

1     **Findings and recommendations from a workshop on “Reducing the uncertainty in**  
2           **measurements of atmospheric Hg” held at the University of Washington**  
3                           **Oct 23-25, 2008**  
4

5     **Summary**

6     Mercury (Hg) is ubiquitous in the environment and a concern for human health, primarily  
7     due to its methylation and bioaccumulation in aquatic food chains. The atmosphere is a  
8     major pathway by which Hg is distributed globally and a source of this contaminant to  
9     terrestrial and aquatic systems. There are significant gaps in our understanding of Hg  
10    sources, sinks and atmospheric chemistry. This lack of understanding is hindered by the  
11    methods available for measurement of atmospheric Hg, the available data, and our  
12    understanding of atmospheric reactions. To address these uncertainties an international  
13    group of experts was convened in Seattle, Washington in October 2008 to develop an  
14    assessment of our current capabilities for measurement of atmospheric Hg concentrations  
15    and fluxes, and to develop a set of recommendations for future research.  
16

17    **Background**

18    Because of the very low concentrations in the atmosphere,  $\sim 1.5 \text{ ng/sm}^3$  (standard  $\text{m}^3$ ) for  
19    gaseous elemental mercury (GEM) and  $\sim 10$ 's of  $\text{pg/sm}^3$  for reactive mercury,  
20    measurements of Hg are challenging. Mercury in the air is measured as operationally  
21    defined forms that include gaseous elemental mercury (GEM), reactive gaseous mercury  
22    (RGM, e.g.  $\text{HgO}$ ,  $\text{HgCl}_2$ ,  $\text{HgBr}_2$ ,  $\text{Hg}(\text{OH})_2$ ) and particle-bound Hg (PHg). The sum of  
23    all gaseous species is often called total gaseous Hg (TGM). The method most often  
24    applied to quantify gaseous Hg involves concentrating on a gold substrate, followed by  
25    thermal desorption and detection as the elemental form using cold vapor atomic  
26    fluorescence spectrometry (CVAFS) (Ebinghaus et al., 1999; Bloom and Fitzgerald,  
27    1988, Munthe et al., 2001). In most environments, gaseous elemental mercury (GEM) is  
28    the dominant form while RGM and PHg are typically a small percentage of the total.  
29    While it is known that oxidized Hg (II) compounds can exist in the gas phase, to date  
30    there has been no unambiguous identification of the chemical form of these compounds  
31    in the atmosphere.  
32

33    For the past 10 years, routine measurements of atmospheric Hg have been made using  
34    instrumentation manufactured by Tekran (Landis et al 2002). The complete system  
35    includes the model 2537A analyzer, that is advertised as measuring total gaseous mercury  
36    (TGM) as well as additional components (Tekran 1130 and Tekran 1135) that, when used  
37    in combination with the 2537A, allow for an operationally defined measurement of GEM,  
38    RGM and PHg. There is some disagreement as to whether gaseous Hg (II) compounds  
39    are quantified when using the 2537A only (Temme et al., 2003). If gaseous Hg (II)  
40    compounds are included in this measurement, then the Hg quantified would properly be  
41    referred to as TGM. Because scientists using this instrument do not agree, some report  
42    these measurements as GEM, while others report TGM. It is also thought that whether  
43    RGM is included depends on the sampling inlet configuration and environmental  
44    conditions.  
45

46 In the Tekran 2537A instrument GEM is concentrated from the atmosphere on a gold  
47 substrate, then desorbed and detected by cold vapor atomic fluorescence spectroscopy  
48 (CVAFS). The method for determination of RGM consists of collection on an annular  
49 denuder coated with KCl. Hg on the denuder is thermally desorbed and analysis is  
50 conducted using CVAFS (Landis et al., 2002). There are concerns regarding the  
51 efficiency of this system for collection of all RGM compounds and interferences due to  
52 environmental conditions. Since RGM concentrations are present at extremely low  
53 concentrations ( $\text{pg}/\text{sm}^3$ ), longer collection times are required as compared to the TGM  
54 measurement. Particle bound Hg has been collected using a variety of sampling systems  
55 (Ebinghaus et al., 1999; Keeler et al., 1995; Wangberg et al., 2003). The Tekran 1135  
56 system uses a quartz particulate filter after the denuder (1130) and before the 2537A unit.  
57 Because of the need to keep coarse particles from entering the denuder these are typically  
58 removed from the air stream by a cyclone which passes only those particles  $<2.5 \mu\text{m}$   
59 diameter in size.

