

FLORIDA DEPARTMENT OF ENVIRONMENTAL PROTECTION

**Division of Environmental Assessment and Restoration
Bureau of Watershed Restoration**

Mercury TMDL for the State of Florida

Appendix G

Quality Assurance Project Plan (QAPP)

Watershed Evaluation and TMDL Section



May 22, 2012

Appendix G: Quality Assurance Project Plan (QAPP)

QUALITY ASSURANCE PROJECT PLAN

Florida Mercury Total Maximum Daily Load Project Atmospheric Sampling and Analysis

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PREFACE

This document is a project-specific Quality Assurance Project Plan (QAPP) for the Atmospheric Monitoring Task of the Florida Mercury TMDL Project. It was developed using the U.S. Environmental Protection Agency (EPA) Quality Assurance document guidelines set forth in *EPA QA/R-5, EPA Requirements for Quality Assurance Project Plans*, *EPA QA/G-5, Guidance for Quality Assurance Project Plans* and *IDQTF UFP-QAPP Manual v1, March 2005*. It is consistent with the *EPA Quality Assurance Handbook for Air Pollution Measurement Systems, Vol I-IV*.

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PROCEDURES AND PROTOCOLS BY ORGANIZATION

Atmospheric Research and Analysis

SpecHg-SOP	Semi-continuous measurement of ambient speciated mercury
ADS-SOP	Determination of ambient acidic and basic gases
AIM-MAN	Semi-continuous measurement of ambient ions
SHARP-MAN	Continuous measurement of ambient particulate mass
ASPS2-SOP	Automated collection of daily event precipitation
PMdichot-MAN	Automated collection of ambient fine and course PM
Met4A-MAN	Collection of BP, RH and T data
OCEC-SOP	Automated collection of EC and OC in ambient fine PM
AMBGAS-SOP	Automated collection of trace gas and flow data
SRsensor-MAN	Collection of SR data
LWS-MAN	Collection of leaf wetness data
Sonic-MAN	Collection of WD and WS data via sonic anemometer
Rainfall-MAN	Collection of incident precipitation data
FL-DOC	FirstLight data management software documentation

Florida Department of Environmental Protection

HGpcp-SOP	Analysis of mercury in precipitation by CVAFD
PMmass-SOP	Measurement of mass on sample filters
Data-SOP	Standard Operating Procedure for Records Maintenance and Storage
Report-SOP	Standard Operating Procedure for Reporting Qualified Data

University of Michigan

ACtable-SOP	Acid cleaning steps for all sampling supplies
TEpcp-SOP	Analysis of trace elements by ICP-MS
IONSpcp-SOP	Analysis of ions by IC
HGisotopes-SOP	Determination of Mercury Isotopic Composition in Precipitation

U. S. Environmental Protection Agency

TEpcp-SOP	Extraction and analysis of trace elements on Teflon® filters
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ACRONYMS AND ABBREVIATIONS

ADS	Acid Denuder System (URG Model 3000C)
AIM	Ambient Ion Monitor (URG Model 9000C)
AQL	University of Michigan Air Quality Laboratory
ARA	Atmospheric Research & Analysis, Inc
ASPS	Automated Sequential Precipitation Sampler II
CNR	Consiglio Nazionale della Ricerche, Inst. for Atmos. Pollution, Rende, Italy
CVAFS	Cold Vapor Atomic Fluorescence Spectroscopy
EOQ	End of the calendar quarter
ED-XRF	Energy Dispersive X-Ray Fluorescence
EPA	U.S. Environmental Protection Agency
EPA ORD-NERL	EPA Office of Research and Development National Exposure Research Laboratory
EPA Region 4 SEDS	EPA Region 4 Science and Ecosystem Support Division
FDEP	Florida Department of Environmental Protection
Hg ⁰	Elemental Mercury
Hg(p)	Particulate Mercury
HR-ICPMS	High Resolution Magnetic Sector Field Inductively Coupled Plasma Mass Spectrometry
IDQTF	Intergovernmental Data Quality Task Force
L/min	liters per minute
MC-ICPMS	Multi Collector Inductively Coupled Plasma Mass Spectrometry
MDL	Method Detection Limit
MMAD	Mass Median Aerodynamic Diameter
mL	milliliters
MQ	Milli-Q deionized water, 18 MΩ·cm
MΩ·cm	mega ohm centimeter
m ³	cubic meter
ng/L	nanograms per liter
NDIR	Nondispersive Infrared sensor
NIST	National Institute of Standards and Technology
PI	Principal Investigator
PM _{2.5}	Particulate matter < 2.5 micrometer mass median aerodynamic diameter
QA	Quality Assurance
QAO	Quality Assurance Objectives
QAPP	Quality Assurance Project Plan
QC	Quality Control
RH	Relative Humidity
RGM	Divalent Reactive Gaseous Mercury
SAS	Statistical Analysis Software Package, (SAS Institute, Cary, NC)
SHARP	Synchronized Hybrid Ambient Real-time Particulate monitor (Thermo-Environmental Model 5030)
SRM	Standard Reference Material
SOP	Standard Operating Procedure
TMDL	Total Maximum Daily Load
UFP	Uniform Federal Policy
UM	University of Michigan

UMAQL
UMGS
 $\mu\text{g}/\text{m}^3$

University of Michigan Air Quality Laboratory
University of Michigan Geological Sciences
micrograms per cubic meter

PROJECT PERSONNEL SIGN-OFF SHEET

The following individuals have read the sections of this document that pertain to their role in the project and commit to the implementation of the QA/QC guidelines presented:

[illegible]

1.0 PROJECT DESCRIPTION AND ORGANIZATION

1.1 Introduction

Atmospheric emissions and deposition processes are now recognized as a major route of contamination to many soils, sediments and aquatic systems. Excessive levels of mercury in many species of fish constitute the second-most prevalent indicator, following only eutrophication, of water quality impairment in the US. Both watershed loads plus wet and dry deposition processes must be quantified in order to determine the total loading of any contaminant to an ecosystem.

Earlier studies in South Florida by the UMAQL and others working with the FDEP, EPA ORD-NERL and EPA Region 4 focused on rainfall as the primary pathway (>95%) for delivery of mercury to the Everglades marsh (Dvonch *et al.*, 1995; 1998; 1999). These early measurements included only the wet part of the load, as available technologies could only approximate dry deposition fluxes.

Dry deposition of particulate and gaseous contaminants, including mercury, trace elements, nitrogen species, and other nutrients are also likely very important. The dry deposition flux for some contaminants could be of equal or even greater magnitude than the wet deposition of that contaminant in certain regions. The difference between wet and dry deposition is that the underlying surface or land use type significantly impacts the dry deposition of Hg and other pollutants. Thus, to accurately assess the loadings of Hg and other pollutants to the State of Florida it is necessary to address the spatial differences in land use and the differences in the aquatic ecosystems that are found across the large and diverse state.

To quantify the loadings of mercury across the state, a combined monitoring and modeling approach will be employed. For air quality monitoring and modeling, a combination of long-term comprehensive monitoring sites (Supersites) together with a small number of additional event precipitation sites (Satellite Sites) will be employed for sample collection for a two-year period. In addition, a number of atmospheric deposition monitoring sites (Supplemental Sites) will be deployed surrounding the Supersites to evaluate the spatial patterns and variability in each region during selected months.

The UMAQL has extensive experience in conducting large field efforts such as the Mercury TMDL study. In coordination with the UMAQL and FDEP, ARA will provide for the setup and operation of four Supersite comprehensive monitoring sites across the state. ARA is uniquely qualified to handle this task with their years of experience in running atmospheric monitoring sites similar to those we are proposing in this study. The four proposed Supersite monitoring locations are Tampa, Ft. Lauderdale, Pensacola, and Jacksonville. Two additional wet deposition-only sites will be located in Orlando and in the Everglades National Park. FDEP will coordinate with UMAQL to provide for site operation and maintenance for the two additional wet deposition sites. UMAQL will provide the initial site setup and training of personnel for the two additional wet deposition only sites. ARA will provide instrument upgrades, site installation, site operation and maintenance, and data management support for two complete years of site operation at the four Supersites. In support of the overall project objectives, the Atmospheric Monitoring consists of three major elements: long-term atmospheric monitoring at Supersites, precipitation monitoring at Supersite and Satellite sites, and month-long intensive deposition monitoring at near-field locations (Supplemental sites) surrounding Supersites. These roles and responsibilities of each project team member within these three elements are detailed in the following subtasks.

1.1.1 Subtask 1: Long-Term Atmospheric Monitoring at Supersites

Four Supersites will serve as the basis for the long-term atmospheric monitoring component of the Florida mercury TMDL project. The four proposed site locations include the vicinities of Pensacola, Tampa, Jacksonville, and Fort Lauderdale. The scope of this subtask will include the long-term characterization of key atmospheric constituents necessary for the Florida mercury TMDL assessment. The long-term monitoring at Supersites will include measurements of speciated atmospheric mercury, trace gases, elemental and organic carbon, chemical characterization of fine and coarse particulate matter, as well as surface meteorology. The instruments to be used to carry out the primary and continuous data measures at each Supersite are listed in Table 1.1. Table 1.2 provides a complete listing of the individual constituents to be analyzed, both routinely and during month-long intensive campaigns.

Table 1.1 Instrumentation/Measurements for Atmospheric Monitoring.

