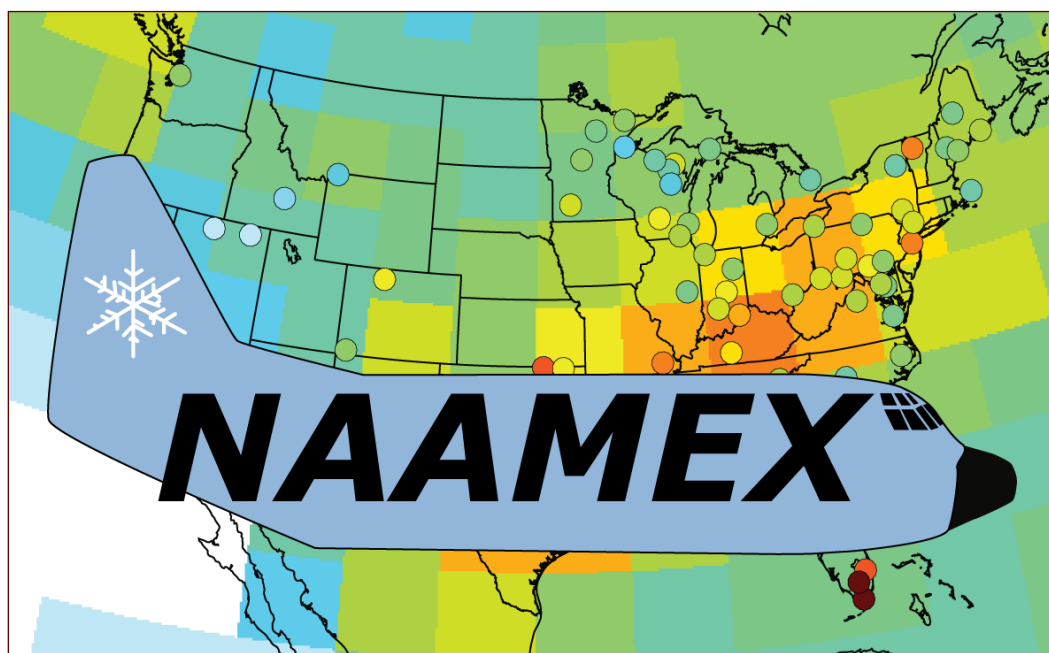


White Paper for:
The North American Airborne Mercury Experiment (NAAMEX)

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Project date: July 2012-June 2015
NAAMEX Field Campaign: June-July 2013



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Project Summary:

The North American Airborne Mercury Experiment is the first comprehensive airborne experiment focused on mercury (Hg) across North America. NAAMEX will provide critical new data to understand the sources, chemical processing and deposition of Hg on a continental scale.

Intellectual Merit

NAAMEX will use the NSF C-130 aircraft to make observations of Hg and related species and combine the data with chemical transport models to address two scientific goals:

- 1) Constrain emissions of Hg from major source regions in the United States
- 2) Quantify the distribution and chemical transformations of Hg in the troposphere.

To address these goals we will use the NCAR/NSF C-130 aircraft equipped with a suite of state-of-the-art instrumentation focused on Hg and related key compounds (CO, CO₂, NO_x, O₃, HO_x, SO₂, reactive halogen species, hydrocarbons and halocarbons). Hg observations on the C-130 will include all of the major atmospheric forms of Hg: gaseous elemental Hg (GEM), gaseous oxidized Hg (GOM) and particle-bound Hg (PHg). All of the primary instrumentation for NAAMEX has been successfully used previously on the C-130 or other aircraft. The experiment is proposed for the summer of 2013. During NAAMEX the C-130 will fly out of two bases, one in the Western U.S. and one in the Eastern U.S.. Using two bases is a critical component of NAAMEX in that it will allow the experimental team to examine a variety of scientific questions focused on the sources and chemical transformations of Hg across the continent. In the Western U.S. the flight objectives will focus on the vertical distribution of speciated Hg, entrainment of free tropospheric reactive Hg into the boundary layer, quantification of regional sources (gold mining in Nevada and industrial sources in California). In the Eastern U.S. the emphasis will be on large-scale transects of industrial sources over the Ohio River Valley, outflow of N. American Hg to the Atlantic, and the impact of convective precipitation on surface wet deposition in the Southeast U.S. Planning in the field will utilize regional and global forecast models to optimize the use of flight time. The C-130 observations will be integrated and analyzed after the mission with several chemical transport and Lagrangian models. These models will be used to examine the consistency between observations and emission inventories, allow the integration of ground-based observations with aircraft observations in a unified framework, constrain source-receptor relationships, and test different hypotheses about the chemical transformations and global cycling of Hg.

Broader impacts

Human exposure to Hg is a significant health risk and a problem of national and global significance. NAAMEX will reduce the uncertainties concerning source-receptor relationships and the relative contributions of domestic, foreign and natural sources of Hg in the U.S. NAAMEX will employ a number of graduate and undergraduate students from 5 different U.S. institutions and thus will expose these students to working on high-level scientific problems of great national significance. In addition to a core group of scientists from the U.S., Hg scientists from Canada, Italy, Germany and Russia will also collaborate on NAAMEX. Thus NAAMEX will strengthen international scientific cooperation on global environmental problems.

1. Introduction

Mercury is a global health concern. The most significant exposure route is through consumption of high trophic level fish. While research has found both beneficial and detrimental aspects of fish consumption, it is clear that reducing Hg concentrations in fish would provide an important health benefit worldwide (Mergler et al., 2007). Mercury accumulates in fish mainly as methylmercury via reductive assimilation of inorganic forms in aquatic systems. In regions with significant Hg emissions, concentrations of Hg in fish tend to be elevated (Hutcheson et al., 2008). But even in the absence of local sources, fish in remote areas have relatively high Hg concentrations due to global atmospheric transport and deposition of Hg (e.g. Schwindt et al., 2008; NRC-BASC, 2009). Nearly all states in the US have fish consumption advisories as a result of elevated Hg concentrations (<http://www.epa.gov/waterscience/fish/advisories/>).

Mercury in the air is present as gaseous elemental Hg (Hg^0 or GEM), gaseous oxidized Hg (GOM) and particle-bound Hg (PHg). Most measurements show that GEM is the dominant form of Hg in the troposphere. GOM and PHg are thought to be more readily removed by wet or dry deposition, and thus have shorter atmospheric lifetimes. All forms are emitted from industrial point sources (Pirrone and Mason, 2009; AMAP/UNEP, 2008) while GEM is the dominant form released from terrestrial and aquatic sources (Schroeder and Munthe, 1998).

GOM is formed by oxidation of GEM in the atmosphere. Oxidation mechanisms involving O_3 , OH, Br and Cl radicals have all been proposed (Pal and Ariya, 2004a,b; Calvert and Lindberg, 2005; Donohoue et al., 2006; Selin et al., 2007; Holmes et al., 2006, 2009; 2010; Seigneur et al., 2009), but the kinetics and mechanisms of these reactions are poorly understood. In the Arctic, elevated levels of GOM in mercury depletion events are caused by bromine oxidation (Steffen et al., 2008). The role of bromine atoms in the production of GOM has also been clearly demonstrated over the Dead Sea (Obrist et al., 2010). Recent aircraft observations during the Western Airborne Mercury Observation project show that stratospheric Hg exists mostly as oxidized species (Lyman and Jaffe, 2011). GOM has also been measured in the marine boundary layer and the free troposphere, although the main oxidant in these regions is not clear (Steffen et al., 2008; Hedgecock et al., 2004, 2008; Swartzendruber et al., 2006; Lindberg et al., 2007; Talbot et al., 2008; Slemr et al., 2009; Holmes et al., 2009). Models and budget calculations suggest an atmospheric lifetime of between 0.5-1.5 years for total gaseous mercury (TGM) (Bergan and Rodhe, 1999; Seigneur et al., 2006; Selin et al., 2007; Holmes et al., 2010).

Global natural and anthropogenic Hg emissions are in the range of 5,000-11,000 tons/year (Pirrone and Mason, 2009, Selin et al., 2008; AMAP/UNEP, 2008 NRC-BASC 2009). A significant fraction of Hg emitted from surface sources was originally emitted from anthropogenic sources, deposited, and then re-emitted (Pirrone et al., 2008), this is referred to as "legacy mercury". In their global inventory for the year 2005, Pacyna et al. (2010) found that human activities account for 1930 tons of Hg, but other estimates are nearly a factor of two higher (Selin et al., 2008). The burning of fossil fuel, mostly coal, is the largest single source of anthropogenic Hg, responsible for ~50% of emissions. While anthropogenic emissions are relatively well known compared to other sources such as the ocean and land, large uncertainties remain. North American industrial emissions are believed to be 153 tons year, with a range of 90-305 tons/year (AMAP/UNEP, 2008). In addition, there are significant uncertainties in the chemical speciation of anthropogenic Hg emissions.

Given the relatively modest emissions in North America, a single source can be important in the regional distribution. For example recent stack testing data from a cement factory in

Durkee Oregon indicate emissions of GOM+PHg of 816 kg/year (State of Oregon, 2007), making it the largest point source of GOM+PHg in the U.S. These previously unidentified emissions could be responsible for a substantial amount of regional wet and dry deposition. Observations collected at sites several kilometers downwind of coal-burning power plants in the SE U.S. have shown that GOM accounts for only 8-21% of total Hg (Edgerton et al., 2006; Weiss-Penzias et al., 2011). This is significantly lower than expectations based on stack measurements (40-80% GOM), and might be due to rapid reduction of GOM to GEM in power plant plumes (Lohman et al., 2006). Such a shift in the speciation might explain the “Pennsylvania anomaly”: the lack of wet deposition enhancement downwind of the main Hg emitting regions in the Ohio River Valley (Seigneur et al., 2003). The speciation of anthropogenic Hg has direct implications for the fraction of Hg emissions that is deposited locally as opposed to transported away (Zhang et al., 2011). Furthermore, releases of Hg from soils and vegetation over N. America (both due to direct natural emissions and re-emission of anthropogenic/natural Hg) could account for nearly twice as much as direct anthropogenic emission (Gbor et al., 2007). Overall, this suggests the need for a careful evaluation of US anthropogenic and natural emissions using atmospheric observations.

Models, combined with observations can play a key role in advancing our understanding. An example of data-model integration that has proven to be useful is the early study of Asian pollution outflow. Asian anthropogenic emissions (800-1,500 tons/year) are much larger than North American emissions and thus are a substantial contributor to the global Hg pool. Observations of GEM, GOM and PHg were made in 2004 on the island of Okinawa, Japan (Jaffe et al., 2005; Chand et al., 2008). Aircraft observations of GEM and PHg were made during the ACE-Asia experiment (Friedli et al., 2004). All these observations have been used to constrain the Asian outflow of GEM using the Hg/CO ratio, indicating that Asian emissions were higher than current inventories (Jaffe et al., 2005; Selin et al., 2007; Strode et al., 2008; Pan et al., 2007; Shetty et al., 2008). This was hypothesized to be due to higher anthropogenic emissions and/or a significant contribution from soil emissions. Surface observations of GOM and PHg at Okinawa suggest very low export of these compounds, due to their short lifetimes (Chand et al., 2008), with GOM concentrations controlled by in-situ oxidation (Holmes et al., 2009).