60  
61 Despite the fact that atmospheric mercury is an important global pollutant, there are still  
62 significant gaps in our understanding of the forms, spatial-temporal behavior, and fluxes  
63 between environmental compartments. There are also significant concerns regarding our  
64 ability to measure Hg (e.g. Lindberg et al., 2007; Pirrone et al., 2008). For this reason,  
65 the National Science Foundation provided support to convene a workshop focused on  
66 discussing uncertainties in atmospheric Hg measurements. The workshop was organized  
67 by Dan Jaffe (University of Washington) and Mae Gustin (University of Nevada). A  
68 group of 30 of the world's experts on mercury measurements participated in the  
69 workshop held on the University of Washington campus in October 2008. A list of the  
70 participants is given in Appendix A.

71  
72 Prior to the workshop, the following questions were posed to the group as a means to  
73 focus the presentations and discussions at the workshop:

- 74 1) What are the detection limits and uncertainty of current methods for total (TGM),  
75 particulate (PHg), elemental (GEM) and reactive mercury (RGM)?
- 76 2) How consistent are measurements of GEM, TGM, RGM and PHg from place to  
77 place and group to group from ground based observations?
- 78 3) How consistent are measurements of GEM and TGM by aircraft?
- 79 4) What is known about oxidized Hg in the atmosphere?
- 80 5) What is the status of Hg calibration systems?
- 81 6) What new methods are on the horizon for atmospheric TGM and Hg species, and  
82 how should we compare these to existing methods?
- 83 7) What surrogate methods can be used for determining spatial patterns of  
84 atmospheric Hg?
- 85 8) How can measurements be used to partition surface concentrations that are due to  
86 area emissions versus down-welling of free tropospheric air? What ancillary data  
87 are needed to identify sources of Hg?

- 88 9) Is there a need for additional mercury method inter-comparisons? If so, how,  
89 when and where should these be organized? What should be the protocol for  
90 airborne measurement comparisons and air-surface measurement comparisons?
- 91 10) What additional strategies can we identify to move mercury science forward?
- 92 11) What type of data (spatial, temporal and chemical specific) need to be collected to  
93 address the broader impacts of atmospheric Hg as a potential contaminant of  
94 ecosystems?  
95

## 96 **Results of the workshop**

97  
98 The workshop took place over 2.5 days (Oct 23-25, 2008). Most scientists gave short  
99 presentations focusing on uncertainties and measurement challenges. Presentations were  
100 grouped by topic. Following each group of presentations a set of "Findings and  
101 recommendations" was developed by the entire group, these are presented below. The  
102 workshop agenda is attached as Appendix B. Where possible, reference is made to  
103 published papers, however where new findings were reported at the workshop these are  
104 referenced as "speaker name, workshop presentation".  
105

## 106 **Overarching finding and recommendations:**

- 107
- 108 1) The atmospheric chemistry of Hg remains poorly understood, especially the  
109 oxidation pathways by which GEM is converted to RGM, the reduction pathway  
110 which converts RGM back to GEM, and the gas-particle partitioning.
  - 111 2) The limitations and potential interferences with our current measurement methods  
112 have not been adequately investigated. Alternate methods to measure  
113 atmospheric Hg are needed. These would increase our confidence in existing  
114 methods.
  - 115 3) There is a need for identification of the chemical forms of oxidized mercury in the  
116 atmosphere and methods to measure these compounds individually.
  - 117 4) Since Hg is emitted and transported with other atmospheric species it is important  
118 to collect other chemical data simultaneously (e.g. CO, O<sub>3</sub>, aerosols).
  - 119 5) For both atmospheric concentrations and Hg deposition, there is a need for data  
120 across large spatial scales.
  - 121 6) Large scale integrated experiments with measurements on multiple scales (e.g.  
122 surface, aircraft, satellite, mountain-top) that compare observations between  
123 groups and have integrated modeling would play a major role in advancing our  
124 understanding.
  - 125 7) A permanent network of ground based monitoring sites and observations of  
126 mercury and/or related species on a global scale and with remote sensors would  
127 be highly desirable. These data are needed to test and validate model processes  
128 and predictions, understand the source-receptor relationships and understand  
129 long-term changes in the global mercury cycle.
- 130  
131