Class	Variable(s)	Detection	Manufacturer	Model	Time
Hg	Hg ⁰	CVAFS	Tekran	2737A or B	5-minute, 1-hour
	RGM	CVAFS	Tekran	2737A or B	1-hour
	Hg _{PM2.5}	CVAFS	Tekran	2737A or B	1-hour
Cont. Gas	O ₃	UV absorption	Thermo-Env.	49c or i	5-minute, 1-hour
	CO	NDIR	Thermo-Env.	48c or i	5-minute, 1-hour
	SO ₂	UV fluorescence	Thermo-Env.	43c or i	5-minute, 1-hour
	NO	NO-Q CL	Thermo-Env.	42c or i	5-minute, 1-hour
	NO _y	NO-Q CL	Thermo-Env.	42c or i	5-minute, 1-hour
Discrete Gas Sampler	HNO ₃ /HNO ₂ /NH ₃ /SO ₂ /HCl	IC	URG	3000C-ADS	weekly, day/night
Discrete Particle	PM _{2.5} Major Ions	IC	URG	ADS	weekly, day/night
Cont. Particle	PM _{2.5} Major Ions	IC	URG	AIM	1-hour
	PM _{2.5} OC/EC	NDIR	Sunset Labs.	RT-ECOC	1-hour
	PM _{2.5} Mass	Light Scattering	Thermo-Env.	Sharp	5-minute, 1-hour
Dichotomous Sampler	PM _{2.5} and PM _{2.5-10} Mass	Gravimetric	R&P	2025	daily
	PM _{2.5} and PM _{2.5-10} Trace Elements	EDXRF or ICPMS	R&P	2025	daily
Wet	Total-Hg	CVAFS	UM	ASPS	event
	Trace Elements	ICP-MS	UM	ASPS	event
	Hg Isotopes	ICP-MS	UM	ASPS	event
	Major Ions	IC	UM	ASPS	event
Meteorology	Wind Speed	sonic anemometer	RMYoung	81000	5-minute, 1-hour
	Wind Direction	sonic anemometer	RMYoung	81000	5-minute, 1-hour
	Temperature	thermistor	Paroscientific	Met4A	5-minute, 1-hour
	Relative Humidity	thermistor	Paroscientific	Met4A	5-minute, 1-hour
	Barometric Pressure	manometer	Paroscientific	Met4A	5-minute, 1-hour
	Solar Radiation	pyranometer	Campbell Sci.	LI200 X-L	5-minute, 1-hour
	Precipitation	rain gauge	ETI	NOAH-IV	5-minute, 1-hour
	Surface	conductivity	Campbell Sci.	237	5-minute, 1-hour

Table 1.2 Data Capture and Analytes Quantified for Atmospheric Monitoring.

Class	Variable(s)	Detection	Minimum # of Samples	Laboratory	Analytes
Hg	Hg ⁰	CVAFS	Daily (85% data	ARA (in field)	Hg ⁰
	RGM	CVAFS	Daily (85% data	ARA (in field)	RGM
	Hg _{PM2.5}	CVAFS	Daily (85% data	ARA (in field)	Hg _{PM2.5}
Cont. Gas	O ₃	UV absorption	Daily (85% data	ARA (in field)	O ₃
	CO	NDIR	Daily (85% data	ARA (in field)	CO
	SO ₂	UV fluorescence	Daily (85% data	ARA (in field)	SO ₂
	NO	NO-O ₃ CL	Daily (85% data	ARA (in field)	NO
	NO _y	NO-O ₃ CL	Daily (85% data	ARA (in field)	NO _y
Discrete Gas Sampler	HNO ₃ /HNO ₂ /NH ₃ /SO ₂ /HCl	IC	Weekly (85% data	UMAQL	HNO ₃ , HNO ₂ , NH ₃ , SO ₂ , HCl
Discrete Particle	PM _{2.5} Major Ions	IC	Weekly (85% data	UMAQL	sulfate, nitrate, nitrite, phosphate, ammonium, and sodium
Cont. Particle	PM _{2.5} Major Ions	IC	Daily (85% data	ARA (in field)	sulfate, nitrate, nitrite, phosphate, ammonium, sodium, calcium, potassium and
	PM _{2.5} OC/EC	NDIR	Daily (85% data	ARA (in field)	OC, EC
	PM _{2.5} Mass	Light Scattering	Daily (85% data	ARA (in field)	PM _{2.5} mass
Dichotomous Sampler	PM _{2.5} and PM _{2.5-10} Mass	Gravimetric	Daily (85% data	FDEP	PM _{2.5} mass, PM _{2.5-10} mass
	Trace	EDXRF or ICPMS	Daily (85% data	USEPA-NERL	Mg, Al, P, S, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Rb, Sr, Mo, Cd, La, Ce, Sm, Pb
Routine Wet	Total-Hg	CVAFS	75*	FDEP	Hg
	Trace	HR-ICP-MS	75*	UMAQL	Mg, Al, P, S, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Rb, Sr, Mo, Cd, La, Ce, Sm, Pb
	Hg Isotopes	MC-ICP-MS	22*	UMAQL	$\delta^{203}\text{Hg}$, $\delta^{201}\text{Hg}$, $\delta^{200}\text{Hg}$, $\delta^{199}\text{Hg}$, $\gamma^{201}\text{Hg}$, $\gamma^{199}\text{Hg}$
	Major Ions	IC	75*	UMAQL	sulfate, nitrate, nitrite, chloride, ammonium, and sodium
Intensive Wet	Total-Hg	CVAFS	50**	FDEP	Hg
	Trace	HR-ICP-MS	50**	UMAQL	Mg, Al, P, S, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Rb, Sr, Mo, Cd, La, Ce, Sm, Pb
	Hg Isotopes	MC-ICP-MS	15**	UMAQL	$\delta^{203}\text{Hg}$, $\delta^{201}\text{Hg}$, $\delta^{200}\text{Hg}$, $\delta^{199}\text{Hg}$, $\gamma^{201}\text{Hg}$, $\gamma^{199}\text{Hg}$
	Major Ions	IC	50**	UMAQL	sulfate, nitrate, nitrite, chloride, ammonium, and sodium
Intensive Dry Deposition	Total-Hg	CVAFS	50**	UMAQL	Hg
	Trace	HR-ICP-MS	50**	UMAQL	Mg, Al, P, S, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Rb, Sr, Mo, Cd, La, Ce, Sm, Pb
	Major Ions	IC	50**	UMAQL	sulfate, nitrate, nitrite, chloride, ammonium, and sodium
Meteorology	Wind	sonic anemometer	Daily (85% data	ARA (in field)	wind speed
	Wind Direction	sonic anemometer	Daily (85% data	ARA (in field)	wind direction
	Temperature	thermistors	Daily (85% data	ARA (in field)	temperature
	Relative Humidity	thermistors	Daily (85% data	ARA (in field)	relative humidity
	Barometric Pressure	manometer	Daily (85% data	ARA (in field)	barometric pressure
	Solar Radiation	pyranometer	Daily (85% data	ARA (in field)	solar radiation
	Precipitation	rain gauge	Daily (85% data	ARA (in field)	precipitation
	Surface	conductivity	Daily (85% data	ARA (in field)	surface wetness

* Per site for each full year, based upon climatological norms. ** Per intensive, based upon climatological

1.1.1.1 Roles and Responsibilities: Supersite Data Management and Reporting Timelines

For Subtask 1, ARA will provide field operation of the four Supersites, including field operation of all Supersite instruments described in Table 1.1, as well as QA of all associated data generated in the field. For subsequent laboratory analyses related to samples collected as part of Subtask 1, FDEP Central Laboratory will provide for the pre- and post-weighing of filters for the dichotomous samplers. EPA ORD-NERL will provide for the trace element analysis of dichotomous sample filters. ARA will provide sample media and UMAQL will conduct the ion chromatography analysis for the weekly-integrated discrete gas/particle samplers. Data for all continuous analyzers (Hg speciation, gas analyzers, particle analyzers, meteorological parameters) will be reported by ARA to the UMAQL and FDEP one calendar quarter *after* the end of a quarter's worth of data collection. FDEP will report data for PM mass determinations to the UMAQL within 20 weeks after the end of a quarter's worth of data collection. UMAQL will report data for ion chromatography analysis to FDEP within two calendar quarters after the end of a quarter's worth of data collection. EPA ORD-NERL will report data for trace element analysis to UMAQL and FDEP within 22 weeks after the end of a quarter's worth of data collection. The initial quarter of data collection for all Subtask 1 activities is defined to conclude on December 31, 2008; subsequent project quarters will be coincident with calendar quarters (e.g., ending March 31, June 30, September 30).

1.1.2 Subtask 2: Long-Term Precipitation Monitoring at Supersites/Satellite Sites

In addition to the four Supersite locations in the vicinities of Pensacola, Tampa, Jacksonville, and Fort Lauderdale, two additional Satellite sites have been identified for daily collection of wet deposition only. Combined, these six sites will form a spatially diverse long-term wet deposition monitoring network. ARA will provide for field operations of precipitation monitoring at the four Supersites, and FDEP will provide for field operation of the two Satellite sites, one in Orange County and one in Everglades National Park. The scope of Subtask 2 includes the long-term characterization of key constituents of precipitation necessary for the Florida mercury TMDL assessment. The long-term monitoring at the six wet deposition sites will include sample collection and analysis for total mercury, major ions (sulfate, nitrate, nitrite, chloride, ammonium, and sodium), trace elements (Mg, Al, P, S, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Rb, Sr, Mo, Cd, La, Ce, Sm, Pb), and stable mercury isotopic composition ($\delta^{202}\text{Hg}$, $\delta^{201}\text{Hg}$, $\delta^{200}\text{Hg}$, $\delta^{199}\text{Hg}$, $\Delta^{201}\text{Hg}$, $\Delta^{199}\text{Hg}$). The methodologies to be used to carry out the collection and analysis of the constituents in precipitation measures at each site are listed in Table 1.1. Table 1.2 provides a listing of the individual constituents to be analyzed for the wet deposition samples.

1.1.2.1 Roles and Responsibilities: Precipitation Monitoring Data Management and Reporting Timelines

For Subtask 2, ARA, as described above for Subtask 1 will be providing field operation of the four Supersites that will include the ASPS precipitation collector. FDEP will provide for field operation of the two Satellite sites, one in Orange County and one at Everglades National Park. For subsequent laboratory analyses related to Subtask 2, FDEP Central Laboratory will provide for analysis of total mercury in precipitation samples,

and UMAQL will conduct the trace element analysis as well as the ion chromatography analysis and mercury isotope analysis for the precipitation samples. FDEP Central Laboratory will report data for total mercury in precipitation to UMAQL within 23 weeks after the end of that quarter's worth of data collection. UMAQL analyses of trace elements, major ions, and mercury isotopes in precipitation samples will be completed within 2 calendar quarters after the end of a quarter's worth of data collection. UMAQL will integrate these data with data from FDEP analyses of total mercury in precipitation for subsequent project reporting to FDEP. The initial quarter of data collection for all Subtask 2 activities is defined to conclude on December 31, 2008, with subsequent quarters being the calendar quarters (e.g., March 31, June 30, September 30).