Deposition of atmospheric Hg to terrestrial and marine ecosystems occurs via both wet and dry processes. In the US, wet deposition has been monitored for the past 15 years as part of the Mercury Deposition Network (MDN) (Prestbo and Gay, 2009). Highest wet deposition rates are generally found in the SE US, and this has been attributed to oxidation of GEM to GOM and subsequent washout by deep convective systems (Sillman et al., 2007; Selin and Jacob, 2008), but there is no observational verification of this mechanism. At many sites in the Eastern US, there is evidence for a downward trend in Hg concentrations in precipitation, consistent with a decrease in regional emissions (Butler et al., 2008; Prestbo and Gay, 2009). In Florida, trends in Hg wet deposition have been minimal, despite large reductions in regional emissions of Hg (Vijayaraghavan et al., 2011). This suggests the importance of global sources and a role for deep convective scavenging in controlling wet deposition in that region.

1.1. Observations of Hg

Surface measurements of atmospheric Hg have been made for more than 20 years (e.g. Sprovieri et al., 2010 and references therein). Based on long-term observations at several surface sites and ship measurements, Slemr et al. (2011) conclude that the global atmospheric burden of

Hg has declined by 20-38% since 1996. This is contrary to estimates of increasing anthropogenic emissions of Hg over the past 50 years (Streets et al., 2009, 2011) and suggests a change in the global cycling of Hg in the environment.

While there is a long record of surface observations, the vertical distribution has only been measured during the past 10 years (e.g. Ebinghaus and Slemr, 2000; Banic et al., 2003; Friedli et al., 2004; Swartzendruber et al., 2006; 2008; Radke et al., 2007; Talbot et al., 2008; Slemr et al 2009). There are significant differences in observed profiles, which could be due to real variability in the vertical distribution of Hg in the atmosphere, or might be caused by the use of different measurement techniques (Swartzendruber et al 2009; Gustin and Jaffe, 2010). For example, in many of these aircraft studies it is unclear whether measurements represent TGM or GEM, since no inlet tests or calibrations with oxidized Hg compounds were reported.

The University of Washington (UW) group has focused on reducing these ambiguities and developing more robust methods for aircraft measurements of Hg and GOM (Swartzendruber et al., 2009; Lyman et al., 2010; Lyman and Jaffe, 2011). In Swartzendruber et al. (2009), two methods were used to determine the vertical distribution of GOM by aircraft: a high time response GOM measurement using the difference between TGM and GEM and a standard, low time resolution method based on collection of GOM on a KCl coated quartz denuder. With both methods the GOM vertical profile peaks in the middle troposphere. While the correlation between the two GOM methods was good, there was a factor of 2 difference in concentrations due to problems with the KCl coated quartz denuder method (Swartzendruber et al., 2009). The KCl method, used by many Hg researchers for more than 10 years, appears to be biased low when exposed to ozone (Lyman et al., 2010). The high time response method, using thermal decomposition, does not have this problem.

Based on these results, the UW aircraft instrument, called the UW-Detector for Oxidized Hg Species (UW-DOHGS), was further improved for the Western Airborne Mercury Observations (WAMO) project, undertaken in 2010 on the NCAR C-130. The UW-DOHGS instrument features many of the elements of the original design, while improving the detection limit, reliability and ability to be calibrated with both GEM and GOM compounds. The instrument consists of dual atomic fluorescence detectors that measure GEM and TGM. The difference is due to the sum of GOM and PHg (hereinafter Hg(II)). For the GEM channel, GOM compounds are removed using quartz wool and for the TGM channel, GOM compounds are decomposed to GEM using a high temperature (650°C) furnace. The instrument has been extensively tested in the lab using GEM and GOM compounds (HgCl_2 and HgBr_2), as well as potential interfering compounds (O_3 and H_2O). To our knowledge, the UW-DOHGS is the only instrument in the world that has these capabilities and has been tested as extensively.

Figure 1 shows data from a WAMO flight going from Bangor, Maine to Boulder, Colorado on November 5, 2010. The aircraft was flying near 6 km asl when it encountered a stratospheric intrusion. These are the first ever simultaneous measurements of GEM and GOM made in a stratospheric intrusion (Lyman and Jaffe, *Nature Geosciences*, In-press October 2011). These results demonstrate the capability of the instrument to detect GEM and GOM simultaneously at reasonable time resolution (2.5 minutes). More details on the instrument configuration and inlet during WAMO are available in Lyman and Jaffe (2011).

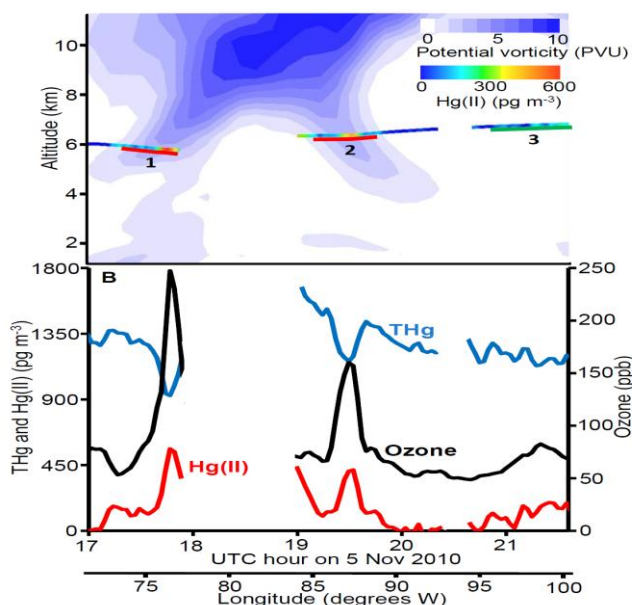


Figure 1. Mercury and ozone during the 5 Nov 2011 flight through stratosphere-influenced air. The top panel shows the flight track, colored by Hg(II) concentration, along 40 to 44° latitude. Background is colored by potential vorticity. Solid red lines indicate stratosphere-influenced air (PV >1.5 PVU; Events 1 and 2) and the solid green line indicates high-Hg(II) air that was not recently influenced by the stratosphere (Event 3). The bottom panel shows the concentrations of THg, Hg(II), and ozone. The data gap from 18:00 to 19:00 exists due to diplomatic restrictions on sampling in Canadian airspace. (from Lyman and Jaffe, 2011)

Subsequent to WAMO the UW instrument participated in the Reno Atmospheric Mercury Intercomparison Experiment (RAMIX), organized by the Universities of Washington and Nevada. This project brought together the conventional commercial method (e.g. Tekran 2537/1130/1135) with new methods being developed by 4 different research groups (D. Jaffe, U. Washington; D. Obrist, Desert Research Institute; R. Talbot, U. Houston and A. Hynes, U. Miami). The experiment took place in August-September 2011, so final results are not yet available. However we do know a few key results: First, the UW DOHGS was the only instrument, besides the Tekrans, that successfully measured Hg(II). Second, the UW-DOHGS instrument also showed a good linear relationship with the quantity of added HgBr₂ to the instrument manifold, as measured by an independent method.

1.2. Modeling of Mercury

Several large-scale atmospheric Hg models have been developed over the past 15 years. Initially Lagrangian trajectory models with simplified assumptions of chemistry and scavenging were used (e.g., Peterson et al., 1995; Shannon and Voldner, 1995; Bullock et al., 2000). Subsequently, more sophisticated regional/continental-scale Eulerian or mixed models (e.g., Pai et al., 1997; Xu et al., 2000; Petersen et al., 2001; Bullock and Brehme, 2002; Cohen et al., 2004, 2007; Hedgecock et al., 2005, 2006) and hemispheric/global-scale models (Bergan et al., 1999; Shia et al., 1999; Christensen et al., 2004; Dastoor and Larocque, 2004; Travnikov, 2005; Selin et al., 2007; Jung et al., 2009) were developed. Many of these first global models had relatively coarse horizontal resolution (2-5 degrees latitude by 5-10 degrees longitude) and were unable to capture the high spatial variability of Hg wet deposition. The regional models could capture this variability, but were found to be highly dependent on assumed boundary conditions (Bullock et al., 2008). This has led to the development of global models with high horizontal resolution (Durnford et al., 2010), the extension of regional models to hemispheric scale (Pongpruesksa et al., 2011), and the implementation of nested-grid simulations imbedded within parent global models (Zhang et al., 2011). These models have been applied in numerous studies that have helped improve our understanding of Hg, specifically: the inter-hemispheric gradient, the

seasonal cycle, the spatial and seasonal variations in wet deposition, long-range transport, the role of ocean and land emissions, Arctic Hg processes, source attribution for Hg deposition and the sensitivity to different assumptions about oxidants.

Yet, as discussed above many of the basic mechanisms controlling the emission and fate of Hg in the atmosphere are still poorly known. As a symptom of these uncertainties, we see large differences in chemical transport models (CTMs), which make divergent assumptions about emissions, chemistry, and deposition. This was highlighted in several model intercomparison studies for regional (Bullock et al., 2008, 2009; Ryaboshapko et al., 2007a,b) and global models (Skov et al., 2008). In the North American Mercury Model Intercomparison Study (NAMMIS), Bullock et al. (2008, 2009) evaluated differences in Hg deposition and concentrations over N. America for three regional models. Predicted atmospheric concentrations and deposition varied considerably among the regional models, despite using identical lateral conditions, anthropogenic emissions and meteorological fields (Figure 2). Mean deposition averaged over N. America varied by a factor of 4 for dry deposition and 70% for wet deposition. Locally, order of magnitude differences were seen. The predicted concentrations and deposition were also sensitive to the choice of boundary conditions. In the AMAP/UNEP report Skov et al. (2008) compared four CTMs. They showed that assumed natural emissions varied by a factor of 2, while anthropogenic emissions varied by $\pm 50\%$. Over N. America predicted mean wet deposition varied by a factor of 2 and dry deposition differed by up to an order of magnitude. Yet, these models all displayed general agreement with the limited observations of wet deposition and surface TGM concentrations, illustrating that existing observations are not sufficient to constrain models. ***Large-scale speciated Hg measurements in both the boundary layer and free troposphere obtained during NAAMEX will address this gap and allow direct validation of regional and global models.***