132 **Session 1: Issues concerning ground-based measurements**

133

134 **Findings:**

- 135 1) There has been good progress in our ability to measure atmospheric Hg in the past  
136 10 to 15 years. An automated instrument is available to measure gaseous Hg with  
137 sufficient sensitivity (Tekran 2537A), and this instrument is in wide use around  
138 the world. In general, the community has good confidence in ground based  
139 measurements of Hg using this instrument (Ebinghaus et al., 1999). However,  
140 there was debate and discussion regarding whether the Tekran 2537A alone  
141 collects RGM, and thus whether it determines TGM or GEM. In most cases this  
142 is not a significant concern since RGM is a small fraction of GEM. However if  
143 one is interested in understanding the atmospheric oxidation of GEM or the  
144 deposition of Hg then this is a critical concern. Given the affinity of RGM  
145 compounds to stick to surfaces, the inlet configuration plays a significant role in  
146 whether RGM is delivered to the detector or not.
- 147 2) Injection of air from a saturated Hg vapor source maintained at a constant  
148 temperature is usually used for primary calibration of CVAFS. For this to be  
149 accurate the Hg vapor pressure versus temperature relationship must be known  
150 accurately (e.g. Dumarey et al., 1985). For the past 20+ years most mercury  
151 researchers have used the Dumarey equation (ISO 6978) to provide a  
152 concentration of mercury for calibration. A recent re-analysis and curve fit of  
153 past data on this relationship in a vacuum has been published by NIST (2006) and  
154 Huber et al., (2006). The new vapor pressure curve differs from the Dumarey  
155 equation by approximately 7% at relevant temperatures. In order to resolve this  
156 difference a laboratory study was completed by Brown et al. (2008a). They  
157 reported that the Dumarey equation better predicts the concentration of saturated  
158 mercury vapor in air at ~1 atmosphere, compared to the NIST/Huber relationship.  
159 Also unpublished research by Tekran has shown that the Dumarey equation is  
160 consistent with calibrations using NIST standard reference materials (e.g. SRM  
161 3133). Because of this discrepancy, scientists at NIST Gaithersburg (S. Long)  
162 have done new measurements of the saturated vapor pressure at atmospheric  
163 pressure. The recent NIST measurements are not yet published, but appear to be  
164 consistent with the Dumarey relationship. The community expects that NIST will  
165 finalize its recommendations in the near future.
- 166 3) Because the Tekran 2537A is typically calibrated at only two points, zero and the  
167 other at  $\sim 15 \text{ ng/sm}^3$  there is concern regarding the assumption of linearity of the  
168 calibration. This appears to be most significant at very low concentrations or low  
169 mass loadings of the gold traps (Swartzendruber et al., 2009a).
- 170 4) The uncertainty of GEM measurements is 12-20% (2 sigma), excluding the  
171 contribution from the vapor pressure uncertainty. This is based on field  
172 intercomparisons (Aspmo et al., 2005; Temme workshop presentation) and  
173 estimates from propagation of errors (Temme et al., 2007; Brown et al., 2008b).  
174 Including the uncertainty from the vapor pressure relationship could increase the  
175 uncertainty by approximately 7%, if this remains unresolved.
- 176 5) RGM concentrations are quantified based on an operationally defined method  
177 using KCl denuders. There are very limited tests for interferences, specificity and

178 calibration that have been published (c.f. Landis et al., 2002; Temme et al., 2007).  
179 The uncertainty in RGM measurements is much greater than for GEM.  
180 Differences of 30-40% (Lyman et al., 2007) or more (Aspmo et al., 2005) have  
181 been reported for co-located RGM measurements. Tests based on desorption of a  
182 known amount of  $\text{HgCl}_2$  loaded on a denuder from solution have been used with  
183 some success to give information on instrument performance but they do not  
184 indicate the efficiency of RGM collection from air (Prestbo, workshop  
185 presentation). Thus, how efficiently the denuder collects and retains RGM and  
186 whether it collects all forms of RGM is not presently known.