1.1.3 Subtask 3: Short-Term Intensive Deposition Monitoring

In order to support and supplement the long-term air quality monitoring and modeling, a number of atmospheric deposition "Supplemental" monitoring sites will be deployed surrounding the Supersites to evaluate the spatial patterns and variability in each region during selected months. These deposition measurement intensives will take place at near-field locations surrounding each of the four proposed Supersites: in the vicinities of Pensacola, Tampa, Jacksonville, and Fort Lauderdale. There will be one deposition intensive at each Supersite during the two-year duration of the mercury TMDL field project. Each of these deposition intensives will last one month in duration, for a total of four atmospheric deposition measurement intensives. The field intensives will be conducted by UMAQL staff in coordination with the on-going long-term atmospheric monitoring at the Supersites, as well as the long-term wet deposition monitoring at the Supersites and Satellite sites.

Two of the measurement intensives will take place during summer 2009 and two will take place during summer 2010. The primary purpose of the measurement intensives is to evaluate and characterize the spatial patterns and variability surrounding each Supersite, which will be information critical to the successful execution of the overall mercury TMDL atmospheric modeling component. The short-term intensive monitoring at a minimum of four Supplemental sites surrounding each of the Supersites will include collection and analysis for total mercury, major ions (sulfate, nitrate, nitrite, and chloride), and trace elements (Mg, Al, P, S, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Rb, Sr, Mo, Cd, La, Ce, Sm, Pb) in both wet and dry deposition. In addition, a subset of the wet deposition samples with appropriate levels of total Hg will be analyzed for Hg stable isotope ratios ($\delta^{202}\text{Hg}$, $\delta^{201}\text{Hg}$, $\delta^{200}\text{Hg}$, $\delta^{199}\text{Hg}$, $\Delta^{201}\text{Hg}$, $\Delta^{199}\text{Hg}$). The specific analytes, methodologies and laboratories to be used to carry-out the laboratory analysis of the constituents in deposition measures from the intensive periods at each site will match those used for the long-term measurements at the Supersites, as described for Subtasks 1 and 2 and listed in Table 1.1 and Table 1.2.

1.1.3.1 Roles and Responsibilities: Intensive Deposition Monitoring Data Management and Reporting Timelines

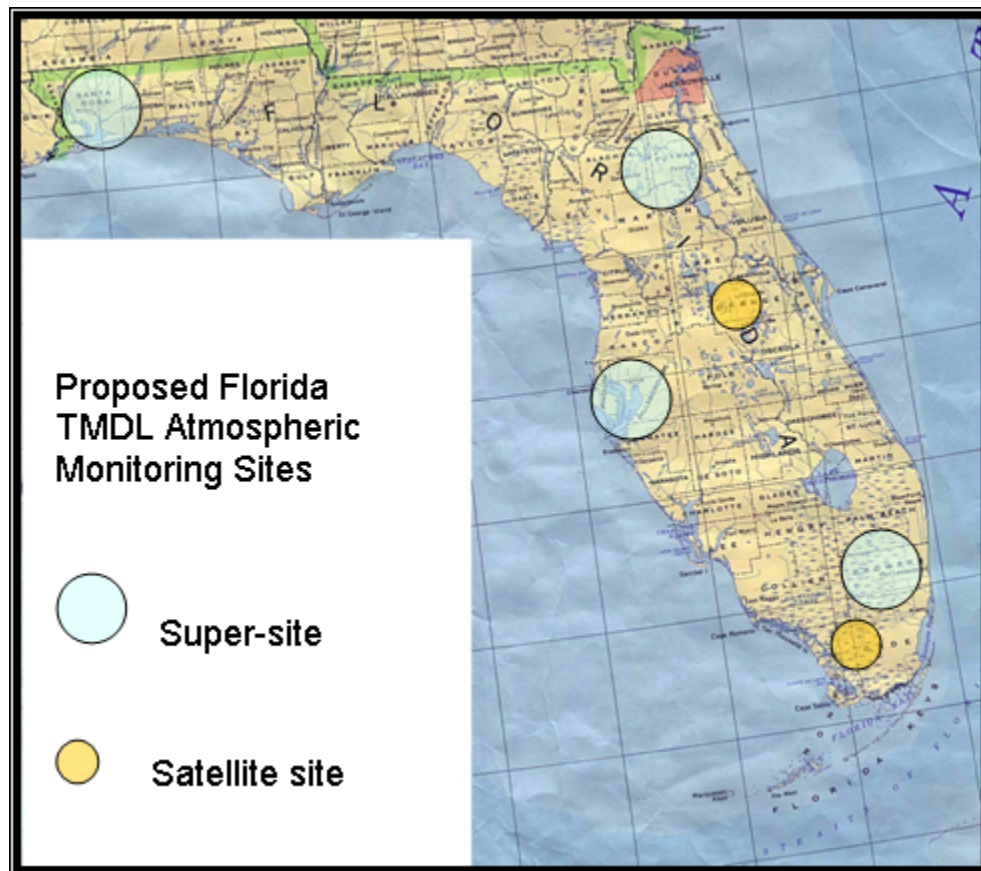
For Subtask 3, ARA will provide on-going field operation of the four Supersites, including the ASPS precipitation collection. UMAQL will provide for set-up and collection of all other samples described for Subtask 3, including daily wet deposition and dry deposition sample collection at each of the four Supplemental field sites and surrounding Supersites during each deposition measurement intensive period. For subsequent laboratory analyses related to Subtask 3, FDEP Central Laboratory will provide for analysis of total mercury in precipitation samples, and UMAQL will conduct the total Hg in dry deposition analysis, the trace element and major ion analysis for both wet deposition and dry deposition samples, as well as Hg isotope analysis of a subset of the precipitation samples with sufficient volume. Data from intensive monitoring for trace elements and major ions

in wet deposition and dry deposition, total Hg in dry deposition, and Hg isotopes in wet deposition will be reported by UMAQL to FDEP by March 31st, 2010 for samples collected during measurement intensives #1 and #2 (conducted in-field during summer 2009), and by March 31st, 2011 for samples collected during measurement intensives #3 and #4 (conducted in-field during summer 2010). The FDEP Central Laboratory will report data for total mercury determinations in precipitation from the intensive samples to the UMAQL by December 31st, 2009 for samples collected during measurement intensives #1 and #2 (conducted in-field during summer 2009), and by December 31st, 2010 for samples collected during measurement intensives #3 and #4 (conducted in-field during summer 2010).

1.2 Site Locations

Six general regions for the sampling sites have been identified and include the counties of Escambia, Duval, Orange, Hillsborough, Broward, and Miami-Dade. These site locations provide state-wide coverage for the atmospheric monitoring and are representative of major land use areas and Hg emission sources across the state. Figure 1.1 shows the locations of Supersites and Satellite (i.e., precipitation only) sites. The Escambia County Supersite is located on U.S. Navy property approximately 19 km NW of downtown Pensacola (lat. 30.5500, long. -87.3751). The Duval County Supersite is located on a farm managed by the City of Jacksonville-Parks and Recreation approximately 29 km WSW of downtown Jacksonville (lat. 30.2475, long. -81.9516). The Hillsborough County site is located on private property approximately 8 km SE of the City of Tampa (lat. 27.9137, long. -82.3749). The Broward County site is located at a county-operated air monitoring site (Site #8) located approximately 12 km SW of the City of Fort Lauderdale (lat. 26.0854, long. -80.2407).

Figure 1.1. Atmospheric Monitoring - Approximate Site Locations.



1.3 Atmospheric Sampling Objectives

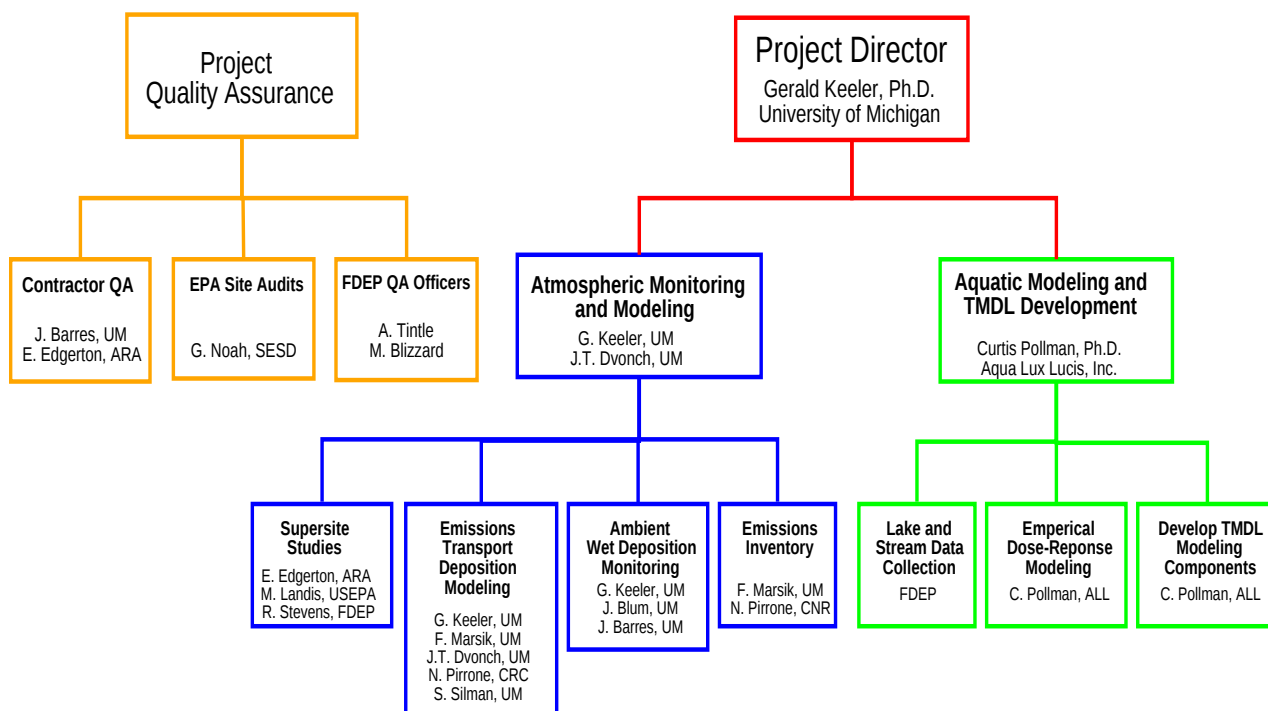
- This project task has the following goals:
- Establish enhanced monitoring and research field sites located in strategic areas throughout the state of Florida that are representative of the diverse land use patterns in Florida.
- Provide high quality long-term characterization of the atmospheric constituents required to perform state-wide Mercury TMDL calculations.
- Provide short term high resolution characterization of atmospheric processes also in support of the Mercury TMDL calculations.