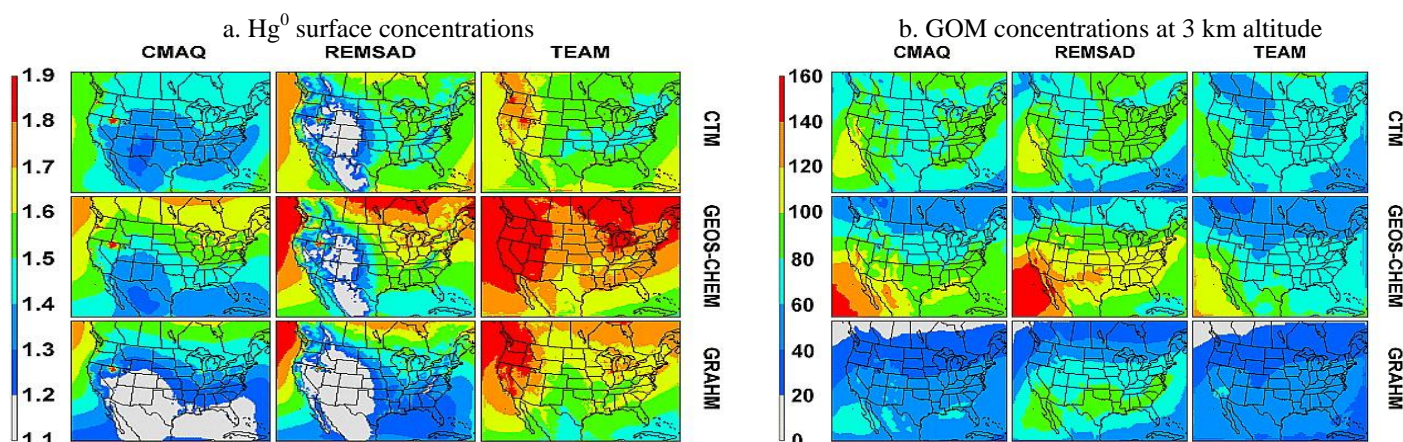


Figure 2. a) Annual mean surface atmospheric concentrations of Hg⁰ (in ng/m³) calculated by 3 regional models (CMAQ, REMSAD, TEAM) using initial and boundary conditions from 3 global models (CTM-Hg, GEOS-Chem, and GRAHM); b) GOM (in pg/m³) at 3 km altitude (Bullock et al., 2008).

Several recent assessments have highlighted the need for observations of Hg across large spatial scales, with instrumentation that have been carefully evaluated. A report from the National Academy of Sciences (NRC-BASC 2009, pg. 7) states: “***Our ability to quantify the magnitude and rates of exchange among these Hg reservoirs is limited by incomplete knowledge about atmospheric chemical processing, dry deposition, and the re-suspension of***

deposited Hg back to the atmosphere, and by insufficient observational data needed to evaluate models". The UNEP/HTAP study (Pirrone and Keating 2010, pg 9) gives more specific recommendations regarding aircraft studies: *"Measurements of Hg concentration and speciation in the free troposphere are crucial to better understanding of global Hg cycling. Airborne measurement campaigns must be a major priority and focus of future field campaigns, and more long-term measurement sites with speciated Hg are needed in the free troposphere (e.g. on mountains or making use of commercial aircraft)".*

The NAAMEX project presents an unprecedented opportunity to gather a high quality Hg dataset that can be used to constrain models. Given the recent advances in instrumentation and the clear scientific and policy need, a continental scale study of Hg is timely. NAAMEX will enhance our understanding of the domestic and global sources of Hg, which is critical to predicting the impacts of domestic emission reductions. Since NAAMEX will include extensive measurements within the boundary layer, it will also allow for an assessment of the spatial representativeness of existing surface measurements.

2. Goals and scientific questions/Intellectual Merit

Goal 1: Constrain emissions of mercury from major source regions in the United States.

- ❖ Specific questions: What is the spatial distribution of atmospheric Hg in the western US, Midwest, and Eastern U.S.? Are observations consistent with bottom up emissions inventories? Can we separate U.S. sources from global sources to establish boundary conditions with which to assess regional Hg cycling over the U.S.?

Goal 2: Quantify the distribution and chemical transformations of speciated mercury in the troposphere.

- ❖ Specific questions: How does the speciation of Hg change with increasing height in the free troposphere over the Western and Eastern U.S.? How is this speciation affected by atmospheric oxidation, precipitation, cloud-processing, and stratospheric intrusions? Can we use the spatial distribution of Hg(II) to provide information on its production mechanism? Does free tropospheric Hg(II) mix down to the surface and enhance dry deposition? How does the partitioning of Hg evolve downwind of major emission regions?

3. Experimental plan

3.1. Instruments

To meet the NAAMEX goals we will include a variety of instrumentation on the C-130 including speciated Hg measurements and a suite of other gas and aerosol measurements (Table 1). All of the major instrumentation has successfully flown previously on the C-130 or another aircraft. The Hg measurements will be the responsibility of the UW group (Jaffe/Ambrose). As mentioned above, the high time resolution system (UW-DOHGS) was successfully flown on the C-130 for the WAMO project (Lyman and Jaffe, 2011). The system detects GEM and GOM+PHg simultaneously with 2.5 min resolution. At present, we have not tested the response of the UW-DOHGS instrument to particle bound Hg (PHg), however we expect that this is quantitatively detected in the GOM channel, due to the high temperature (650° C) in the pyrolyzer. This will be verified in lab studies prior to NAAMEX. During WAMO we used a rear-facing PFA coated inlet, maintained above 50° C. While this inlet will transmit most GOM compounds with reasonable efficiency, a higher temperature inlet can achieve near 100% transmission. We have confirmed this in the lab with HgCl₂ and HgBr₂. In addition to the high

time resolution system, UW will deploy a denuder/filter pack system for PHg (with 60 minute time resolution and 8 samples per flight). This will strip out GOM compounds and collect PHg onto filters for post-flight analysis. The denuder/filter pack system will be constructed in the summer of 2012 and extensively tested in the year prior to NAAMEX.

Table 1. C-130 Measurements for NAAMEX

Measurement	Detection limit	Time resolution	Who
GEM	0.02 ng/sm ³	2.5 min	Jaffe, Ambrose-UW
GOM+PHg	0.04 ng/sm ³	2.5 min	Jaffe, Ambrose-UW
GOM/PHg	0.01 ng/sm ³	60 min	Jaffe-UW
CO	10 ppbv	1 sec	Campos-NCAR
CO ₂	0.5 ppmv	1 sec	Campos-NCAR
O ₃	3 ppbv	1 sec	Weinheimer-NCAR
NO, NO ₂	5/10 pptv	1 sec	Weinheimer-NCAR
BrO, Br ₂ , ClNO ₂ , HO ₂ NO ₂ , HNO ₃ , SO ₂	1 pptv	1 min	Huey-GIT
OH, HO ₂ , RO ₂ and H ₂ SO ₄	0.01 pptv	1 min	Cantrell, Mauldin-U. Colo.
Speciated NMHCs and Halocarbons	5 pptv	1 min, ~60 samples/flight	Blake-UCI
Aerosol number/size and optical properties	NA	10 sec	NCAR
Meteorological parameters	NA	1 sec	NCAR

All of the other primary instruments have previously flown and we here include a brief description of each major system. The GIT group will fly a CIMS instrument with two channels. The first will utilize Γ^- chemistry to detect halogens (e.g. Liao et al., 2011). The second channel will utilize either SF_6^- or SF_5^- chemistry to measure SO₂, HNO₃, and HO₂NO₂ (e.g. Kim et al., 2004). The UCI group will measure speciated NMHCs, including halocarbons in 60 whole air samples per flight (Colman et al., 2001). The Univ. of Colorado group will measure a variety of HO_x and other species using CIMS. For this ambient air is sampled into two inlets, one for OH and H₂SO₄, and one for peroxy radicals. Within the inlets, reagent gases are added to convert the analytes into H₂SO₄ (³⁴S labeled for OH measurements). Sulfuric acid is ionized by reaction with negatively charged nitrate ions. The reagent and product ions are sampled by a mass spectrometer where the ions are mass-separated and counted. The ratio of count rates of product to reagent ions is proportional to the ambient concentration of the target species (Cantrell et al., 2003; Mauldin et al 2003; Hornbrook et al., 2011). Other key measurements are provided by NCAR. This includes measurements of CO and CO₂ (T. Campos), NO_x and O₃ (A. Weinheimer). Aerosols and meteorological parameters will also be measured by the NCAR/C-130 team.

Species like CO, CO₂, SO₂, NO_x and NMHCs have some of the same combustion sources as Hg and will be essential to identify anthropogenic sources as well as biomass burning sources. We will use Hg/CO and Hg/SO₂ correlations to constrain Hg sources. Reactive species (O₃, HO_x, BrO and Br₂) will provide information on the oxidative environment leading to the production of GOM. NO_x/HNO₃ and NMHC ratios will serve as chemical clocks to track the aging of air masses. NMHCs will further allow for source fingerprinting. Aerosol properties will help

constrain the gas/particle partitioning of GOM and PHg, as well as characterize source properties.

Additional information on each measurement:

Speciated Hg (UW)

The UW-DOHGS detects total Hg, GEM and Hg(II) by difference. GEM is detected by removing Hg(II) compounds with a quartz wool trap. Total Hg is detected by decomposing all Hg(II) compounds in a high temperature furnace. An early version of this instrument first flew in 2008. At that time we compared the dual channel method with the more traditional denuder approach (Swartzendruber et al 2008). This led to the discovery that O₃ was a significant interference in the denuder method (Lyman et al., 2010). More recent improvements in the instrument have improved the stability and reduced the detection limit. The instrument flew on the C-130 during the WAMO experiment in the configuration shown in Figure 3.

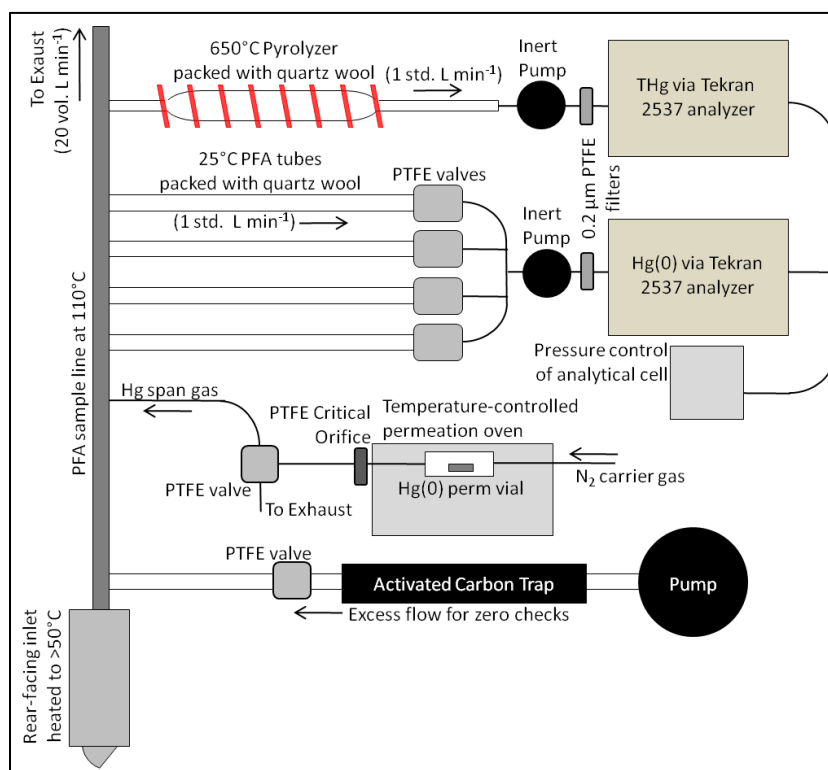


Figure 3. Schematic diagram of the UW-DOHGS instrument for THg, GEM and Hg(II) (by difference).