- 187 6) Limited studies have been done to characterize the measurements of particle-  
188 bound Hg. There is one report of loss of PHg on filters during extended sampling  
189 in a marine environment (Malcolm and Keeler, 2007). Another study indicted  
190 that PHg may be lost from the particle phase at elevated temperatures in the  
191 Tekran 1130 and be detected as RGM (Rutter and Schauer, 2007).
- 192 7) Different groups may apply different operating parameters for the Tekran  
193 instruments, thus impacting the comparability of the data between sites.  
194 Environment Canada has developed a standard operating procedure for the Tekran  
195 system and a series of steps for quality assuring the data. A similar protocol is  
196 being developed in the United States by the Mercury Deposition Network.(see  
197 <http://nadpweb.sws.uiuc.edu/amn/>)  
198

### 199 **Recommendations:**

- 200 1) GEM- TGM measurements.
- 201 a) A systematic investigation to determine whether the Tekran 2537A detects GEM  
202 or TGM in different environments is needed. The impact of inlet configuration on  
203 the measurement of GEM and TGM is also needed.
- 204 b) It is recommended that all experimentalists report the temperature for primary  
205 calibrations and the mercury equation used.
- 206 c) All groups should report Hg data in either mass concentrations at STP, where STP  
207 is clearly defined, or as volumetric mixing ratios.
- 208
- 209 2) RGM measurements
- 210 a) The collection efficiency of the KCl denuder for the measurement of RGM needs  
211 to be assessed using gaseous oxidized mercury compounds. Potential  
212 measurement interferences need to be determined. Tests are needed to determine  
213 whether all forms RGM in the atmosphere are collected by the denuder.
- 214 b) A method for field calibration of the RGM measurement needs to be developed.  
215
- 216 3) HgP measurements.
- 217 a) The potential for gas-particle interconversion and interferences in the method  
218 need to be better understood.
- 219 b) The inlet configuration for HgP needs adequate care to ensure appropriate particle  
220 throughput in the desired size ranges.  
221  
222

223 **Session 2: Issues concerning aircraft measurements**

224

225 **Findings:**

- 226 1) GEM can be measured by aircraft. The uncertainty is greater than ground  
227 measurements due to a more challenging calibration environment and the smaller  
228 mass of Hg collected (Talbot, workshop presentation, Swartzendruber et al., 2008;  
229 2009a).
- 230 2) There is evidence for a non-linearity in the Tekran system at low mass loadings  
231 on the gold traps (Swartzendruber et al., 2009a). This is especially important for  
232 aircraft sampling given the reduced pressure at altitude and the shorter collection  
233 times typically used.
- 234 3) There is general consistency among published reports on a relatively flat mean  
235 vertical profile for GEM (Banic., 2003; Swartzendruber et al., 2008; Talbot et al.,  
236 2008; Slemr et al., 2008), with one exception (Radke et al., 2007). However in  
237 one direct intercomparison, a significant discrepancy in the absolute  
238 concentrations was reported (Swartzendruber et al., 2008).
- 239 4) Two reports suggest significantly reduced Hg in the stratosphere. One set of data  
240 indicates essentially zero GEM in the stratosphere (Talbot et al., 2007). Another  
241 dataset suggests a ~50% reduction in THg from tropospheric values (Slemr et al.,  
242 2008). This difference could be explained by the presence of RGM. However  
243 given that both instruments used high flow inlets with no method to remove  
244 RGM, it is difficult to understand why one instrument responded to RGM  
245 whereas the other did not.
- 246 5) Currently there are very few measurements of RGM in the free troposphere.  
247 Three studies have reported periods with high RGM in the free troposphere, but  
248 there is inadequate data to develop any broad understanding regarding the overall  
249 concentration and variability across space and time (Sillman et al., 2007;  
250 Swartzendruber et al., 2006; 2009)
- 251 6) Particulate mercury is generally very low ( $<5 \text{ pg/sm}^3$ ) in the free troposphere  
252 (Murphy et al., 2006; Swartzendruber et al., 2006), except when sampling in  
253 plumes downwind of major industrial source regions (e.g. Friedli et al., 2004) or  
254 fires (Finley et al., 2009).
- 255 7) There are limited data collected from an aircraft and significant challenges in  
256 making airborne measurements of Hg. There are concerns regarding the inlet  
257 system, calibration of the instruments, flow measurement, and the detector  
258 sensitivity and linearity at low concentrations,

259

260 **Recommendations:**

- 261 1) All experimentalists must clearly identify the target component (GEM or TGM)  
262 and demonstrate how their measurement system either includes or excludes RGM.
- 263 2) All aircraft investigators need to carefully evaluate their inlet. A standardized  
264 inlet would be desirable.
- 265 3) Development of in-flight calibration methods for GEM and RGM are needed.
- 266 4) Measurement of GEM by the CVAFS system needs to be assessed at the low  
267 mass loadings used in aircraft systems.

