampling is performed both upwind and downwind (e.g., 10 kilometers) of a source as a simple weather system moves across the country. This kind of data would be highly useful to determine the local mercury deposition contribution from combustion point sources. Currently, EPA is largely limited to modeling local mercury deposition from combustion plumes.

Finally, emphasis needs to be placed on developing improved field calibration techniques for speciation of mercury using CEMs. Without real-world calibration techniques for mercury speciation in flue gas, the data will always be subject to relatively high uncertainty.

Gerald Keeler, School of Environmental Engineering, University of Michigan

Dr. Keeler, from the University of Michigan's School of Environmental Engineering, proposed in 1995 that MDN set up an intensive monitoring event sub-network as part of the regional long-term monitoring network. This sub-network would allow a number of research questions to be answered (including how different forms of mercury are being removed). Data collected from a number of specific source areas (e.g., coal burning and oil burning) would aid in determining source-receptor relationships. Dr. Keeler suggested that EPA consider this proposal for application in the near future.

According to Dr. Keeler, the biggest uncertainty associated with TMDL efforts is the uncertainty associated with the forms and amounts of mercury emissions and ambient air concentrations. In order to improve the performance of TMDL models coupled to watershed effect studies, better data are needed. Furthermore, major source categories need to be studied, particularly with respect to day-to-day and seasonal variation in emission patterns.

Finally, opportunities to perform coupled emission deposition studies should be utilized, so that researchers/modelers can investigate the chemistry and transport of mercury in the atmosphere. Aircraft measurements, receptor site measurements of the major forms of mercury (mercuric

chloride, elemental and particle bound mercury), and speciated mercury emissions are vital inputs to the current source-receptor models.

Karl Kamme, Opsis, Inc.

Karl Kamme, Opsis Inc., related his experience with mercury measurements using the DOAS technology. His studies suggest that both fence-line and source characterization are needed to address source emission characteristics. The DOAS technology is currently being used by ORD and EPA's Office of Enforcement to measure fugitive mercury emissions from chlor-alkali operations in the United States. In addition, the DOAS technology is approved by the European testing laboratory, TUV, to measure in-stack emissions of elemental mercury from incinerators and fossil fuel powered electric utilities. Mr. Kamme also noted that his company's efforts to get industry to install "fence-line" applications have been hindered by concerns that the data obtained using these systems can be used against them.

Matthew Landis, US EPA Research Triangle Park (RTP)

Dr. Landis, US EPA RTP, observed that when developing a model for estimating emission transport, deposition, bioaccumulation, etc., the ultimate goal is to set up a model with predictive ability, so that the model can be used to test different load reduction scenarios and their effect on deposition to water bodies and endpoint concentrations in fish. Dr. Landis then noted that researchers and regulators need to make sure that the knowledge, tools, and models needed to support ongoing aquatic systems research are in place so we can "go from the source to deposition in the water body."

C.4.3 Open Discussion

Robert Stevens, Florida DEP

Before opening the floor to questions/comments, Mr. Stevens noted that setting up a station under a plume is not a trivial exercise. In fact, two stations will be set up (west of Ft. Lauderdale, Florida, and north of Columbus, Ohio) within the next year to characterize local and regional emissions. The data from these "super sites" will be used to characterize atmospheric concentrations of various forms of mercury, both in the atmosphere and in wet deposition.

Thomas Brown, DOE NETL (formerly FETC)

According to the panel, there needs to be a connection between the source and the deposition. Under the EPA ICR, both EPRI and DOE are funding testing at sites for mercury speciation in flue gas. DOE and EPRI have also contributed funding to examine static plume dilution and total and total speciating mercury CEMs. Mr. Brown is interested in discussing the potential for performing deposition studies for these sites. One utility site in particular is an excellent location for performing a joint EPA/DOE deposition study (a 1,100 megawatt plant, with three stacks and speciated mercury in the flue gas, which is located in an isolated, relatively pristine area in Minnesota).

Fredric Chanania, US EPA OSW

Information on specific sources and their impacts on mercury receptors may eventually be obtained from data submitted to fulfill permit reporting requirements. Currently, Mr. Chanania knows of one permit in which a hazardous waste cement kiln is required to periodically submit ambient monitoring data. More permits with local ambient monitoring requirements are expected in the future, particularly in areas where the local permittees are uncertain that emission goals will be met within their area. It may also be possible that EPA will be willing to offer regulatory incentives (e.g., flexibility) to facilities willing to perform ambient monitoring.

The CAA requires that the Administrator must reduce mercury emissions by 90% in the near future. The CAA does not, however, directly address "tying in" a particular emission effect to a specific source. From a regulatory perspective, this can be interpreted as "do what you can now, we'll figure out the details later." Thus, if the goal is to build momentum behind source control, care needs to be taken to ensure that researchers/regulators do not display too much uncertainty regarding the fate and transport data/methods.

Perhaps an alternative approach would be to focus on cutting the mercury in wet deposition in half and to dedicate resources on deposition studies (via MDN networks) rather than trying to identify the "right" sites to control based on fate and transport research.

Thomas Atkeson, Florida DEP

In 1992 Dr. Atkeson was privy to the results of a Swedish study of forested catchment lakes. The study concluded that there was such a large proportion of the deposited mercury tied up in the watershed that if deposition was cut by 50%, it would take 500 years for the lake to re-equilibrate to a new load. A recent study from Sweden, however, appears to indicate that reductions in Eastern Europe emissions have resulted in reduced deposition in Southern Sweden and surprisingly rapid decreases in lake effects.