The UW-DOHGS instrument also participated in the Reno Atmospheric Mercury Intercomparison Experiment (RAMIX). This experiment took place outside of Reno NV in August-September 2011. While the results are not published yet, here we highlight two important results obtained for the DOHGS instrument. First, we modified the fluorescence cells of our Tekran Hg vapor analyzers to improve the signal-to-noise ratio for the instrument. This lowered the limit of detection for Hg(II) $39 \pm 20 \text{ pg/m}^3$, which is 42% lower than the $68 \pm 20 \text{ pg/m}^3$

value estimated from the WAMO dataset by Lyman and Jaffe (2011). Second, tests performed during the RAMIX study demonstrate a near unity response to oxidized Hg (HgBr_2) in an ambient air matrix over an atmospherically relevant range of Hg(II) concentrations. Figure 4 shows the DOHGS response as a function of added HgBr_2 .

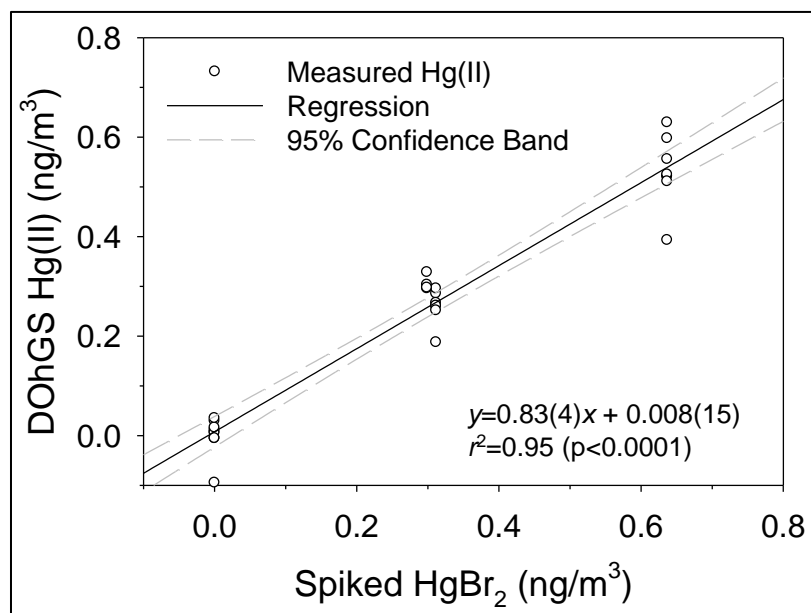


Figure 4. Response to oxidized Hg for the DOHGS instrument during the Reno Atmospheric Mercury Intercomparison Experiment (RAMIX). HgBr_2 was spiked into ambient air in a heated ($115\text{ }^\circ\text{C}$) PFA sampling manifold at concentrations of $0.299\text{--}0.637\text{ ng/m}^3$ ($\pm 11\%$). The spiked concentrations were determined by an independent method using high temperature decomposition of HgBr_2 . The Hg(II) concentrations measured with the DOHGS have a total 1σ uncertainty of $\sim 0.05\text{ ng/m}^3$. For this test, the recovery of spiked HgBr_2 by the DOHGS was 83%.

CO/ CO_2 / CH_4 (NCAR)

The NCAR/NSF G-V vacuum UV resonance fluorescence instrument is a commercial version of the instrument described by Gerbig, et al (1999). The source is a flowing RF discharge gas lamp emitting in the VUV. An optical filter provides a narrow band of radiation centered at 151 nm with a 10 nm bandpass. The CO fluorescence is detected using photon counting. The internal data system can accommodate sampling rates from 1-18 samples/second. The instrument was integrated into the HAIS ozone instrument rack and shared a pressure-controlled inlet. In-flight calibrations are conducted using a working standard and a catalytically scrubbed zero trap for background subtraction. A series of NOAA ESRL/GMD primary standard compressed gases are used in lab measurements to quantify the concentration of the working standard cylinder. Two to three replicates of these standardizations are conducted prior to and after the intensive field phase of the experiment. Additional characterizations are performed as needed upon replacement or re-filling of the working standard cylinder.

The CO mixing ratio in ppbv is displayed on the analyzer in real-time. Real-time in flight data are transmitted to the Aircraft Data System (ADS) and can be displayed at any station in the

aircraft or on the ground using Aeros. Users can connect remotely with the analyzer's internal Windows-based PC and control it through a standard Remote Desktop connection or with similar remote login software. Post-processing of data is necessary but field data typically is delivered real-time to the RAF data system and is typically accurate to better than 20%. These data (containing signal background measurements and calibrations) are typically available within hours of the end of a flight as part of the RAF data release.

The Picarro CO₂/CH₄ Flight Analyzer is a real time trace gas monitor. The measurement principle is based on Wavelength-Scanned Cavity Ring Down Spectroscopy (WS-CRDS). The analyzer maintains high linearity, precision, and accuracy over changing environmental. Precise temperature and pressure control systems designed into the analyzer ensure accurate measurements over long periods of time. The analyzer is ruggedized for aircraft use. No consumables other than calibration gas are required. The analyzer requires an external pump (dimensions about 12x8x6inches, 27 pounds) as well as an inlet compressor (shared with VUV CO instrument; 8x6x6 inches, 15 pounds). The gas concentration is displayed on the analyzer in real-time, and is continuously archived to the analyzer's internal hard drive. Real-time in flight data (CO₂ and CH₄ in ppmv) are transmitted to the Aircraft Data System (ADS) and can be displayed at any station in the aircraft or on the ground using Aeros. Users can connect remotely with the analyzer's internal Windows-based PC and control it through a standard Remote Desktop connection or with similar remote login software. Post-processing of data is necessary but field data is delivered real-time to the RAF data system and is typically accurate to better than 20%. These data (containing in-flight calibrations) are available within hours of the end of a flight as part of the RAF data release. In-flight calibrations are conducted using a working standard and a catalytically scrubbed zero trap for background subtraction, similar to CO.

For NAAMEX, the VUV CO analyzer can be integrated into one standard GV rack together with the Picarro CO₂/CH₄ instrument and the fast-ozone instrument, with the NO/NO₂ analyzer integrated into a second rack. These racks need to be mounted side-by-side because they share some components (data system, pumps, gases). A similar configuration is currently being flown on the GV for the DC3 mission. One calibration gas cylinder (shared with Picarro CO₂/CH₄) is required on the aircraft. The instrument also requires N₂ for purging and CO₂ in Ar as lamp gas. These two small cylinders can be installed in the rack if required but a full size cylinder is preferred. N₂ can often be shared with other investigators.

O₃/NO/NO₂ (NCAR)

The 2-channel NO-NO₂ instrument is integrated with the 1-channel O₃ instrument. Both are based on chemiluminescence detection employing the reaction of NO with O₃ to form excited NO₂, which is detected via photon counting. For NO-NO₂, one sample channel is used to measure nitric oxide via addition of reagent O₃, and the second measures nitrogen dioxide by first flowing sample air through a glass cell illuminated by light-emitting diodes at 395 nm, for the conversion of NO₂ to NO via photolysis. The instrument is similar to instruments previously built at NCAR [Ridley and Grahek, 1990]. The O₃ instrument operates similarly, except with addition of reagent NO to the sample stream.

The instruments can fly as stand-alone instruments, but for NAAMEX there will be a significant sharing of components. This will result in considerable weight, space, and power savings for the overall payload. The items to be shared include these: data acquisition and control system, power distribution and power supplies, vacuum pump, pressure-control valve, zero air

bottle, and inlet. The entire installation will occupy approximately three-fourths of a pair of racks plus some floor space. One rack is devoted to NO-NO₂, and the companion rack is devoted to O₃ along with the VUV instrument for CO and the Picarro instrument for CO₂ and CH₄. Thus the O₃ instrument is fully integrated with NO-NO₂, electrically and in the plumbing and in the data acquisition, and the rack pair houses NO-NO₂, O₃, CO, and CO₂-CH₄ instruments.

Data will be recorded at 10 Hz, though the true frequency response is not that fast. Data will be archived at 1 Hz. The precision of 1-s values of NO and NO₂ are estimated to be in the range of 5-10 pptv, depending on performance characteristics determined in flight. The overall uncertainty of 1-sec values is estimated to be 10% or better for large mixing ratios (> 50 pptv). For O₃, overall uncertainty is 5% and the detection limit is better than 0.1 ppbv.

BrO, Br₂, ClNO₂, HO₂NO₂, HNO₃, SO₂ (Georgia Tech)

Two CIMS instrument will be deployed on the NCAR C-130 for the NAAMEX mission. Each CIMS consists of a low pressure ion molecule reactor (IMR) coupled to a quadrupole mass filter by an actively pumped collisional dissociation chamber (CDC) and an octopole ion guide. One CIMS, devoted to measure BrO, utilizes a 160 mm OD vacuum chamber evacuated by two turbopumps (250 l s⁻¹). The mass filter is a set of 19 mm dia. quadrupole rods housed in the vacuum chamber. The IMR is evacuated with a scroll pump (300 l min⁻¹) that also serves as the backing pump for the mass spectrometer. The other CIMS, devoted to measurement of sulfur dioxide, utilizes a smaller vacuum chamber (100 mm OD), 9.5 mm quadrupole rods, and is evacuated with two small turbo pumps (70 l s⁻¹). The acid IMR is evacuated with a small scroll pump (100 l min⁻¹). The CDC of each CIMS instruments is a short 80 mm diameter chamber that houses an octopole ion guide and is evacuated with a hybrid molecular drag pump.

The first CIMS will be configured to detect BrO, and other halogens such as Br₂, Cl₂, and ClNO₂. These species will be detected utilizing iodide chemistry. BrO will be detected by the ion molecule reaction below. The other species are detected by analogous reactions.



Detection limits for the halogen species are expected to be of the order of a few pptv for a one second integration period and to scale with the square root of the averaging time. BrO will be measured each second with a duty cycle of 60%, with the other species having a combined duty cycle of 40%. The accuracy of the measurements are expected to be of the order of 30%. The second CIMS will be configured to detect sulfur dioxide (SO₂), nitric acid (HNO₃), pernitric acid (HO₂NO₂), and hydrochloric acid (HCl). SO₂ will be detected by the ion molecule reaction below. The other species are detected by analogous reactions.



Detection limits for all species are expected to be of the order of tens of pptv for a one second integration period. Each species will be measured every second with a duty cycle of 20% except for SO₂ which will be measured with a duty cycle of 40%. The accuracy of the measurements are expected to range from 10% for SO₂ to 35% for HO₂NO₂.

The CIMS instruments will be mounted in one or two standard C-130 racks. The rack(s) will house the CIMS, pumps, calibration sources, control and acquisition electronics, and an automated zeroing valve. Gas cylinders will be mounted external to the rack. Both instruments will be calibrated semi-continuously with isotopically labeled standards for Br₂ and SO₂. The background signals will be measured periodically by scrubbing the sampled air with activated

carbon (SO₂) or glass wool (halogens).