- 268 5) GEM, RGM and PHg measurements by aircraft need further development and  
269 evaluation. Comparison of high elevation mountain top observations could be  
270 used to help evaluate aircraft measurements.  
271 6) The published data and our evaluation indicates the need for a carefully  
272 performed aircraft intercomparison for GEM and, if possible, RGM.  
273

### 274 **Session 3: Issues concerning new measurement methods**

#### 275 **Findings:**

- 277 1) There are a small number of new methods being developed for the measurement  
278 of atmospheric Hg, but these are in their infancy and need further development  
279 and evaluation.  
280 2) Several new methods for detection of GEM are under development. Two-photon  
281 laser induced fluorescence (LIF) has the potential to provide rapid and sensitive  
282 data for GEM (Bauer et al., 2002; 2003). Cavity Ring-Down Spectroscopy  
283 (CRDS) is another tool that may be useful. Previous work has shown that CRDS  
284 can rapidly measure GEM, but at concentrations well above ambient (e.g. Spuler  
285 et al., 2000). Current research is extending this method to ambient and sub-  
286 ambient for flux applications (Obrist, workshop presentation, Moosmüller et al.,  
287 2009)  
288 3) Passive sampler methods appear to have promise for obtaining air concentrations  
289 of GEM and RGM data over large spatial scales (Skov et al., 2007; Lyman et al.,  
290 2007).  
291 4) Identification of the chemical forms of gaseous oxidized mercury may be possible  
292 based on their desorption profile from a KCl or uncoated denuders (Hynes  
293 workshop presentation; Donohue, 2008) and or mass spectrometry e.g. API-  
294 MS/MS/MS; ESI/MS/MS/MS (Ariya workshop presentation). However these  
295 methods need further development.  
296 5) Specific compounds such as HgCl<sub>2</sub>, HgBr<sub>2</sub> and HgO can be generated using a  
297 permeation source. Thus calibration of Hg instruments using specific compounds  
298 may be feasible (Lyman, workshop presentation; Hynes, workshop presentation).  
299 6) Two groups (UW and NCAR) are developing aircraft instrumentation for GEM,  
300 PHg and RGM measurements. While both groups instruments' utilize  
301 modifications to the existing Tekran/ CVAFS method, there are significant  
302 differences in the approach being taken. Using these methods it may be possible  
303 to get time response for RGM and GEM down to as low as 2.5 minutes. These  
304 systems are very promising but need continued development and comparison  
305 against other methods (Swartzendruber et al., 2009b; Friedli workshop  
306 presentation).  
307

#### 308 **Recommendations:**

- 309 1) New experimental methods would add greatly to our understanding of the  
310 global cycle of Hg.  
311 2) It would be useful to have independent methods for quantifying the various  
312 chemical forms of gaseous oxidized Hg.

- 313 3) Less expensive methods that allow us to measure the spatial and temporal  
314 variations in air concentrations would be useful.