The atmospheric sampling task will establish a network of monitoring sites in Florida. The network will include sites that are close to major emission sources across the state, sites downwind from these sources, and sites that are more distant from major anthropogenic sources.

1.4 Project Personnel

The management structure associated with this project is summarized in the Figure 1.2. A biographical sketch of the primary participants in the measurement aspects of this study are also provided below.

Figure 1.2. Project Management Structure.



Gerald J. Keeler, Ph.D. (Principal Investigator, UM) is an expert on atmospheric mercury and trace elements. He founded the UMAQL in 1990 and has since become an international leader in atmospheric sampling and characterization of toxic metals. He has participated on several state and federal review and advisory committees and is frequently requested to lead panel discussions and present plenary lectures at international conferences and workshops. Dr. Keeler has extensive experience on the sampling, analysis and modeling of atmospheric mercury in all its forms. Dr. Keeler will serve as PI for the project and will be responsible for all coordination with subcontractors and the Florida Department of Environmental Protection. He will be responsible for all atmospheric data preparation and reporting.

J. Timothy Dvonch, Ph.D. (Co-Investigator, UM) is an environmental health expert with extensive experience in measurements of atmospheric pollutants for human health and environmental exposure projects. Dr. Dvonch also has considerable experience in the development and evaluation of atmospheric Hg speciation methodologies. He has experience and publications dealing with receptor modeling methodologies and the source apportionment of airborne pollutants including Hg. Dr. Dvonch was a key participant in the South Florida Atmospheric Mercury Monitoring and Modeling Study and published one of the first research papers on characterization of the sources of mercury in wet deposition. He will take part in project management, data analysis and reporting.

Frank J. Marsik, Ph.D. (Co-Investigator, UM) is a meteorologist at the University of Michigan with extensive experience in atmospheric measurement campaigns. Dr. Marsik has considerable experience in the use of synoptic and micro-meteorological parameters for the characterization of the atmospheric transport and deposition of Hg (both wet and dry). These include modeling of these parameters to calculate meteorological air mass back-trajectories as well as the measurement and modeling of Hg dry deposition. Dr. Marsik also has experience in the first known use of NEXRAD radar data for evaluation of impacts of cloud chemistry and local source emissions on the wet deposition of Hg. He will be responsible for the atmospheric modeling tasks of the project and will also participate in the data analysis and report writing.

Joel D. Blum, Ph.D. (Co-Investigator, UM) is an expert in trace element and isotope geochemistry and biogeochemistry, with emphasis on heavy-metal pollutants in the environment. He has conducted extensive research on mercury in freshwater ecosystems, terrestrial ecosystems, wildfires, the arctic atmosphere, and in foodwebs. He has also directed investigations using trace elements and high precision measurements of Pb, Sr, Nd and Os isotopes to study heavy element mobility in soils, groundwater and atmospheric particles. In the past 8 years Dr. Blum pioneered development of very high precision mercury isotope ratio measurement and the application of mercury isotopes as tracers of atmospheric sources of mercury and as tracers of mercury redox transformations in the environment. He will be involved in trace element and mercury isotope measurement and interpretation, as well as data analysis and report writing.

James A. Barres, M.S. (AQL Lab Manager, UM) is responsible for the day-to-day management of all activities associated with the Laboratory. As such, he is responsible for insuring that laboratory personnel are properly trained for their assigned tasks and that there is strict adherence to UMAQL standard operating procedures (SOPs), which have been established to insure that QA goals are met. Mr. Barres has extensive experience in field measurement and laboratory management through his work with both the University of Michigan Air Quality Laboratory and the University of Michigan Center for Great Lakes and Aquatic Studies. His research has focused on the measurement of trace element concentrations in near surface waters in the Great Lakes region, with emphasis on the development of procedures and methods of collection, storage and analysis of trace elements. For this project, Mr. Barres will be responsible for directing the fabrication of the ASPS units and for installation, training and support of the units. He will be responsible for QA related activities associated with precipitation supply preparation, sample collection, transport, preservation, analysis and data processing.

Eric Edgerton, M.S. (President/Scientist, ARA) is an expert in the design, setup and operation of long-term atmospheric monitoring networks. His areas of expertise include atmospheric chemistry, measurement of trace atmospheric species (including Hg), development of continuous methods for atmospheric constituents, and geochemical cycles of sulfur, nitrogen and carbon. Mr. Edgerton received his B.A. in Atmospheric Chemistry from Cornell University (1974) and his M.S. in Environmental Engineering from the University of Florida (1981). Mr. Edgerton will be responsible for the direction, oversight and QA/QC of the continuous measurements at the 4 Supersites. This includes coordinating the site selection, set-up and oversight of the continuous measurements database.

Matthew S. Landis, PhD: (Research Sci., EPA ORD-NERL) As the EPA-NERL atmospheric mercury research principal investigator, Dr. Landis has the responsibility to identify the gaps in EPA's understanding of atmospheric mercury transport, transformation and deposition. His expertise and current research activities include a dynamometer study to quantify mercury emissions from mobile vehicles, a study to investigate the oxidation of elemental mercury (Hg^0) to divalent reactive gaseous mercury in the free troposphere, a study to evaluate the impact of coal combustion on mercury deposition in the Ohio River Basin, a study to investigate the benefit of continuous ambient mercury speciation data to successful application of source apportionment models, development of an automated surrogate surface mercury dry deposition sampler, and an effort to develop HR-ICPMS analysis methods for the quantification of trace elements in highly time resolved (~30 minutes) and low mass PM_{2.5} samples. For this study, Dr. Landis will be responsible for deployment and technical support for his automated particulate collector, speciated mercury technical support, and oversight of the trace element analysis on the sequential particulate filters.

Curriculum vitae are found in the Appendix.

1.5 Personnel Training

Training of laboratory analysts and field operators will be provided as appropriate. The UMAQL, ARA, FDEP and EPA have extensive combined experience in the laboratory and field procedures required for this project. Operators for the monitoring sites will receive specific instruction on the operation and maintenance of all instrumentation and in the proper handling of samples using clean techniques. Laboratory analyses will be performed by experienced personnel. Training will be provided as required to ensure high quality results.

1.6 Quality Objectives and Criteria

The measurements to be made during this research program can be divided into three major categories: continuous chemical measurements, continuous meteorological measurements and discrete precipitation, particulate and gas measurements. The Quality Assurance Objectives for each category will be discussed separately.

1.6.1 Continuous Chemical Measurements

1.6.1.1 Mercury in Air

The integrated Tekran Instruments Corporation (Knoxville, TN) ambient mercury speciation system (Models 2537A/1130/1135) will be used to measure ambient Hg^0 , RGM, and $\text{Hg}(\text{p})$ continuously throughout the course of the project (Landis et al. 2002). Target accuracy and detection limits are provided in Table 1.3. Internal, automated zeros and calibrations (i.e., span checks) will be performed every 3 days using an internal Hg^0 permeation source (i.e., located within the Model 2537A analyzer). Manual standard addition injections will be performed each month and manual calibrations of the model 2537A internal permeation tube will be performed every six (6) months. Manual standard addition and calibrations will be performed by making multiple injections of Hg^0 through the injection port on the front of the 2537A, using a Tekran Model 2505 primary calibration system and a Hamilton Company (Reno, NV) NIST traceable digital micro-syringe. The permeation rate for the internal permeation source is set in the following manner. First, multiple calibrations of the instrument are performed using the internal permeation source. Second, multiple injections are performed using the Tekran 2505 primary standard. The results of this procedure are used to calculate and enter a new permeation rate into the Tekran setup parameters. Refer to the Appendix (SpecHG-SOP) for the details regarding the calibration procedures and maintenance of the Model 2537A.

Table 1.3 Instrumentation, Accuracy and Detection Limits for Hg in Air

Variable	Instrument	Accuracy	Detection Limit (pg/m3)
Hg^0	Tekran 2537A	$\pm 5\%$	50
RGM	Tekran 2537A/1130	$\pm 15\%$	2
$\text{Hg}(\text{p})$	Tekran 2537A/1135	$\pm 15\%$	2

1.6.1.2 Trace Gases in Air

Trace gases will be measured continuously at each Supersite at a reference height of 8-10 m above ground level by placing inlets, and the NO_y converter, in a weatherproof housing atop a 10-m tilt-down tower. Data will be acquired as 1-minute averages, then aggregated and reported as 5-minute and 60-minute averages. Table 1.4 provides information on accuracy and detection limit targets for the trace gas measurements. See AMBGAS-SOP in the Appendices for more details.

Ozone analyzers will be subjected to automated zero, span and precision checks each night using a Thermo-Environmental Model 49PS primary standard. Manual calibrations with the Model 49PS will be performed once a month. The remaining trace gases will be calibrated automatically every third day using tank standards (Scott-Marrin, Riverside, CA) diluted with zero air. Automated zeros will be performed every day for NO and NO_y and every 120 minutes for CO and SO_2 in order to track baseline stability. Manual calibrations of each trace gas analyzer will be performed monthly.

Table 1.4 Instrumentation, Accuracy and Detection Limits for Trace Gases in Air

Variable	Instrument	Accuracy	Detection Limit (ppb)
Ozone (O ₃)	TE 49c	±5%	1
Carbon Monoxide (CO)	TE 48C	±10%	20
Sulfur Dioxide (SO ₂)	TE 43C	±10%	0.1
Nitric Oxide (NO)	TE 42c	±10%	0.05
Reactive Odd Nitrogen (NO _y)	TE 42c	±15%	0.1

1.6.1.3 Fine Particulate Anions, Acidic Gases, EC/OC and Fine Particulate Mass in Air

The URG-9000C Ambient Ion Monitor (AIM) will be used to obtain semi-continuous (i.e. hourly) measurements of fine particulate sulfate, nitrate, nitrite, phosphate and chloride, and gaseous nitric acid, nitrous acid, sulfur dioxide and hydrochloric acid. Other anions and gases can be measured with the AIM (e.g., fluoride and bromide), but are virtually always below the analytical detection limit. The AIM samples air at a flow rate of 3.0 L/min through a size segregating PM_{2.5} impactor inlet and then into a parallel plate membrane diffusion denuder which scrubs the acidic gases in a dilute solution of hydrogen peroxide. Particulate anions are then nucleated (grown) at high RH and collected in deionized water via cyclonic separation. Gases and particles are collected in this manner for 60 minutes. After the collection period, the solutions containing particulate anions and acidic gases are injected into an ion chromatograph and analyzed for target ions. Procedures for determination of precision, accuracy and blank values are still under development and will be appended to this document on or before June 30, 2009.