Whole Air Sampling for NMHCS, halocarbons, and other compounds (UCI)



The University of California Irvine (UCI) research group will collect up to 62 whole air samples per flight for NAAMEX (see photo at left). Each sample will be analyzed for more than 60 trace gases at the Irvine laboratory, including C₂-C₁₀ NMHCs, C₁-C₂ halocarbons, C₁-C₅ alkyl nitrates, selected sulfur compounds, methanol, ethanol, acetaldehyde, acetone, MVK and MAC using GC/FID, GC/ECD and GC/MSD (e.g., Colman et al., 2001 and Simpson et al., 2011).

We anticipate collecting whole air samples from beyond the laminar boundary layer of the aircraft into a stainless steel gas-handling manifold employing a two-stage metal bellows pump. We will collect up to 62 air samples per flight, with 1-minute sampling every 10 minutes during horizontal flight legs, and more frequently during ascents and descents.

The range of accuracies for the gases we report is 2-20%. The precision of the measurements varies by compound and by mixing ratio. For example, the measurement precision for alkanes and alkynes is 1% or 1.5 pptv (whichever is larger), for the alkenes the precision is 3% or 3 pptv (whichever is larger). The measurement precision for OCS is 5%, CFC-12 at 550 pptv is ± 3 pptv, while that for methyl iodide at 0.02 pptv is ± 0.01 pptv. The limit of detection (LOD) is 3 pptv for the NMHCs, and better than 20 pptv for OCS. Although the LOD is different for each halocarbon, the halocarbons that we report are usually present at mixing ratios above their LOD.

The UCI group has extensive prior experience with airborne field missions (NSF/NCAR-130 and NASA) and has demonstrated many times the power of the VOC tracers listed above to diagnose and characterize different air masses and their sources, including oceanic, urban/continental, biomass burning, natural vegetative emissions, and air mass transport. Recent field missions include: TOPSE [Blake et al., 2003a], TRACEP [Blake et al., 2003b; Simpson et al., 2003], INTEX-A and B [Blake et al., 2008] and ARCTAS- A and-B [Harrigan et al., 2011, Simpson et al., 2011]. This VOC tracer capability is central to finding and differentiating source regions and correlating them with mercury emissions.

OH, H₂SO₄, HO₂ and RO₂ (University of Colorado)

The HO_x free radicals and sulfuric acid are measured using a 4-channel mass spectrometer system previously deployed on several missions including TRACE-P, MIRAGE/MILAGRO, and PASE. It consists of a large vacuum system that houses 4 quadrupole

mass filters with an ion detector for each channel. The vacuum chamber mounts to a custom instrument rack that houses electronics, flow controllers, pump controllers, the foreline pump, heater controllers and other items. The chamber supports the weight of the inlets and a pressure seal is formed between the chamber and the aircraft wall via rubber impregnated canvas.

Custom inlets are attached to outer part of the chamber that is configured to allow electrical and gas connections between the aircraft cabin and the inlets. For NAAMEX, only two inlets will be installed: the OH and H₂SO₄ inlet which consists of a shrouded sampling tube (4 in diameter) set slightly off-axis from the free stream flow and constricted at the exit (Eisele et al., 1997, Figure 1), and the HO₂ and RO₂ inlet which samples perpendicular to the free stream flow (Cantrell et al., 2003; Hornbrook et al., 2011, Figure 2). For the OH/H₂SO₄ inlet, once the flow is straightened to align with the axis of the main sampling tube, the flow is sub-sampled by smaller tubes of 2 in diameter and 0.75 in diameter. The 2 in diameter tube is also constricted at the exit, while the 0.75 in diameter tube brings ambient air into the instrument chemical and ion reaction region. The 0.75 in diameter tube must also turn the sampled air 90 degrees to align with the axis of the mass spectrometer. This arrangement serves to slow the flow from the ambient free stream rate of about 100 m/sec to 6-10 m/sec.

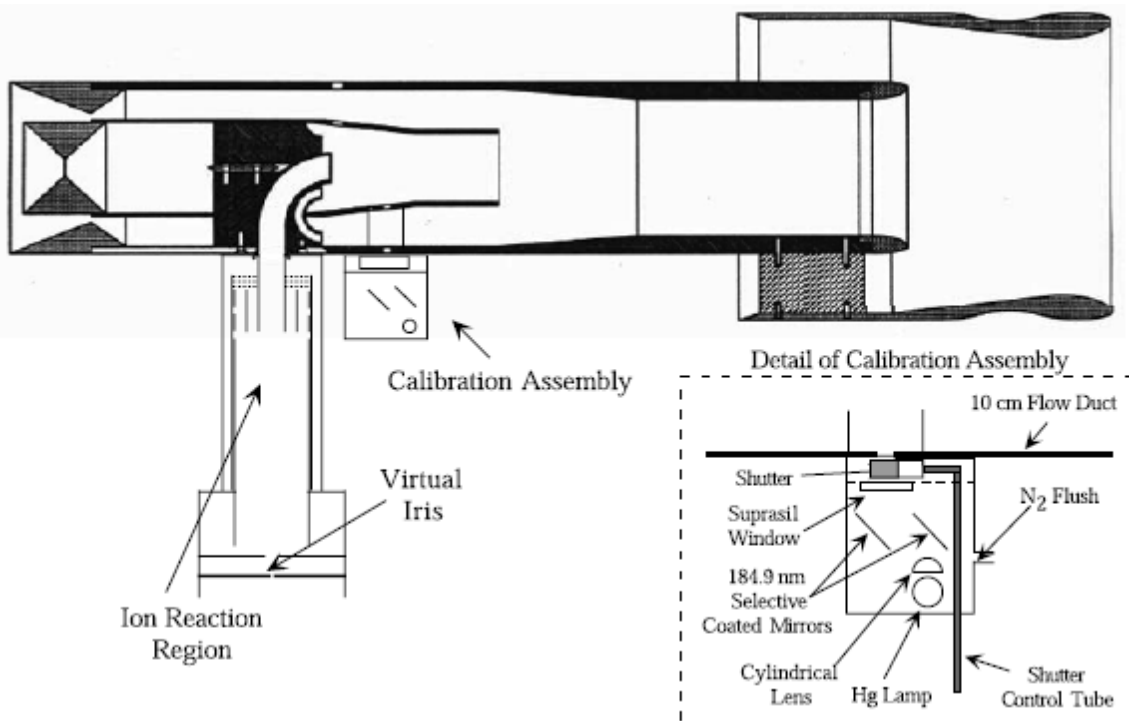


Figure 5. Inlet for measurements of OH and H₂SO₄

Within the chemical reaction region of the OH inlet, reagent gases are added to control the conversion of OH into sulfuric acid. This is accomplished by reagent gas injectors constructed of narrow diameter stainless steel tubing. In the OH measurement mode, a mixture of sulfur-34 labeled SO₂ in nitrogen is added to the front injector, while a flow of propane is added the rear injector. OH reacts with the SO₂ to form sulfur-34 labeled H₂SO₄. The propane serves to minimize the conversion of ambient HO₂ into OH primarily via its reaction with ambient NO. In the OH background mode, propane is added to the front injector in an amount to

react with OH must faster than SO₂ and thus remove ambient OH. Ambient H₂SO₄ moves through the chemical reaction region unaffected (except for a small wall loss).

In the ion reaction region, negatively charged nitrate ions are produced by passing ambient air that is scrubbed of SO₂ contained ppmv levels of nitric acid over an Americium-241 gold foil. This happens in a sheath flow so that the sampled air is not exposed to the alpha particles or gamma rays emitted by the radioactive source. The sheath flow and sample flow enter a drift tube maintained at a negative polarity relative to the sample tube. This serves to bring the nitrate ions and sulfuric acid into contact, leading to the formation of bisulfate ions (HSO₄⁻) from sulfur-34 labeled or ambient sulfuric acid. The nitrate and bisulfate ions pass through a dry nitrogen buffer and through a pinhole into the vacuum system.

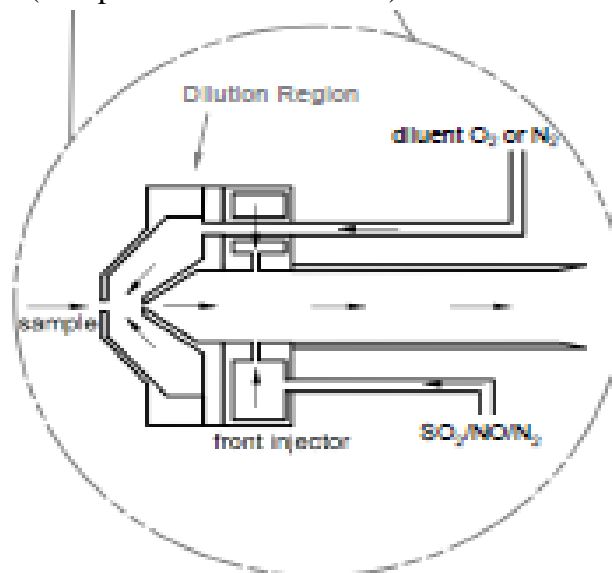


Figure 6. Inlet for HO₂ and HO₂+RO₂

The first chamber of the vacuum chamber is at moderate pressure (about 0.1 Torr). Here, the ions undergo moderate acceleration which serves to break up clusters of water and nitric acid. The sampled mixture enters a main chamber (pressure about 2 mTorr) where the ions are directed into the next chamber via an octopole ion guide. The quadrupole chamber (pressure about 10⁻⁵ Torr) contains a mass filter that separates ions based on their mass (NO₃⁻, m/z 62; H³²SO₄⁻, m/z 97; H³⁴SO₄⁻, m/z 99). The ions exited the quadrupole filter are counted using an ion detector biased in the negative ion mode. A typical measurement cycle (30 seconds) involves switching a valve to direct the reagent gases for the OH measurement mode. While the transient signals are stabilizing, the count rate of nitrate ions is measured for a few seconds. Then the count rate of sulfur-34 labeled bisulfate ions is measured for about 8 seconds. The valve is switched to change the chemistry into the OH background mode and allowed to stabilize. During this period, the count rate of bisulfate ions from ambient sulfuric acid is determined. Next the background count rate of sulfur-34 labeled bisulfate ions is measured. The electronic background (with detector count rate with the quadrupole filter biased in the opposite direction) is also measured during this cycle.

The count rates (S_x) for the various instrument conditions and m/z ratios are used to determine the concentrations of OH and H₂SO₄ as follows:

$$[\text{OH}] = C \frac{S_{\text{OH, meas}} - S_{\text{OH, bkg}}}{S_{\text{NO}_3^-}}$$

$$[\text{H}_2\text{SO}_4] = C \frac{S_{\text{H}_2\text{SO}_4} - S_{\text{elec}}}{S_{\text{NO}_3^-}}$$

The factor, C, is related to the kinetics of the nitrate ion reaction with sulfuric acid, the wall loss rate of OH and sulfuric acid and the count rate efficiency of the detector for various masses. It is determined from calibrations using the photolysis of water vapor at 184.9 nm

(Cantrell et al., 1997). From the lamp intensity (measured with NIST calibrated photodiodes), the water vapor concentration, and the water vapor absorption cross section, a known amount of OH is produced within the OH inlet. The signals from this calibration are used to determine the factor, C , which is then used to determine OH and H_2SO_4 concentrations from ambient air signals.