315

316 **Session 4: Issues of concern in measuring Hg fluxes**

317

318 **Findings:**

- 319 1) It is currently not certain whether terrestrial or marine ecosystems are net sources  
320 or sinks for atmospheric Hg. Fluxes associated with most terrestrial and marine  
321 systems are small and require careful protocols for accurate measurements.  
322 (Gustin and Lindberg, 2005). Better information on fluxes and controlling  
323 processes is needed to improve model predictions of mercury impacts.
- 324 2) Both GEM and RGM may be dry deposited and emitted. Because of this, it is  
325 important that we identify whether our measurements capture this bi-directional  
326 flux or a one-way flux.
- 327 3) Currently there is a standard method for wet deposition measurements and these  
328 data are collected in a few regions with sufficient coverage to test model  
329 predictions. Wet deposition depends directly on precipitation amounts. Models  
330 must capture the variations in precipitation correctly in order to capture Hg wet  
331 deposition. Uncertainty in wet deposition measurements is on the order of 12 to  
332 24 %.
- 333 4) There are significant uncertainties regarding dry deposition and there is not a  
334 standard method to measure it. Several methods are being used including  
335 surrogate surfaces (Gustin et al., 2006, 2008; Marsik et al., 2003), flux chambers  
336 (Lyman et al., 2007) and micrometeorological methods (Poissant workshop  
337 presentation., Obrist workshop presentation). A dry deposition method  
338 intercomparison was hosted in August 2008 by the University of Michigan and  
339 results of this study are being compiled.
- 340 5) Dry deposition is influenced by meteorological variables, surface characteristics  
341 and the form of Hg (Zhang et al., 2003). As a result there is significant variability  
342 from site to site. RGM appears to have a larger deposition velocity than GEM,  
343 although little is known about deposition of specific chemical compounds  
344 (Schroeder and Munthe, 1998). Temporal/spatial variability of RGM deposition  
345 appears to be significant.
- 346 6) The fraction of deposited Hg that is re-emitted back to the atmosphere is not  
347 known and is likely to vary from ecosystem to ecosystem. Limited work suggests  
348 that elemental Hg that has been dry deposited to soils is readily re-emitted to the  
349 atmosphere (Gustin et al., 2006, 2008). Additionally, it is not known if recently  
350 deposited RGM is quickly re-emitted, sequestered in ecosystems, or mobilized to  
351 other ecosystem compartments. Limited isotope work has indicates that re-  
352 emission of Hg following aqueous application of Hg<sup>+2</sup> is on the order of 10-40%  
353 (Hintelmann et al., 2002; Ericksen et al., 2005; Harris et al., 2007; Southworth et  
354 al., 2007).

355

356

357 **Recommendations:**

358

- 359 1) There is need for standardized methods to measure dry deposition and re-  
360 emission.
- 361 2) Additional isotope or other tracer studies focused on deposition and re-emission  
362 would be useful.
- 363 3) For wet deposition fluxes, precipitation amount needs to be accurately measured.  
364

365

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**Appendix A: Workshop participants**

Parisa Ariya, McGill University	Steve Lindberg, unaffiliated
Cathy Banic, Environment Canada	Seth Lyman, Univ of Nevada Reno
Steve Brooks, NOAA	Hunting Mao, Univ of New Hampshire
Chris Eckley, Univ of Nevada Reno	Robert Mason, University of Connecticut
Eric Edgerton, ARA Inc.	Daniel Obrist, Desert Research Institute
Brandon Finley, Univ. of Washington	Mark Olson, USGS
Hans Friedli, NCAR	Nicola Pirrone, CNR (Italy)
David Gay, NADP	Eric Prestbo, Tekran Instruments Corp.
Mae Gustin, Univ of Nevada Reno	Laurier Poissant, Environment Canada
Christopher Hall, US EPA, Region X	Henrik Skov, Aarhus Univ. (Denmark)
Eric Hinsta, NSF	Sandy Steffen, Environment Canada
Anthony Hynes, Univ of Miami	Phil Swartendruher, Univ. of Washington
Lyatt Jaegle, Univ. of Washington	Robert Talbot, Univ. of New Hampshire
Dan Jaffe, Univ. of Washington	Christian Temme, ERGO (Germany)
Bob Kotchenruther, US EPA, Region X	Arnout Ter Schure, EPRI
Leonard Levin, EPRI	Ingvar Wangberg, IVL (Sweden)
Jerry Lin, Lamar University	

**Appendix B: Workshop agenda**  
**Workshop on reducing the uncertainty in measurements of atmospheric Hg**  
**Parrington Hall-Commons, University of Washington, Seattle, Washington**  
**Oct 23-25, 2008**

**Thursday, 10/23/2008**

900: Meet and greet.