Quarterly calibrations are done on the AIM system and on the associated Dionex Model ICS-2000 ion chromatograph (IC). System calibrations set the parameters of ambient temperature, orifice temperature, orifice delta pressure, ambient orifice delta pressure, ambient pressure and inlet flow. For the IC calibration, aqueous multi-anion standards, plus an independent, mid-range calibration verification solution (CVS), are prepared by the ARA laboratory and distributed to the sites each quarter. The calibration standards are injected into the instrument in sequence to generate a calibration curve. The CVS is then analyzed and the new calibration curve is accepted if ion recoveries from the CVS are within +/- 10 percent. Immediately prior to the next calibration, the CVS is again analyzed to determine detector drift. In addition, monthly standard addition injections will be performed. The full operation manual may be found in the Appendices (AIM-MAN).

Fine particulate mass will be measured continuously with a Thermo-Environmental (Franklin, MA) Model 5030 synchronized hybrid ambient real-time particulate (SHARP) monitor. The model 5030 uses nephelometry and beta attenuation to provide continuous (5-minute and 60-minute) PM_{2.5} mass data. Ambient air is drawn through a size segregating cyclone inlet at 16.67 L/min, then heated, if necessary, to reduce sample RH to ≤40%. Sample then travels through a nephelometer section which measures light scattering at 880 nanometers. Sample air then passes through a section of filter tape and PM_{2.5} mass deposited on the tape is measured via beta attenuation. Beta attenuation data are used to continuously mass calibrate the output of the

nephelometer. Table 1.5 provides accuracy and detection limit information for continuous PM_{2.5} and acid gas measurements. The full operation manual may be found in the Appendices (SHARP-MAN).

Fine particulate organic and elemental carbon will be determined with a Sunset Laboratory Inc. (Tigard, OR) Semi-Continuous Carbon Aerosol Analyzer. Ambient air is drawn through a size segregating cyclone inlet into the system and collected on a quartz filter mounted in the quartz furnace. After collection, carbon on the filter is thermally desorbed as CO₂ and quantified by non-dispersive infrared (NDIR). The NDIR is calibrated with external sucrose and methane standards (Appendix OCEC-SOP).

Table 1.5 Instrumentation and Accuracy Specifications for AIM and SHARP Measurements

Variable	Instrument	Accuracy	Detection Limit (µg/m ³)
SO ₄ ²⁻	AIM	±10%	0.1
NO ₃ ⁻	AIM	±10%	0.1
NO ₂ ⁻	AIM	±10%	0.1
Cl ⁻	AIM	±10%	0.05
PO ₄ ³⁻	AIM	±10%	0.2
SO ₂	AIM	±20%	0.2
HNO ₃	AIM	±20%	0.2
HNO ₂	AIM	±20%	0.2
HCl	AIM	±20%	0.1
PM _{2.5} Mass	SHARP	±5% ^a	0.5

Note: accuracy based on comparison with 24-hour FRM samples.

1.6.2 Continuous Meteorological Measurements

For this study, meteorological measurements are made to characterize the mean meteorological conditions at the site during each measurement period. The measurements obtained at the site will not require stringent precision and accuracy criteria, given that these measurements will only be used to generate time-averaged (5-minute and 60-minute) values of the quantities measured. The measurements to be made for this purpose are presented in Table 1.6, along with the manufacturer's accuracy specifications. Individual documents in the Appendices provide more detail. See Met4A-MAN, LWS-MAN, Rainfall-MAN, Sonic-MAN, and SRsensor-MAN.

Table 1.6 Instrumentation and Accuracy Specifications for Meteorological Measurements.

Variable	Instrument	Accuracy
Temperature (8 m)	ParoScientific Met4A	±0.25 deg C
Relative Humidity (8 m)	ParoScientific Met4A	±2.0 %
Barometric Pressure (8 m)	ParoScientific Met4A	±0.1 mbar
Wind Direction (10 m)	R.M. Young Model 81000 Sonic Anemometer	±3 deg
Wind Speed (10 m)	R.M. Young Model 81000 Sonic Anemometer	±0.1 m/sec
Global Radiation (2 m)	Licor LI200X Pyranometer	+/- 5% of reading
Incident Precipitation (1 m)	ETI Model NOAH-IV rain gauge	±0.02"
Surface Wetness (0.2 m)	CSI Sensor 237	---

Note: Reference height, above ground level, in parentheses

1.6.3 Discrete Measurements

1.6.3.1 Total Mercury in Precipitation

During the course of this project, precipitation samples will be collected to determine total mercury concentrations and to calculate wet deposition. The determination of the mercury content in collected samples will be performed using CVAFS at FDEP. Project QAO goals associated with the wet mercury analysis are summarized in Table 1.7. The standard reference material that will be used for verifying the accuracy of mercury analysis in water samples by CVAFS is NIST 1641d. A summary of the analytical methods to be used is presented in Section 2.2 of this document.

Table 1.7 Data Quality Objectives for Total Mercury in Precipitation.

QA Criteria	QA Operation/Type	Frequency	Acceptance Criteria	Control Action	Reporting Units
Precision	Analytical Replication*	5%	rsd < 20%	Re-analyze/ flag	Percentage
Accuracy	SRM Analysis NIST 1641d	Daily	± 15% of Certif. Concentration	Re-analyze/ Flag	Percentage
Blanks	Procedural	Daily	<MDL	Re-analyze/ flag	Mass/vol
Calibration	Standard Curve	Daily	r ² >0.995	Repeat until criteria met	---

rsd = relative standard deviation (standard deviation/mean x 100)

MDL = method detection limit

*: Matrix spike duplicates are analyzed from the same sample. If a replicate value is below the practical quantitation limit, precision is reported from the relative percent difference of the matrix spikes.

Method Detection Limits (MDL) will be determined for mercury in precipitation using EPA Method 200.1. This entails measuring seven replicate analyses from a sample with a low concentration of mercury from each medium and calculating the MDL as follows:

$$\text{MDL} = (t) \times (S)$$

where t = Student's t value for a 99 percent confidence level and a standard deviation estimate with n-1 degrees of freedom (t = 3.14 for seven replicate analyses), and S = standard deviation of the replicate analyses.

1.6.3.2 Trace Metals in Air and Precipitation

During the course of this project, samples will be collected to determine the levels of a suite of trace metals in ambient aerosols and precipitation. Daily precipitation samples will be collected with the ASPS and daily or weekly particulate samples will be collected with the sequential Dichotomous sampler and day/night denuder/filter pack sampler (ADS). The determination of the elemental content in precipitation and ADS filter samples will be performed using HR-ICPMS at UMAQL. Dichotomous sampler filters will be analyzed by ED-XRF or HR-ICPMS at EPA ORD-NERL. Details of the HR-ICPMS analysis for both precipitation and filters are given in Appendix TEpcp-SOP. If ED-XRF becomes the method of choice for the dichotomous sampler filters, the appropriate SOP will be appended to this QAPP.

Method Detection Limits obtained with the UM Thermo Finnigan Element2 HR-ICPMS running precipitation from Steubenville, Ohio and filter extractions from Detroit, Michigan are shown in Table 1.8. MDLs specific to the current project (for both precipitation by UM and filter extraction analysis by EPA) will be determined when the trace element analysis begins and will be appended to this QAPP on or before June 30, 2009. The method of calculating the MDLs is given later in this section. MDLs reflect instrument limitations from the sample matrix, preparation and analysis.

Table 1.8 Trace Element Method Detection Limits (MDLs).

Element	MDL (ppb)	
	Precip	Filt Extr
Rb85	0.0029	0.0012
Sr88	0.0113	0.0112
Mo95	0.0304	0.0069
Cd111	0.0251	0.0067
In115	0.0015	
Sn118	0.0070	
Sb123	0.0639	0.0062
La139	0.0009	0.0042
Ce140	0.0014	0.0056
Sm147	0.0002	0.0034
Pb208	0.0320	0.0379
Mg24	0.4900	0.1946
Al27	3.4900	0.1876
P31	0.1380	0.5646
S32	6.8000	6.5289
Ti47	0.0834	0.0337
V51	0.0045	0.0094
Cr52	0.0089	0.0101
Mn55	0.0700	0.1766
Fe57	0.9690	1.0474
Co59	0.0013	0.0049
Ni60	0.0810	0.0356
Cu63	1.4800	0.0825
Zn66	1.0600	0.2173
K39	0.9000	0.5494
As75	0.0180	0.0139
Se77	0.0350	

Project QA/QC goals associated with the elemental analysis are summarized in Table 1.9. Precision and accuracy goals were set to be suitable for the modeling while allowing for single pass

analysis even while analyzing a large suite of elements. A summary of the analytical methods to be used is presented in Section 2.2 of this document.

Table 1.9 Data Quality Objectives For Trace Elements in Air and Precipitation.

QA Criteria	QA Operation/Type	Frequency	Acceptance Criteria	Control Action	Reporting Units
Precision	Analytical Replication	15%	rsd < 20%	Re-analyze/Flag	Percentage
Accuracy	Standard Reference Materials	Daily	+/- 25%	Recalibrate/Flag	Percentage
Blanks	Procedural	10%	<MDL	Re-analyze/Flag	Mass/vol
	Field	10%	<10% of sample values	Flag	Mass/vol
Calibration	Standard Curve	Daily	$r^2 > 0.995$	Flag	---

rsd = relative standard deviation (standard deviation/mean x 100)

MDL = method detection limit

The Method Detection Limits (MDL) will be determined separately for metals in ambient aerosol and precipitation samples using EPA method 200.1. This entails measuring seven replicate analyses from a sample with low analyte concentrations and calculating the MDL as follows:

$$MDL = (t) \times (S)$$

where t = Student's t value for a 99 percent confidence level and a standard deviation estimate with n-1 degrees of freedom (t = 3.14 for seven replicate analyses), and S = standard deviation of the replicate analyses.