The neutral and ion chemistry in the HO_2 and RO_2 inlet are similar to that used for OH. The main difference is that NO is added along with SO_2 to the front inlet during the measurement mode, ambient air is diluted with either O_2 or N_2 , and the inlet is operated at a pressure of 150 Torr. HO_2 is measured with N_2 diluent and the NO and SO_2 concentrations elevated. HO_2+RO_2 are measured with O_2 diluent and lower reagent concentrations. A thirty second cycle is required for each measurement, leading to both quantities measured every minute. Calibration accomplished in a way similar to that for OH, except that a synthetic water-air mixture is generated and provided to the inlet via a photolysis probe (Hornbrook et al., 2011).

3.2. Bases of operations and flight plans

Observations and models suggest there are substantial differences in the sources, processing and deposition of Hg between the Western and Eastern US. Figure 7 shows the distribution of anthropogenic Hg emissions over North America (7a) and the combined distribution of biomass burning, land and ocean sources (7b). Anthropogenic emissions dominate the NE US, especially over the Ohio River Valley. Over the Western U.S., natural geogenic sources are more important with a few scattered point sources, including gold mining operations in Nevada and industrial sources in California. Summertime surface concentrations of TGM over the U.S. are shown in Figure 7c. These follow the spatial distribution of Hg emissions, with enhancements up to 1 ng/m^3 over the background near the Ohio River Valley, and somewhat smaller enhancements of $0.3\text{-}0.4 \text{ ng/m}^3$ in the west. Surface GOM concentrations (Figure 7d) display larger enhancements in the West due to subsidence of free tropospheric air with high GOM concentrations (Selin and Jacob, 2008).

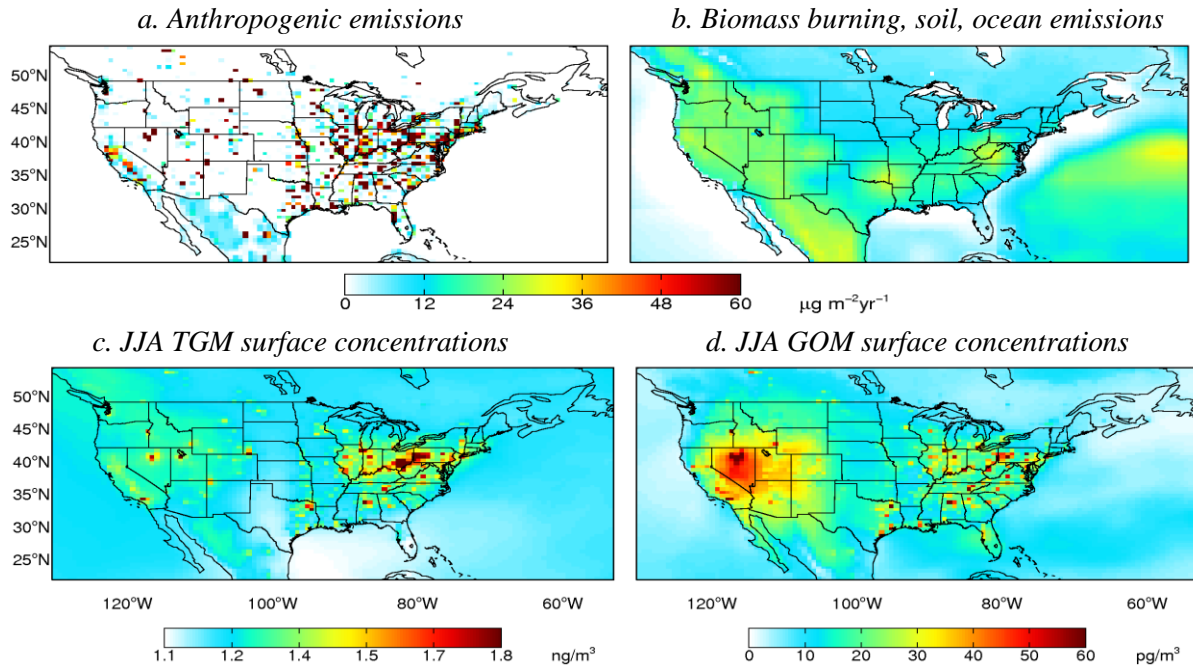


Figure 7. Top: (a) Distribution of Hg emissions from anthropogenic sources and (b) from all other sources (biomass burning, soil, and ocean sources). Anthropogenic sources are from the Environmental Protection Agency's (EPA) National Emission Inventory (NEI) for the year 2005 and the other emissions are from the GEOS-Chem chemical transport model in 2008. Bottom: (c) Summer (JJA) distribution of surface TGM concentrations (ng/m^3) and (d) surface GOM concentrations (pg/m^3) as calculated in GEOS-Chem for 2008. (Zhang et al., 2011).

Figure 8 shows a map of proposed flight tracks for NAAMEX, while Table 2 summarizes the flights along with their objectives.

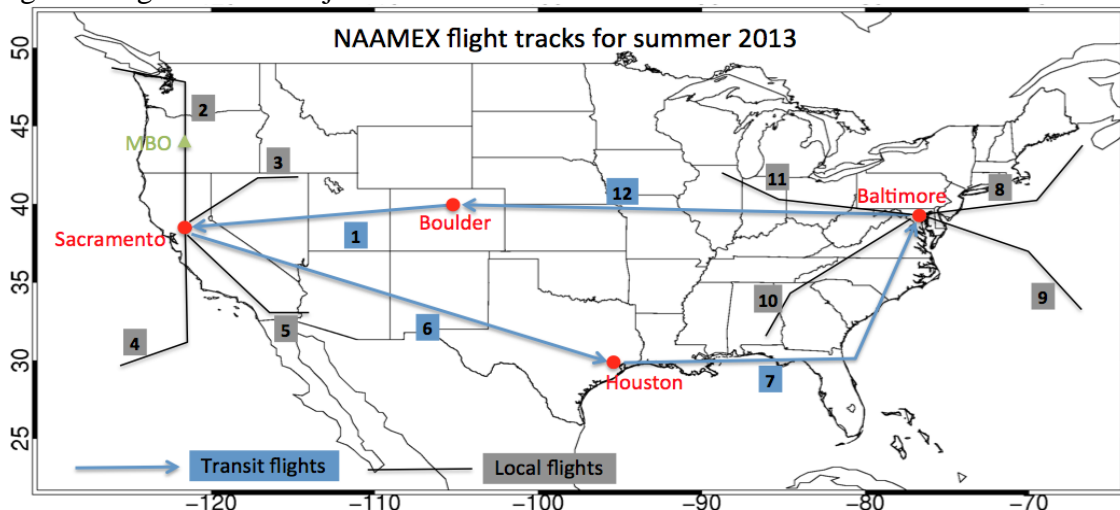


Figure 8. Map of proposed flight tracks for NAAMEX during summer 2013. We assume here that the bases of operation will be Sacramento in the Western U.S. and Baltimore in the Eastern U.S. Proposed tracks for transit flights are indicated in blue, while local flights are in black.

The base in the Western U.S. will focus on the vertical distribution of GEM, GOM, and PHg, the boundary condition inflow over N. America, entrainment of Hg into the boundary layer, comparison of aircraft data with observations at Mt. Bachelor Observatory (MBO) and quantification of major regional natural and anthropogenic Hg sources, such as the gold mining region of Nevada and the industrial region along the U.S.-Mexico border. We anticipate having four flights out of the western base, with each flight targeting multiple objectives (Table 2). Flights from the base in the Eastern U.S. would evaluate the regional boundary layer distribution of speciated Hg from sources in the Ohio River Valley. Curtain flights will be conducted in the outflow region to assess the total Eastern N. American source of Hg. Flights towards the SE will evaluate the vertical distribution of Hg(II) and its removal by wet convective systems. Transits between the two bases of operation will provide data on the large-scale east-west gradients. To intercept plumes from the Eastern U.S. we can use some of the strategies used previously to examine North American outflow (see NAAMEX whitepaper). This will provide a wealth of new data on the consistency of Hg emission inventories with atmospheric observations.

To intercept plumes from the Eastern U.S. we can use some of the strategies used previously to examine North American outflow. Figure 9 shows mean modeled North American outflow for CO July 2000 (Li et al 2005). The outflow flux, calculated using the GEOS-CHEM model, shows a persistent maximum from the northeastern and mid-Atlantic regions, with flow headed towards the North Atlantic. This pattern is consistent with observations (e.g. Real et al 2008). Fang et al (2009) discuss the variability in the outflow and focus on the synoptic conditions that give rise to strong outflow of US pollution. Lee et al (2011) use observations from the ICARTT experiment to identify anthropogenic plumes from New York City. Figure 10 shows a model calculation of an outflow event originating in New York City that was verified with aircraft observations. These outflow events are similar to those we would expect to intercept during NAAMEX. This will provide a wealth of new data on the consistency of Hg emission inventories with atmospheric observations.

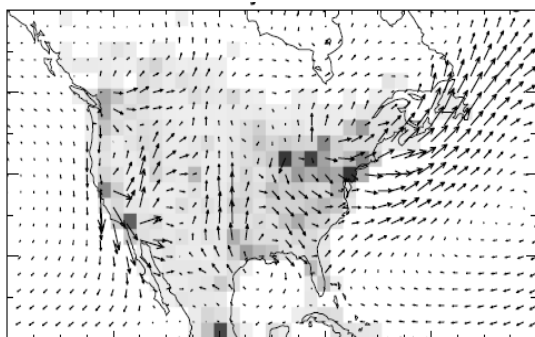


Figure 9. CO emissions (grey background) and North American outflow flux (surface-700 mb, arrows) for July 2000 (Li et al 2005).

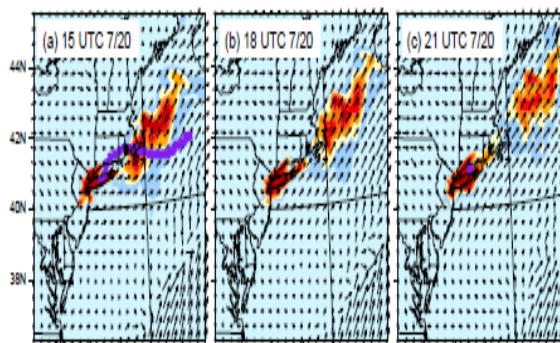


Figure 10. Modeled contribution to CO between ~140-600 meters asl from sources in New York City for July 20, 2004 using the WRF-Chem model with a high-resolution nested grid (Lee et al 2011).