930: Introduction, logistics, goals and outcomes of workshop (D.Jaffe and M.Gustin)

10:00 NSF perspective (E.Hintsa)

10:10 EPRI perspective (L. Levin)

10:20: International perspective (N.Pirrone)

**Opening talks (Moderator: D.Jaffe and M.Gustin)**

10:30 Key uncertainties in atmospheric Hg chemistry, deposition and fluxes (J.Lin)

10:50 The nature of oxidized mercury and identification in the atmosphere (P.Ariya)

11:10 Modeling detailed MBL Hg processes and regional air-sea exchange: reasonable results with inconsistent methods (N.Pirrone)

11:30 From Rio to Seattle: Mercury One Decade Later (S.Lindberg)

11:50 Discussion

**12:00 Lunch**

**12:45 Issue I-Uncertainties associated with ground based measurements**

**Moderators R. Mason and S. Lindberg**

- RGM Measurement: Method development history, challenges, performance and calibration (E.Prestbo)
- Challenges in long-term measurements at multiple sites (E.Edgerton)
- Long term observations of Hg in Canada with an emphasis on quality control (A.Steffen)
- Atmospheric Mercury Instrument Intercomparisons (M. Olson)
- Current status and QA needs for the Atmospheric Mercury Initiative (D.Gay)

**2:40 Coffee break**

**3:00 Issue I-continued**

- Ground based observations of mercury speciation in coastal and ocean environments: Challenges and uncertainties (R.Mason)
- What is the uncertainty in measurements of GEM? Which approach is the best for my application? - Indirect method (GUM) vs. ISO 20988 and ISO 5725 (C.Temme)
- What measurements are needed to advance understanding of mercury chemistry in the atmosphere? (H.Mao)
- Measurements of GEM and RGM on an 8 month circumnavigation: Evaluation of uncertainties (H.Skov)

**4:20 Discussion/summary of key issues**

**5:00 Adjourn for the day**

**Friday, 10/24/2008**

**8:30 Coffee**

**8:40 Summary of recommendations from session I**

**9:00 Issue II -Issues of concern for air craft measurements**

**Moderators D. Jaffe and H. Friedli**

- Specific approaches for aircraft measurements (H.Friedli)
- An international airborne study to advance understanding of the hemispheric-to-global distribution of mercury in the atmosphere (R.Talbot)
- A comparison of published aircraft Hg data: How well are we doing? (D.Jaffe)
- NAAMEX: The North American Airborne Mercury Experiment—Ready, set, go? (D.Jaffe)

**10:10 Coffee break**

**10:40: Discussion and Summary of key issues and recommendations**

**11:30 Issue III-New methods on the horizon**

**Moderators A. Hynes and P. Swartzendruber**

- A prototype instrument to measure speciated mercury in plumes by aircraft (H.Friedli)
- A new instrument to measure GEM and RGM at 2.5 minute resolution by aircraft: Results from the first 5 flights (P.Swartzendruber)

**12:30 Lunch**

**1:30 Issue III-Continued**

- Laser based approaches to the measurement of elemental and reactive gaseous mercury (A.Hynes)
- Using passive samplers to assess spatial variability of gaseous mercury (S.Lyman)

**2:10 Discussion**

**2:30 Summary of key issues and recommendations**

**3:10 Coffee break**

**3:30 Issue IV-Issues of concern in measuring fluxes**

**Moderators: M.Gustin and L.Poissant**

- Measurement of dry deposition using surrogate surfaces and dynamic flux chambers? (M.Gustin)
- Measurement of RGM fluxes method difficulties and uncertainties (H.Skov)
- Field tests of automatic TGM/GEM instruments and samplers for mercury deposition (I.Wangberg)
- The influence of experimental approach and design on the quantification of surface-to-air mercury fluxes (C.Eckley)

**5:00 Adjourn for day**

Saturday, 10/25/2008,

**8:30 Issue IV-Issues of concern in measuring fluxes**

- Intercomparison of methods for measurement of dry deposition (U.Michigan group)
- Ecosystem-level Hg exchange: results from year-long MBR measurements, comparison to plant-derived Hg deposition, and development of a real-time sensor for future Eddy Covariance measurement (D.Obrist)
- Mercury Dry Deposition by modified Bowen method approach: Ann Arbor intercomparison, some preliminary results (L.Poissant)

**9:30 Discussion**

**10:00 Summary of key issues and recommendations**

**10:30 Coffee break**

**11:00 Organization of workshop report and chapter leads for each issue.**

**12:00 Workshop concludes**