1.6.3.3 Stable Mercury Isotopes in Precipitation

During the course of this project, samples will be collected to determine the stable isotopic composition of mercury in precipitation. The determination of the stable isotopic composition of mercury in collected samples will be performed using MC-ICPMS following mercury concentration measurement by CVAFS. High precision mercury isotope ratios are measured relative to the NIST Hg standard reference material (SRM-3133), which is concentration-matched to the samples and analyzed before and after each sample (Blum and Bergquist, 2007). Samples are pre-concentrated, run at a concentration of 2 ng/g Hg, and run in duplicate or triplicate when sufficient sample is available. External standards are analyzed at least every eight samples for QA/QC and isotopic compositions are reported as the per mil (‰, or parts per thousand) deviation in the isotope ratios ($^{202}\text{Hg}/^{198}\text{Hg}$, $^{201}\text{Hg}/^{198}\text{Hg}$, $^{200}\text{Hg}/^{198}\text{Hg}$, $^{199}\text{Hg}/^{198}\text{Hg}$) from the SRM-3133. Project QA/QC goals associated with the mercury isotope analyses are $\delta^{202}\text{Hg}/^{198}\text{Hg} \pm 0.10\text{‰}$ for replication of the external standard and for replication of repeat analyses of samples. A summary of the analytical methods to be used is presented in Section 2.0 of this document.

1.6.3.4 Discrete Filter Measurements of PM_{2.5} and PM₁₀ Mass

Twenty-four hour ambient particulate sample will be collected on Teflon filters using an R&P Model 2025D Sequential Dichotomous air sampler. All filters will be weighed in order to determine PM_{2.5} (fine) and PM_{2.5-10} (coarse) mass. See Appendix PMmass-SOP. As described above, selected filters will also be analyzed for trace elements via ED-XRF or HR-ICPMS. Data quality objectives for filter-based measurements of PM_{2.5} and PM_{2.5-10} are shown in Table 1.10. Acceptable weighing room temperature and relative humidity ranges ensure consistency for pre- and post weights which may be weeks apart. Collection completeness is the percentage of filters that yield mass results after losses due to filter damage or loss, balance problems, etc.

Flow checks, leak checks and time checks in the field will be performed every other week (see Table 1.10b). Flow checks will employ an inlet adapter provided by R&P and a NIST traceable BIOS Defender primary flow standard. Flow controllers will be recalibrated if they fall outside tolerances. Time checks will compare the time displayed by the Model 2025D with an atomic clock. Time will be adjusted on the Model 2025D if the display differs from the atomic clock by more than 2 minutes. Data from the Model 2025D will be downloaded, via connection to the RS232 port, and ingested into the project database each day. See Appendix PMdichot-MAN.

Table 1.10a Laboratory Data Quality Objectives –PM_{2.5}/PM₁₀ (Dichotomous Sampler)

Requirement	Frequency	Acceptance Criteria	Action / Information
Reporting Units	All data	µg	
Filters Visual defects Collection efficiency Conditioning Equilibration time Temperature range Humidity range	All filters Purchase spec All filters “ “	Defect free >99 % ≥24 hours 20-23±2° C on a 24-hr avg 30-40 ±5 % RH on a 24-hr avg	Discard defective filters Reject shipment Repeat equilibration Record T° & RH continuously Do not work outside range
Equipment Analytical balance Mass reference stds	Purchase spec “	0.1 µg sensitivity NIST traceable	
Balance calibration Instrument Reference weights	Annually Annually	Manufacturer Specs Manufacturer Specs	Manufac Recommendation Manufac Recommendation
QC checks Balance zero Laboratory Blank Tare Weight Laboratory Duplication Balance calib check - (100 mg & 200 mg)	Every filter 1/Batch* 1/Batch* Every Batch**	0.0000 ± 15µg ± 15µg ± 3µg	Rezero Reweigh or Flag samples Reweigh or Flag samples Reweigh or Flag samples

* Batch-maximum of 15 samples

** Frequency of verification is before and after every batch

Table 1.10b Field Data Quality Objectives –PM_{2.5}/PM₁₀ (Dichotomous Sampler)

Requirement	Frequency	Acceptance Criteria	Action / Information
Equipment Sampler Flow rate transfer std	Purchase spec “	USEPA method ± 2% accuracy	
Collection Completeness	Quarterly	75%	Report < 75%
Sampler calibration Flow control device Flow rate transfer std	Monthly or on Flow check failure Annually	± 5% ± 2%	Manufacturer recertification
QC checks Field Blanks Field flow check Field Leak Check Time Check	Monthly Fortnightly Fortnightly Fortnightly	± 5% <30 mm Hg +/- 2 minutes	Report Data Recalibrate Sampler Troubleshoot/repair leak Reset Time

2.0 SAMPLING AND MEASUREMENTS

Continuous measurements (e.g. meteorology) generally do not involve exchange of sample media between the field and a remote laboratory or preparation center. However, a discussion of sample preparation is appropriate for the Tekran Models 1130 and 1135, due to their use of annular denuders and particulate traps, respectively, to quantify RGM and Hg(p). Sampling procedures for filter-based measurements and precipitation measurements are discussed, as well.

2.1 Sampling Procedures

2.1.1 Preparation

Quartz annular denuders used for sampling RGM will be cleaned and prepared according to the procedures outlined in Appendix RGMprep-PRO. Quartz particulate traps are prepared by the manufacturer. Prior to sampling they will be checked and conditioned. This involves checking the amount of quartz wool that is packed in the trap (should not be too firm) and baking the trap at 800°C for approximately 30 minutes. Traps are then sealed to prevent contamination and shipped directly to field sites.

All filters used for sampling will be prepared and handled according to the procedures outlined in Appendix PMmass-SOP. Site operators will inform the FDEP PM_{2.5} Lab of their specific filter requirements at least two weeks in advance to ensure adequate time for filter preparation and shipping by the lab.

Preparation of precipitation sampling media will follow the procedures outlined in Appendix HGpcp-SOP, section 2. All fluorinated polyethylene, Teflon®, polypropylene and glass collection bottles and apparatus, reagent bottles and analytical supplies that come into contact with the samples will be cleaned according to the procedures outlined in Appendix ACtable-SOP. Prior to use, sample bottles are labeled, sealed and weighed, then triple-bagged for transport into the field. All other items are dried in a HEPA filtered air-drying box and triple-bagged in polyethylene zip-lock bags for storage and transport.

2.1.2 Sample Identification

Each sample deployed and collected will be identified by a unique sample ID. Sample IDs will indicate the type of sample (e.g., Day or Night denuder), the year of collection, site of collection and sequence number. Sequence number will be related to collection date in electronic or paper field logs. Sample IDs for the day/night denuder filter pack will be prefixed with the letters DSC, DCA and DFP for daytime sodium carbonate denuder, citric acid denuder and filter pack, respectively. Corresponding nighttime samples will be prefixed with NSC, NCA and NFP. For example, DCA08-7*0001 refers to the first daytime citric acid denuder collected at OLF (site 7) in 2008.

Fine and coarse sequential Dichot filters will use similar nomenclature for sample IDs and will be prefixed with the letters DFRMF and DFRMC, respectively.

Sample IDs for bottles used to collect precipitation samples in the ASPS are slightly different. The base tape on the bottle is labeled with the site code, the date on, the rack position, and the funnel ID number during setup. When a bottle contains a sample, the operator applies a 2nd label preprinted with the site code, a sequential sample number, a 'PCP' for precipitation, and either a 'HG' or 'MET' tag. The ASPS records the date and time of

the first tip of the rain gauge. The date is used as the sample date and will be hand written on the preprinted label when the site operator collects the sample, as well as recorded in permanent records.

An example of the labeling for the 22nd Pensacola sample collected since the beginning of the project is given below:

Base tape: **OLF 12/23/08**  **647** (hand-written site code, on date, position in the rack, and funnel ID code with a Sharpie® when the bottle rack is loaded on 12/23/08)

Preprinted label: **OLF-22-PCP-HG Precip Date: 12/27/08** (preprinted label applied to the base tape when the sample is removed from the collector 1 or 2 weeks later, date of rain hand-written with a Sharpie® on the preprinted label)

As noted, all samples deployed will be given a unique sample ID. IDs are written on sample tracking forms and transferred to spread sheets for future data processing. In the event that a sample filter/container/bottle is contaminated during the deployment (e.g., filter/container/bottle is dropped on the ground), that sample will be marked as voided on the field and tracking logs.

2.1.3 Sample Collection

2.1.3.1 Continuous Measurements

2.1.3.1.1 SPECIATED MERCURY

In order to effectively monitor ambient levels of Hg^0 , RGM, and $\text{Hg}(\text{p})$ in the atmosphere, a Mercury Speciation System manufactured by Tekran Instruments Corporation (Knoxville, TN) is used. The system includes a Mercury Vapor Analyzer Model 2537A, a Mercury Speciation Unit (Denuder Unit) and Pump Module Model 1130, and a Mercury Particulate Unit Model 1135 (The Tekran 1130/1135 speciation units are programmed to collect one-hour composite RGM and $\text{Hg}(\text{p})$ samples at 10 L/min volumetric. The Tekran 2537A will continuously sample at 1 L/min and the 1130 pump module will pump 9 L/min during the denuder/quartz filter sampling period. During the denuder/quartz filter sampling period, RGM is collected onto a KCl-coated quartz annular denuder and $\text{Hg}(\text{p})$ is collected onto the quartz filter. During this period Hg^0 is passed through the system and quantified by the 2537A every 5 minutes (12 five-minute elemental Hg^0 determinations for each one-hour denuder/quartz filter sampling period). Following the one-hour denuder/quartz filter sampling period, the 1130 pump module will flush the system with zero air (15 minutes). The Pyrolyzer will be preheated to 800°C (5 minutes), the quartz filter will then be heated to 800°C (15 minutes), and the denuder will be heated to 500°C (15 minutes). During the heating cycle, the $\text{Hg}(\text{p})$ collected on the quartz filter and the RGM collected on the denuder are thermally decomposed to Hg^0 and purged into the 2537A. After the heating cycle, the system will be cooled and purged with zero air for another 10 minutes before resuming another one-hour collection period.

2.1.3.1.2 AMBIENT IONS

Ambient air is drawn into the AIM at 3 L/min through a PM_{2.5} size segregating cyclone inlet to remove the coarse particulate matter. Sample air is then drawn through a parallel plate membrane liquid diffusion denuder to remove acidic and basic gases that would otherwise create a positive particulate phase artifact. Steam is injected to nucleate aerosols which are collected in an inertial separator cyclone. Denuder and cyclone aqueous samples are collected into 5 mL syringes and subsequently injected into the IC. After the particulate analysis is complete the gas phase ions are also analyzed.