John Munthe, IVL Swedish Water and Air Pollution Research Laboratory

In response to Dr. Atkeson's comments, deposition reductions of close to 50% have been observed in the West Coast of Sweden. There has also been a reduction in mercury concentrations in fish approaching 10%.

Thomas Atkeson, Florida DEP

The most advanced aquatic models indicate that shallow wetlands, like the Florida Everglades, will experience more rapid and quantitatively significant responses to deposition changes than less dynamic, less shallow water bodies.

Russell Bullock, US EPA NERL

Mr. Bullock, US EPA NERL, commented that when Congress mandated research and science directed emission cuts in 1990, researchers and regulators did not realize at that time that speciation of mercury would make a significant difference. At that point, researchers and EPA were focused on gaseous and particulate mercury.

Given the new appreciation of speciation issues and effects, significant benefits can be realized if researchers and regulators are able to determine which forms of mercury cause the most problems and concentrate on controlling just those emissions. In order to provide appropriate modeling scenarios, speciated mercury measurements are needed from the representative source types (i.e., medical waste incinerators, resource recovery incinerators, and coal and oil-fueled power plants). Currently the official method for measuring mercury emissions provides only total gaseous and particulate mercury. According to Mr. Bullock, "I and my ORD colleagues consider this unacceptable."

James Kilgroe, US EPA NRMRL

After voicing his support for much of the work the panel mentioned, Mr. Kilgroe noted that if the government decides to regulate mercury, the Agency will need good information to develop/evaluate cost-effective strategies to control emissions and make good policy decisions. In addition to reliable data on plant emissions (speciated and total), cloud chemistry, and mercury transport, the Agency will also need to know which types of emissions can be considered local, global, and/or regional problems.

Paul Mathai, US EPA Office of Toxic Substances

EPA is developing a national action plan for addressing mercury for all media (air, water, etc.). This work needs to be "tied-in" with other program activities and measurement studies so that a more holistic plan is developed. Sector-based measurement techniques also need to be developed which define how to plan to measure the success of a reduction in each of these sectors (e.g., utilities and medical waste).

In response to Mr. Mathai's comment, Dr. Atkeson noted that mercury is just a trace gas in emissions, an ultra-trace gas in the atmosphere, and an ultra-trace gas in water. As a result, "it has no direct significance to anything, except that it bioaccumulates in fish." Thus bioaccumulation in fish can be used to indicate the outcome.

Comment (Unknown Participant)

The CAA amendments of 1990 were an amalgam of efforts specified by Congress for EPA. Among these "efforts" was an attempt to force EPA to perform mercury risk assessments before risk management steps were taken. These studies were a good first step to require EPA to use the risk paradigm in decision making. Since researchers/scientists do not have a benign tracer that can be used to track mercury emissions from sources to their receptors (fish), they have to use models to assess risk and impact. Unfortunately, since there currently are not enough data to check whether the models are right, and there are not enough models of different processes to check against current data, progress has been slow.

Two field studies are currently being performed in an attempt to get the information needed to help eliminate this "Catch 22." The first study is being performed at a power plant near Lake Superior; this study is examining mercury transport from the power plant, downwind into the water system, and through the methylation process taking place along the margins of Lake Superior. The other study is being performed cooperatively with Canada; the purpose of this study is to determine what type of mercury in the lake system is taken up by the fish (e.g., newly deposited mercury or mercury from disturbed sediments). If the second study determines that the mercury in fish is from accumulated mercury sources in the watershed (e.g., disturbed sediments), then management steps for sources may take decades to show an impact. If the study indicates that mercury in the fish "originates" from new deposition, more rapid responses may be realized from the management steps.

By the time these studies are completed (in approximately 5 years), hopefully new information on the health effects of mercury, which is the second branch in the EPA risk assessment paradigm, will be available. When combined with information regarding exposure levels, this information can be used to make informed risk management decisions regarding mercury emissions.

John Ackerman, US EPA Region IV

EPA ORD has a research plan which is currently available for comment and should be finalized within the next couple of months. Since long-term monitoring is often classified as routine, the NADP MDN was developed. It may be a good idea, within the next year, to address what is known about monitoring and develop an approach to monitoring across media. Furthermore, researchers need to make correlative measurements which can be related to the mercury concentrations. Finally, within the next 2 years, researchers, EPA, and others need to establish a baseline and specify future monitoring requirements.

It is also very important that States use the correct scale of model when estimating TMDLs. Unfortunately, finding a model which is bigger than an urban airshed model (50 kilometers), but smaller than the entire US (hopefully near about 200 kilometers) will be difficult. [Note: During these efforts, Region IV has gained some experience with the Regulatory Modeling System for Aerosols and Deposition (REMSAD) model, which it can share with others.] Also, the results of the mercury pilots mentioned by Thomas Atkeson should be available next spring.

Russell Bullock, US EPA NERL

The REMSAD model uses the exact same parameterization for the deposition of elemental mercury (via a chemical reaction, chemical oxidation, precipitation, and wet deposition) as specified in the RELMAP. This parameterization was originally developed by Petersen et al. in Europe using a Lagrangian model with a horizontal resolution of 150 kilometers. Since the REMSAD is a fixed-grid Eulerian-type model (which resolves the atmosphere in a much different manner), Mr. Bullock cautioned that the REMSAD mercury model should be tested using good emission and deposition data before it is broadly applied.

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