While a decision on the exact bases of operation will be made in consort with NCAR Earth Observing Laboratory, our desired headquarters are located near Nevada in the Western U.S. and Maryland in the Eastern US. Given the range for the C-130 of 2900 nautical miles, these two bases of operations would allow us to achieve our science objectives within each region of the country. During the WAMO experiment, the C-130 operated out of a base in Sacramento and this location would also be acceptable for the western base during NAAMEX.

The summer timing of NAAMEX was chosen to coincide with maxima in several of the key processes. Summer is a primary season to observe the outflow of North American pollution. Summer is also the peak in photochemistry, which is believed to control the concentration of GOM. It is a time with the highest observed wet deposition fluxes in the Eastern U.S. In addition stratosphere-tropospheric exchange peaks in late spring/summer (Tang et al., 2011), and could thus influence GOM.

Table 2. Proposed NAAMEX flights

Flight	Location	Objectives
1	Transit from-Boulder to Sacramento	Nevada natural and anthropogenic sources; Tropospheric profiles of Hg speciation; Free tropospheric influence on surface GOM; Large-scale distribution of Hg
2	Local flight-Sacramento: North transect	Characterization of Hg boundary conditions; Vertical profiles; MBO intercomparison
3	Local flight-Sacramento: Nevada sources	Nevada sources; Boundary-layer/Free troposphere exchange; Profiles
4	Local flight-Sacramento: South transect	Characterization of Hg inflow; Vertical profiles; Influence of oxidation
5	Local flight-Sacramento: California sources	California sources and speciation; Large-scale characterization; Influence of oxidation
6	Transit to from Sacramento to Houston	Large-scale distribution; Vertical profiles; Texas sources; Influence of PBL/FT exchange on surface deposition
7	Transit from Houston to Baltimore	SE large-scale horizontal and vertical distribution; Convective scavenging; MBL chemistry
8	Local flight-Baltimore: N. American outflow and North transect	Evolution of N. American pollution outflow; Large-scale characterization; MBL chemistry
9	Local flight-Baltimore: N. American outflow and South Transect	Evolution of N. American pollution outflow; Large-scale characterization; MBL chemistry
10	Local flight-Baltimore: SE sources	SE anthropogenic sources; Convective scavenging; Influence of PBL/FT exchange on surface deposition
11	Local flight-Baltimore: Ohio River valley sources	Large-scale anthropogenic source characterization; Vertical profiles
12	Transit from Baltimore to Boulder	Large-scale Hg distribution; west-east evolution of distribution; Vertical profiles

3.3. Ground-based operations

A number of long-term, regionally representative, ground based monitoring stations exist for GEM, GOM, and/or PHg, including the Canadian Atmospheric Mercury Measurement Network (CAMNet) sites; sites in the Southeastern Aerosol Research and Characterization

(SEARCH) network; participants in the National Atmospheric Deposition Program's Atmospheric Mercury Network (AMNet); and independent University operated sites at MBO in Oregon (Weiss-Penzias et al., 2007); Storm Peak, Colorado (Fain et al., 2008), sites in Nevada (Weiss-Penzias et al., 2009) and New Hampshire (Mao et al., 2008). While these sites are not formally included in NAAMEX, their incorporation in our analyses will contribute to the goals of NAAMEX. Many of these sites will likely be operational during the NAAMEX field campaign. For example, variations in Hg at MBO are associated with long-range transport of Asian pollution (Jaffe et al., 2005; Weiss-Penzias et al., 2006, 2007) and variations in GOM are influenced by large-scale subsidence (Swartzendruber et al., 2006). The observations at MBO will also be important to constrain boundary conditions for regional modeling and to help validate the absolute concentrations seen on the aircraft. Because Mt. Bachelor is an isolated peak (2.8 km asl) it is suitable for aircraft comparisons. During the 2006 INTEX campaign, the NCAR C-130 flew within a few hundred meters of the summit during an early morning flight (downslope conditions) to inter-compare the ground and airborne measurements.

Observations of GOM at sites across northern Nevada showed synchronized daily variations that were hypothesized to be due to entrainment of free tropospheric air into the boundary layer (Weiss-Penzias et al., 2009). Similar data during NAAMEX would be valuable to help constrain our understanding of synoptic variations in Hg(II) and how free tropospheric air influences surface GOM concentrations. NAAMEX profiles of Hg(II) before and after convective storms in the SE will provide invaluable constraints on the scavenging of GOM. This will be related to surface observations of Hg wet deposition from the MDN network.

3.4. Use of models to address NAAMEX objectives

Models will be used to examine the consistency between observations and anthropogenic emission inventories. They will also allow the integration of ground-based observations with aircraft observations in a unified framework. Sensitivity simulations with different assumptions about speciation and chemical evolution of anthropogenic emissions will help assess what assumptions are consistent with the observed geographic distribution.

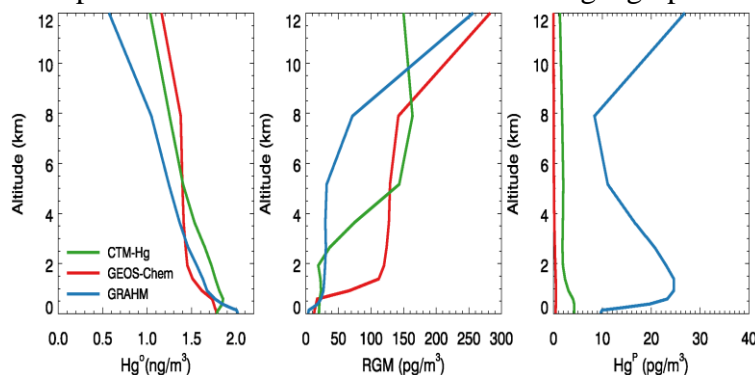


Figure 11. Model-calculated mean vertical profiles of GEM (Hg^0), GOM (RGM), and PHg (Hg^p) for August over the NE Pacific (10-50°N and 120-35°W). The results are for the 3 global models used as boundary conditions for the NAMMIS study (Bullock et al., 2008).

Figure 2a shows the simulated surface Hg^0 concentrations for 3 regional models using boundary conditions (BC) from three global models. The predicted Hg^0 South-North and West-East gradients differ among models. Differences in free tropospheric GOM concentrations of 50-100% can be seen both due to BC and assumptions in regional models. The proposed East-West and North-South curtain flights will be extremely useful to constrain the longitudinal and latitudinal gradients in Hg and its speciation. Similarly, the modeled vertical profiles of Hg show

large differences between models. Figure 11 shows mean vertical profiles of GEM, GOM, and PHg calculated by 3 global models for August in the NE Pacific. All models predict that the concentration of GOM increases and GEM decreases with altitude, due to the surface source of GEM, its oxidation to GOM, and the longer lifetime of GOM at higher altitudes caused by the lack of removal by deposition and in-cloud reduction. While calculated boundary layer concentrations of GEM and GOM are similar, large differences become apparent in the free troposphere. For PHg, concentrations differ by 1-2 orders of magnitude. By providing robust constraints on the distribution and speciation of Hg, NAAMEX will help constrain these global models, and thus reduce uncertainties in calculated source-receptor relationships.

Inverse models, as used in Roustan and Bocquet (2006) and Pan et al. (2007), will be useful tools to derive top-down anthropogenic and natural emissions based on the observed distribution of Hg obtained during NAAMEX. Thus the integration of models and observations will lead to constrained budgets of Hg over N. America during summer.

The GEOS-Chem Hg simulation

We will make extensive use of the GEOS-Chem Hg simulation before, during, and after NAAMEX. This effort will be led by the University of Washington (Jaeglé) and MIT (Selin) modeling groups in collaboration with the NAAMEX science team. The GEOS-Chem model is driven by assimilated meteorological observations from the NASA Goddard Earth Observing System (GEOS). The most recent meteorological fields (GEOS-5) have a spatial resolution of 0.5° latitude by 0.667° longitude, with 72 hybrid sigma-pressure levels. For input to the GEOS-Chem simulation, these fields are degraded vertically to 47 levels. The horizontal grid can also be degraded to either $4^\circ \times 5^\circ$ or $2^\circ \times 2.5^\circ$ resolution, in order to drive the global Hg simulations. We have recently developed a high-resolution nested-grid Hg simulation, keeping the native horizontal resolution ($0.5^\circ \times 0.667^\circ$, about 50 km) over N. America (Zhang et al., 2012).

The GEOS-Chem atmospheric Hg simulation is described and evaluated in Selin et al. (2007), with recent updates by Holmes et al. (2010) and Amos et al. (2011). The model includes three mercury species: Hg^0 (GEM), Hg^{II} , and primary particulate Hg from anthropogenic sources (Hg_p). Global anthropogenic Hg emissions are from the 2005 inventory of Pacyna et al. (2010). We use anthropogenic Hg emissions from the 2005 EPA NEI inventory over the U.S. and from the 2005 Canadian National Pollutant Release Inventory over Canada. Natural sources include emissions from the ocean and from land as well as smaller sources from biomass burning and snow re-emissions. There are two options for defining GEM oxidants in GEOS-Chem: (1) assume that OH and O_3 are the main oxidants (as described in Selin et al., 2008), or (2) that Br accounts for GEM oxidation (Holmes et al., 2010). Both mechanisms produce Hg fields consistent with measured global distribution of atmospheric GEM, interhemispheric gradients, and wet deposition. We will evaluate the performance of these schemes with NAAMEX observations.

Zhang et al. (2012) have evaluated the high-resolution nested-grid GEOS-Chem simulation over N. America finding that the Hg simulation captures the seasonal and spatial evolution of Hg wet deposition observed by the MDN network. It also reproduces the seasonal cycle of surface observations of TGM, GOM, Hg_p at AMNet and CAMNet sites. The model reproduces the variability in aircraft measurements of TGM during the ARCTAS campaign over California. In contrast to previous versions of GEOS-Chem, which used a resolution of $4^\circ \times 5^\circ$ (e.g. Selin and Jacob, 2008; Amos et al., 2011), the nested simulation shows improved ability to

capture small scale variations near point sources and predicts more efficient convective rain scavenging of Hg over the southeast United States, in agreement with observations.

Use of GEOS-Chem and GEOS forecasts as part of NAAMEX

Mission planning: Prior to the NAAMEX field deployment, we will analyze results from multi-year (2004-2011) runs of the nested Hg and chemistry-aerosol simulations in GEOS-Chem. This will allow us to develop a menu of flights to guide mission execution. We will analyze how interannual variability in meteorology affects GEM and GOM distribution in the free troposphere and transport to the surface during summer. We will examine correlations between simulated GEM/GOM and CO in the free troposphere, to help develop hypotheses of what Hg speciation and correlations we might expect to see in pollution plumes and background air over different regions. We will also focus on conditions leading to enhanced N. American pollution outflow. We will identify meteorological conditions favoring high GOM in the free troposphere (e.g. high pressure, low relative humidity, time since last precipitation, etc.). This will be critical to enable us to use chemical forecasts during NAAMEX to identify regions of interest for flight planning.