2.1.3.1.3 METEOROLOGICAL MEASUREMENTS

The measurement procedures associated with each meteorological instrument will follow those contained in the USEPA Quality Assurance Handbook for Air Pollution Measurement Systems, Volume IV: Meteorological Measurements (EPA-454/B-08-002, March 2008). See Appendices Met4A-MAN, LWS-MAN, Rainfall-MAN, Sonic-MAN, and SRsensor-MAN.

2.1.3.2 Discrete Measurements

2.1.3.2.1 WET DEPOSITION MEASUREMENTS

The sampling method for mercury, trace elements and major ions in precipitation will employ an ASPS to obtain precipitation for analysis. Collection of all precipitation samples will follow the procedures outlined in Appendices ASPS-SOP and HGpcp-SOP. The ASPS uses the MIC-B funnel cover system to facilitate wet-only collection of precipitation and excludes dry deposited material from the samples during non-precipitation periods. It has two specially designed precipitation sensors that allow for complete collection of precipitation events even during light rain. When precipitation falls on the sensor grid, a relay is energized and the motor switches on to move the lid from the collection funnels to the lid support. The electrically heated sensor grid dries when the precipitation stops and a printed circuit controller de-energizes the relay, which switches the motor on again to move the lid back over the collection funnel.

The original MIC-B precipitation collection funnel has been replaced with the University of Michigan custom-made insert that supports four discrete precipitation collection trains. This design allows for separate collection of precipitation for mercury and trace element/ion analysis (Landis and Keeler, 1997). For this study 2 sample trains will be employed, one for mercury and one for trace elements. The major ions sample will be poured off of the trace element samples that have sufficient volume to be split. Separation of sample types makes it possible to provide the best storage and handling for each type. Glass funnels and fluorinated polyethylene sample bottles are the accepted standard for mercury samples. Polypropylene funnels and bottles conform to the current scientific standards for trace element and major ion samples. All acid cleaned parts of the trace element sample train will be subjected to a hot deionized water (MQ) soak to remove hydrochloric and nitric acid residuals. This process has been shown to be effective at removing potential chloride and nitrate artifacts from the major ions subsample.

The ASPS is capable of obtaining eight precipitation samples without operator intervention. The cabinet of the collector is refrigerated so that the samples can be kept from overheating between bottle changes. A microprocessor-controlled system advances collection to a new bottle after each sample and records pertinent meteorological data (Appendix ASPS-SOP).

One of every 10 sample bottles deployed to the sites will be designated as a Field Blank. Preprinted sample labels will be organized with 9 precipitation event ID codes (e.g., OLF-9-**PCP**-HG) and a Field Blank (e.g., OLF-10-**FB**-HG). After the site operator labels 9 precipitation samples, he/she will take one of the empty bottles from the rack and apply the 10th label, designating that bottle as a field blank. Throughout the project collection period, all precipitation ID numbers evenly divisible by 10 (i.e., 10, 20, 30, 40, ...) will be a field blanks.

In the laboratory, deionized water (MQ) will be added to the bottles. They will be processed and analyzed as samples and the analyte mass(es) in the bottle determined.

2.1.3.2.2 SEQUENTIAL PARTICULATE MEASUREMENTS

Both coarse and fine particulate samples will be collected on Teflon® filters using a Dichotomous Partisol®-Plus Model 2025 Sequential Air Sampler (Appendix PMdichot-MAN). The Model 2025 splits a PM-10 sample stream into its fine (PM_{2.5}) and coarse (particles between 2.5 and 10 micron MMAD) fractions using an U.S. EPA-designed virtual impactor for the additional 2.5 micron cutpoint. The unit uses an R&P PM10 inlet operating at 16.7 L/min to make the initial particle size cutoff at a 10 micron MMAD. The virtual impactor or “dichotomous splitter,” follows the inlet and two separate flow controllers maintain the fine particle stream at 15.0 L/min and the coarse particle stream at 1.67 L/min. The system contains two supply and two storage magazines, each having a capacity of up to 16 filter cassettes, as well as a filter exchange mechanism that replaces two filter cassettes at the same time. For this study, samplers will collect samples using Teflon® filters (for mass determination and trace metals analysis).

2.1.4 Sample Handling

There is no sample handling in the case of the collection devices (annular quartz denuders and quartz particulate traps) used to sample RGM and Hg(p). Therefore, a discussion of sample handling is not relevant. However, clean practices are maintained during all maintenance operations that require opening the sample path.

All particulate filters and samples will be handled by FDEP Laboratories and ARA personnel according to Appendix PMmass-SOP. Normally, site operators will receive two magazines from the FDEP PM_{2.5} Lab every week, each containing the requested number of unexposed pre-weighed filters, accompanied by a filter custody log. The filter custody log will be signed and dated with the time of receipt and returned with the next shipment of exposed filters to the lab. A copy of the signed filter custody log will be retained with site records. Site operators will use information from the filter custody log sheet to generate an individual sample ID for each filter in the sample record database that will include the specific sample run date for each filter. All filters in one magazine will be assigned as DFRMF (Fine) samples and all filters in the second magazine will be assigned as DFRMC (Coarse) samples. Magazines will be stored in a secure, dry, controlled environment and will remain capped at all times inside the soft cooler pack until they are deployed. Filters will be deployed for sampling in the order received from the FDEP PM_{2.5} Lab and in accordance with the sample run dates shown in the sample record database. Unexposed filters that do not sample before the filter expiration date shown

on the filter custody log sheet from the lab will be marked as void in the sample record database and in the field filter log.

Site operators will wear clean particle-free gloves at all times when handling filter magazines and will take every precaution to prevent contamination. Under no circumstances will there be any contact with the active surface of the filter (i.e., inside the cassette retaining ring). Should that occur or in the event a filter is otherwise contaminated during deployment (e.g., filter dropped), that sample will be marked as void in the sample record database and in the field filter log.

Precipitation samples contain low levels of trace metals and therefore must be processed with care to avoid contamination. When handling precipitation samples (following procedures outlined in Appendix HGpcp-SOP), operators wear particle-free gloves and position themselves downwind of samples at all times. After collection, samples are triple-bagged in polyethylene bags and transported to the lab as soon as possible for analysis at the designated facility, FDEP for total mercury samples and UMAQL for trace element/ion samples. Upon arrival at the laboratory, all samples processing and handling will take place inside the Class 1000 clean laboratory. A subset of the precipitation samples analyzed for total mercury will be selected, by UMGS and UMAQL, for subsequent mercury isotope analysis. Upon receipt at FDEP and after they have been analyzed for total mercury, these samples will be maintained by FDEP in the Class 1000 clean laboratory at ambient temperature until they are shipped from the FDEP laboratory to UMGS. The mercury isotope samples subsequently will be kept refrigerated by UMGS except during shipping.

2.1.5 Sample Preservation in the Field

All particulate samples on Teflon® filters will be preserved according to the procedures in Appendix PMmass-SOP. On each prescribed filter change out day, site operators will remove the DFRMF and DFRMC magazines and store them in a refrigerator or freezer at a controlled temperature below $\leq 4^{\circ}\text{C}$, along with a resettable min/max thermometer. The time and date the filters are placed in the refrigerator or freezer will be recorded in the field filter log.

All mercury and trace metal/ion precipitation samples collected will be placed in individual, uniquely labeled acid-cleaned containers (fluorinated polyethylene or polypropylene bottles, respectively). The cabinet of the ASPS collector is refrigerated so that the samples can be kept stable between bottle changes. Mercury sample bottles will be pre-charged with 20mL of dilute ultra-pure hydrochloric acid to stabilize the sample preventing loss of the mercury. When eight precipitation events have taken place or 14 days have passed (whichever happens first) the samples will be transported to the analytical laboratory. The sample containers will be triple-bagged using new, polyethylene zip-seal bags. Once at the laboratory facilities, both mercury and trace element/ion samples will be immediately refrigerated. The major ion aliquot will be poured off of the trace element sample and will be refrigerated until analysis.

2.1.6 Sample Transportation

Filters containing particulate matter will be transported to FDEP according to the procedures outlined in Appendix PMmass-SOP. Site operators will ship exposed filters back to the lab in the same coolers in which they were received, packed with “blue ice” to maintain filters below ambient temperature. Where available, site operators will ship via FDEP courier service. Where this service is not available, site operators will ship exposed filters via a commercial carrier providing 2-day delivery service. When a commercial carrier is used, filters will be shipped to the lab on either a Monday or Tuesday to ensure filters are not held over a weekend in the event of a

delivery exception. Shipping via overnight delivery may sometimes be required during holidays. When preparing filters for shipping, field operators will complete the field filter log with the applicable run/storage data and update the sample record database. The field filter log will be signed and dated with the time the filters are relinquished. The completed and signed field filter log will accompany the filter shipment, and a copy will be retained with site records.

Precipitation samples will be prepared for shipment according to Appendices HGpcp-SOP and TEpcp-SOP, and are transported using commercial, "next-day or second-day" transportation services. At this juncture, the major ions samples are still part of the trace element sample. Experience has shown that the transport period without refrigeration does not compromise sample integrity. Mercury samples will be shipped to FDEP and trace element/ion samples to UMAQL.

All samples will be shipped with their respective sample tracking forms, which will be used upon receipt at the designated analytical laboratory for sample validation and tracking during the analytical process.

2.1.7 Sample Receipt and Storage at Laboratory

Samples shipped from the field sites to the UMAQL, ARA, FDEP or EPA will be received by the laboratory's manager. Upon receipt of the shipped samples, all sample tracking logs will be checked against the samples received. Following this initial sample verification, all samples will be refrigerated until they can be processed.

2.1.8 Sample Processing

Upon being conditioned, filters containing particulate matter will be post-weighed at the FDEP facility according to Appendix PMmass-SOP. Once a stable post-weight has been attained, the filters will then be shipped to EPA ORD-NERL for trace element analysis.

Precipitation samples contain low levels of trace metals and therefore must be processed with care to avoid contamination. For proper sample stabilization and preservation, precipitation samples collected for mercury analysis will be oxidized with concentrated BrCl by adding a solution of KBr and KBrO₃ to the preserved sample (acidified with HCl). Samples collected for quantification of additional trace elements will be acidified with HNO₃ (to 0.2% v/v solutions) prior to analysis by HR-ICP-MS (Landis and Keeler, 1997). See Appendix TEpcp-SOP for details.