Mission execution: During NAAMEX, we will provide analysis of chemical transport forecast model results before each flight. We will use chemical forecasts from the NASA Global Modeling and Assimilation Office, based on the GEOS-5 meteorological real-time analysis and forecasts. Forecasted tracers include CO originating from different sources, O₃ and aerosol species. Output from these chemical forecasts will be available immediately via an interactive web interface at UW. The framework for this public access web site has been developed by Jaeglé and was used to display the GEOS forecasts during past field missions, most recently in the NSF-sponsored HIPPO field mission (<http://coco.atmos.washington.edu/cgi-bin/ion-p?page=hippo.ion>). The CO tracers will help target specific plumes during flights (N. America vs. Asian, anthropogenic vs. biomass burning, stratospheric vs tropospheric). The aerosol tracers and precipitation fields will allow us to identify air masses recently exposed to wet scavenging. In addition, we will run the GEOS-Chem Hg high-resolution nested-grid simulation in near-real time (NRT) mode on a dedicated server at MIT. The NRT model results will be available 2-3 days after the flights on the UW interactive web site. Our goal is to be able to rapidly compare model results with observations in order to monitor how the flights are meeting mission goals. This will allow to quickly re-evaluate strategies for flight planning.

Post-mission data analysis: After the mission, we will run GEOS-Chem nested-grid simulations for the entire NAAMEX campaign. Results from the Hg and coupled aerosol-chemistry simulations will be sampled along the C-130 flight track and for individual ground-sites. We will make the results available to the science team. Our analysis of the NAAMEX observations will focus on four objectives:

A) Quantify the origin of Hg over N. America. We will first focus our analysis on aircraft and ground-based observations obtained in the boundary layer over N. America. We will conduct “tagged Hg” simulation in which tracers will be tagged according to source type and source region, as described in Strode et al. (2008), examining whether discrepancies between model and observations are related to specific sources (e.g. soil, anthropogenic, biomass burning).

B) Analyze NAAMEX free tropospheric speciated Hg observations to understand the main controlling factors. We will examine how the speciation of Hg changes with increasing height in the free troposphere over the western and eastern U.S. and how it is affected by oxidation, precipitation, cloud-processing, and stratospheric intrusions. We will use comparisons between GEOS-Chem simulations and NAAMEX measurements to test hypotheses about the chemical (O_3/OH vs Br oxidation) and meteorological controls on Hg speciation in the free troposphere. We will examine correlations in model and measurement data to diagnose chemical processes, the influence of pollutant plumes, and stratosphere/troposphere exchange.

C) Compare GEOS-Chem with wet and dry deposition observations to constrain the sources and processes of Hg deposition over N. America during NAAMEX. We will use a combination of GEOS-Chem simulation results and data from NAAMEX, MDN, and AMNet sites to constrain the sources and processes of Hg deposition over N. America. We will conduct sensitivity simulations with different dry deposition velocities and wet scavenging efficiencies. The GEOS-Chem model predicts that free tropospheric GOM is an important contributor to summertime deposition across the U.S., with a large influence in Southeast wet deposition (deep convective scavenging) and western dry deposition (downwelling of high-GOM air) (Selin and Jacob, 2008). We will test this by contrasting the evolution of wet and dry deposition measured at the surface to free tropospheric NAAMEX observations. We will use the tagged Hg simulation to obtain source-receptor relationships.

D) Examine the evolution of Hg outflow from N. American sources. We will relate the aircraft observations to ground-based observations over source regions in the NE and SE U.S. (AMNet and SEARCH sites). We will examine how Hg speciation and correlation with other species (GEM-CO, GEM-GOM, GOM-SO₂, GOM-O₃, GOM-aerosol) change between sources and outflow regions. We will interpret observed GEM-CO and total Hg-CO correlations with the model to infer the export efficiency of Hg. We will examine how this export efficiency is influenced by the fraction of anthropogenic emissions released as GOM and by GOM/GEM redox chemistry in the outflow.

In addition to the GEOS-CHEM groups, other groups have expressed interest to participate in the NAAMEX experiment. These groups are identified in Table 3 below. In understanding the roles of chemistry and emissions for different air masses, the models will be useful to interpret observed correlations among Hg species (GEM vs. Hg(II)) or between Hg and other species (GEM vs. CO, Hg(II) vs. $O_3-OH-BrO$). In addition to their extensive use for post-mission data analysis, models will be an intrinsic part of mission planning for NAAMEX. We anticipate that several CTMs will be used in NAAMEX (Table 3). Initially, these models will provide hindcast simulations for past summers in order to optimize the design of flights and best address the mission's objectives.

Table 3. NAAMEX modeling teams

Modeling	Model type	Who?
Global/Hemispheric Models	Forecasting	Jaeglé (UW); Selin (MIT); Lin (Lamar U.); Dastoor (Environment Canada)
Global/Hemispheric Models	Near-real time	Jaeglé (UW); Selin (MIT); Lin (Lamar U.); Dastoor (Environment Canada)
Global/Hemispheric/regional Models	Post-mission analysis	Jaeglé (UW); Selin (MIT); Cohen (NOAA); Lin (Lamar Univ.); Dastoor (Environment Canada); Travnikov (MSC-East); Matthias (HRZ-Hamburg); Hedgecock (CNR-Italy)

Members of the GEOS-CHEM modeling teams (and possibly others) will be present in the field to provide an analysis of model forecasts on a daily basis. Some of the forecasting products that will be useful for flight planning, in addition to GEM/GOM/PHg fields, include tracers of pollution (such as CO tagged by emission regions and types: anthropogenic vs. biomass burning, Asia vs. N. America), stratospheric tracers (O₃, CFCs, potential vorticity), and oxidant fields (OH, O₃). We will also use satellite observations for flight planning (e.g. MODIS) to track major anthropogenic plumes and monitors fire activity.

4. Broader impacts

Human exposure to Hg is a significant health risk and a problem of national and global significance. NAAMEX will reduce the uncertainties concerning the source-receptor relationship and the relative contribution of domestic, foreign and natural sources of Hg in the U.S. NAAMEX will employ a number of graduate and undergraduate students from 5 different U.S. institutions and thus will expose these students to working on high level scientific problems of great national significance. The global nature of this problem is evident by the international participation in NAAMEX. In addition to a core group of scientists from the U.S., Hg scientists from Canada, Italy, Germany and Russia will collaborate on NAAMEX. A scientist from NOAA (Mark Cohen) will also participate in NAAMEX. All of these collaborations are documented in the supplemental documents section.

There is also the possibility for cooperation with other airborne experiments happening at the same time. **While these are not essential** for NAAMEX, they would contribute to meeting the scientific goals of the experiment. These aircraft experiments include:

- The NASA Discover-AQ project, which will be operating aircraft near Houston in the same time frame (summer 2013);
- The European CARABIC program, which has measurements of Hg on commercial flights and may operate between Europe and a US East coast location during NAAMEX;
- The European Global Mercury Observation System (GMOS), which may operate an aircraft over Europe and the North Atlantic during NAAMEX.

While the details of each of these experiments are not yet final, it would be desirable to coordinate flight operations with these missions. As NAAMEX and these other missions move forward we will communicate our plans to each other and develop flight plans that build on the synergies of these multiple missions.

We expect to fully collaborate with the European GMOS program coordinated by Nicola Pirrone at CNR-Italy (see letter of support). This includes data sharing and inclusion of European modeling groups into NAAMEX.

5. Plan of Work

NAAMEX will be led by the University of Washington (D. Jaffe, Mission Scientist and L. Jaeglé, co-Mission Scientist), in collaboration with PIs at other institutions (U. California Irvine, D. Blake; U. Colorado, C. Cantrell; Georgia Institute of Technology, G. Huey; Massachusetts Institute of Technology, N. Selin). Specific responsibilities will be as follows:

- **Dan Jaffe** will serve as Lead Mission Scientist. He will coordinate all pre- and post-mission activities for the project with each of the PIs and the NCAR-EOL-C130 team. In consort with the entire group he will coordinate day-to-day flight decisions. He will lead the activities of his own research team to deploy the UW-DOHGS instrument and the filter measurements of PHg. He will also be responsible for developing and maintaining the final NAAMEX data archive, coordinating NAAMEX publications and the outreach component of NAAMEX (with other PIs).
- **Lyatt Jaeglé** will serve as co-Mission Scientist. She will lead the NAAMEX modeling teams for day-to-day flight planning. She will also coordinate with modeling teams for parallel aircraft missions (GMOS, Discover-AQ) and will be present in the field during the entire mission. Her group has recently developed a high-resolution nested grid GEOS-Chem Hg simulation (Zhang et al., 2011), which will be used to analyze NAAMEX observations in detail. The nested grid model will be applied to conduct hindcast simulations and near-real time simulations. Her team will generate merges of the NAAMEX observations, along with model simulations sampled along flight tracks.
- **Don Blake** will lead the UC Irvine research group in collecting whole air samples for the NAAMEX field campaign. He will be responsible for their analysis and quantification for more than 60 trace gases, including C₂-C₁₀ NMHCs, C₁-C₂ halocarbons, C₁-C₅ alkyl nitrates, selected sulfur compounds, methanol, ethanol, acetaldehyde, and acetone, data quality control and archiving. The tracer capability is essential to diagnose and distinguish regional source contributions, which will then be correlated to the Hg data. Prof. Blake will oversee data interpretation, presentation and publication of results.
- **Chris Cantrell and Lee Mauldin** will lead the HO_x group. This team will deploy the four-channel chemical ionization mass spectrometer system for the measurement of OH, H₂SO₄, and MSA on one channel and HO₂ and HO₂+RO₂ in the other channel. The data will be processed using in flight and laboratory calibration information. Field, preliminary, and final data will be submitted to the NAAMEX data archive. They will generate at least two papers describing the results.
- **Greg Huey** will lead the CIMS measurements team. This group will prepare and deploy a two-channel CIMS instrument for the measurements shown in Table 1. The data will be processed post-flight. Preliminary field data and final data will be submitted to the NAAMEX data archive. They will generate at least one paper describing their results.
- **Noelle Selin** will lead the MIT modeling group to deploy forecast and post-mission modeling analysis based on the GEOS-Chem model. NAAMEX support is requested for costs associated with travel to the NAAMEX base in the Eastern U.S., where she will work with Jaeglé on the modeling component (near real time simulations and analysis).

Our schedule for the mission and plan of work is as follows:

Year 1 (2012-2013)	<ul style="list-style-type: none"> • Prepare instruments for deployment; • Conduct hindcast simulations to optimize flight plans; • Pre-mission planning meeting (Boulder, CO, approximately January 2013) • Instrument integration and test flights on C-130 (May-Jun 2013).
Year 2 (2013-2014)	<ul style="list-style-type: none"> • NAAMEX field deployment (Jul-Aug 2013); • Submission of preliminary data by November 1, 2013; • Analysis of observations, interpretation with global models; • Post-mission workshop in Boulder (Jan or Feb 2014).
Year 3 (2014-2015)	<ul style="list-style-type: none"> • Finalize data by Feb 1, 2014; • Prepare results for publication; • Post-mission science meeting at AGU in San Francisco (Dec 2015).

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