Upon receipt of the precipitation samples at the University of Michigan Air Quality Laboratory's analytical laboratory, trace element/ion samples will be logged in and checked to be certain the tracking form matches the bottle label. Samples will be stored under refrigeration until they can be processed. Total sample volume will be determined by weight and recorded. Before the samples are acidified, a small amount is poured off for ion analysis. Then the samples will be acidified with concentrated ultra-pure nitric acid to 0.2% v/v HNO₃. After acidification, trace element samples will be put back in their polyethylene zip-seal bags and stored for 30 days at room temperature to ensure that all particulate material in the samples has been extracted. Ion samples will be stored under refrigeration until they are analyzed.

Precipitation samples to be analyzed for mercury will be sent to the FDEP Mercury Laboratory. Upon receipt by the FDEP Mercury Laboratory, the samples will be taken to the Class 1000 clean laboratory in the container that was used for shipping. In the clean laboratory, the bottles will be removed from the shipping container and plastic bags and arranged on a laboratory bench, where FDEP sample labels will be applied to the bottles. After labels are applied, 350mL of laboratory de-ionized water will be added to the field blank samples. Then, the mass of each bottle with cap will be obtained using a balance in the clean laboratory and recorded in a logbook. The samples will then be

preserved with trace metal grade hydrochloric acid to a pH below 2 and a solution of KBr/KBrO₃ will be added. The samples then will be stored in the clean laboratory at ambient temperature until analysis by Cold Vapor Atomic Fluorescence.

Precipitation Field Blanks will be processed by adding 350 mL of MQ de-ionized water to the sample bottle. After addition of the water, the blank is processed and analyzed as a sample.

The precipitation samples to be analyzed for mercury isotope analysis will already have been processed as total mercury samples by the FDEP laboratory.

2.2 Analytical Procedures

2.2.1 Mercury

2.2.1.1 Ambient Atmospheric Mercury (ARA)

For details of the analysis performed by the 2537A to determine the levels of mercury in each 5-minute sample, refer to Appendix SpecHG-SOP. The system is programmed so that the Hg⁰ determinations are reported in units of ng m⁻³, and zero-air purge, filter heating cycle, and denuder heating cycles are reported in units of pg m⁻³. The Hg(p) and RGM concentrations are automatically corrected for the flow of both the 2537A and the 1130 pump module.

2.2.1.2 Total Mercury in Precipitation (FDEP)

The determination of the mercury content in collected precipitation samples, to be conducted by FDEP, is briefly discussed below. For more details refer to Appendix HGpcp-SOP and the project QAO goals associated with this mercury analysis as summarized in Table 1.7

All analytical procedures for determination of mercury content in precipitation are carried out in a Class 1000 clean room. Nitrogen utilized for purging is 99.998% purity and is stripped of any mercury using a gold-coated bead trap before use in the purge system. Clean room gloves are worn at all times and all glassware with which the samples and reagents come into contact is cleaned weekly using the acid cleaning procedure described earlier.

Dissolved gaseous Hg⁰ is purged from solution in a mercury-free nitrogen stream after appropriate sample pre-treatment and reduction. Hg⁰ liberated from solution is concentrated on a gold trap, which is then analyzed by cold-vapor atomic fluorescence. A mercury-free pre-treated soda lime trap is utilized in the purge system to capture acid gases that may damage the gold trap.

At the start of each day of analysis, the analyzer is calibrated using a five-point calibration curve using various amounts of a 1 ng/ml aqueous standard. Control standards are analyzed every 6 samples to ensure that the CVAFS instrument has not changed in sensitivity. System and reagent blanks are generated on each day of analysis and subtracted from the day's standard curve.

Bottles designated as field blanks will have had 350mL of deionized water (MQ) added to them. They will be processed and analyzed as samples, the mass of mercury in the bottle determined and the results tabulated as part of the QA reports.

2.2.1.3 Mercury Stable Isotopes in Precipitation (UMGS)

A sub-set of precipitation samples will also be analyzed for stable mercury isotope ratios by MC-ICPMS (Blum and Bergquist, 2007). Mercury stable isotope analyses will be conducted by UMGS (HGisotopes-SOP). Mercury stable isotope ratios will be analyzed using a Nu-Instruments Nu-Plasma Multi-Collector ICP-, housed at the UMGS. Clean room gloves are worn at all times and all glassware with which the samples and reagents come into contact is cleaned weekly using the acid cleaning procedure described in previous sections.

2.2.2 Ions

2.2.2.1. Ambient Ions (ARA)

Sample analysis within the URG-AIM system is analyzed as follows: Full details can be found in the Appendix (AIM-MAN).

2.2.2.2. Ions in Precipitation (UMAQL)

Precipitation samples will be analyzed by UMAQL for dissolved anions and cations by ion chromatography (Appendix IONSpcp-SOP). A small aliquot of precipitation will be removed from each trace element sample having a total volume greater than 50 mL before it is acidified. Chloride, nitrate, nitrite, sulfate, sodium, ammonium, and calcium will be quantified. Each sample will be passed through a 0.22 μ m cellulose filter prior to analysis to remove particulates. Two 0.5 mL vials will be prepared at the same time, one for the anion run and one for cation run. Standards, reference materials and samples will be introduced from an auto-sampler into the packed column where the analytes are separated and concentrated. Detection is by suppressed conductivity and the sample response quantified by a standard curve.

2.2.3 Trace Metals

The HR-ICPMS Standard Operating Procedure (TEpcp-SOP) found in the Appendices includes details of both the analysis of precipitation and the extraction and analysis of ambient filters. Analytical results from the EPA and UM instruments have been compared in the past and are considered to give equivalent data.

If ED-XRF becomes the analytical method for the filter samples, the QAPP will be updated to include a Standard Operating Procedure and summary text for that instrument.

2.2.3.1 Ambient Particulate Trace Metals (EPA ORD-NERL)

Sample analysis using the Thermo Finnigan Element2 HR-ICPMS requires that the analytes be in an aqueous medium. For this reason, the material on each filter must be extracted from the Teflon® filters. Sample filters with particulate material are put into 50 mL acid cleaned polypropylene centrifuge tubes and wetted with 100 µl of ethanol prior to being submerged in 40 mL of solution of ultra-pure 0.2% HNO₃ and 0.1% HCl (v/v). The samples are sonicated, then allowed to stand for 30 days before being analyzed by HR-ICPMS.

Just prior to analysis (TEpcp-SOP), a portion of the extract will be transferred to a 15 mL acid cleaned polypropylene centrifuge tube. Sample is introduced into the plasma by pneumatic nebulization into radio frequency plasma where energy transfer processes cause desolvation, atomization and ionization. The ions are extracted from the plasma through a differentially pumped vacuum interface and separated on the basis of their mass-to-charge ratio and kinetic energy. Resolution selection and peak characteristics for each target trace element is considered in the method to eliminate interferences from polyatomic ions derived from the plasma gas, reagents, or sample matrix. Instrument drift and suppression, or enhancement of instrument response caused by the sample matrix, will be corrected by internal standardization.

2.2.3.2 Trace Elements in Precipitation (UMAQL)

Trace metals will be analyzed using a Finnigan Element2 HR-ICPMS (details in Appendix TEpcp-SOP), housed at the University of Michigan analytical laboratory. Clean room gloves are worn at all times and all labware with which the samples and reagents come into contact is cleaned weekly using the acid cleaning procedure described in previous sections. Just prior to analysis, a portion of the sample will be transferred to a small polypropylene auto sampler vial. Sample is introduced into the plasma by pneumatic nebulization into radio frequency plasma where energy transfer processes cause desolvation, atomization and ionization. The ions are extracted from the plasma through a differentially pumped vacuum interface and separated on the basis of their mass-to-charge ratio and kinetic energy. Resolution selection and peak characteristics for each target trace element is considered in the method to eliminate interferences from polyatomic ions derived from the plasma gas, reagents, or sample matrix. Instrument drift and suppression, or enhancement of instrument response caused by the sample matrix, will be corrected by internal standardization.

Bottles designated as field blanks will have had 350mL of deionized water (MQ) added to them. They will be processed and analyzed as samples and the masses of the suite of trace elements in the bottle determined.

2.3 Calibration Procedures and Frequency

Automated and manual calibration schedules for Hg and trace gas analyzers are shown in Table 2.1. Tekran analyzers will be subjected to automated zero and span checks every third day, using an internal, temperature-controlled permeation tube filled with Hg⁰. Manual standard addition injections will be performed each month and manual calibrations of the model 2537A internal permeation tube will be performed every six (6) months. Manual standard addition and calibrations will be performed by making multiple injections of Hg⁰ through the injection port on the front of the 2537A, using a Tekran Model 2505 primary calibration system and a Hamilton Company (Reno, NV) NIST traceable digital micro-syringe. The digital syringe will be recertified annually by the manufacturer. Complete descriptions of calibration procedures and frequency for analysis of Hg⁰, RGM, and Hg(p) by the Tekran speciation system can be found in Appendix SpecHG-SOP.

Quarterly calibrations are done on the AIM system and on the associated Dionex Model ICS-2000 ion chromatograph (IC). System calibrations set the parameters of ambient temperature, orifice temperature, orifice delta pressure, ambient orifice delta pressure, ambient pressure and inlet flow. For the IC calibration, aqueous multi-anion standards, plus an independent, mid-range calibration verification solution (CVS), are prepared by the ARA laboratory and distributed to the sites each quarter. The calibration standards are injected into the instrument in sequence to generate a calibration curve. The CVS is then analyzed and the new calibration curve is accepted if ion recoveries from the CVS are within +/- 10 percent. Immediately prior to the next calibration, the CVS is again analyzed to determine detector drift. In addition, monthly standard addition injections will be done. The full operation manual may be found in the Appendices (AIM-MAN).

Ozone analyzers will be subjected to automated zero, span and precision checks each night using a Thermo-Environmental Model 49PS primary standard. Manual calibrations with the Model 49PS will be performed once a month. The remaining trace gases will be calibrated automatically every third day using tank standards (Scott-Marrin, Riverside, CA) diluted with zero air. Automated zeros will be performed every day for NO and NOy and every 120 minutes for CO and SO2 in order to track baseline stability. Manual calibrations of each trace gas analyzer will be performed monthly.

Table 2.1 Automated and Manual Calibration Schedules for Hg and Trace Gas Analyzers

Instrument	Automated Calibration	Manual Calibration
Tekran 2537A	Every 3 days (zero/span)	Bi -annually
TE 49c (O3)	Daily (zero/span/precision)	Monthly
TE 48c (CO)	Zero – every 120 minutes Span- every 3 days	Monthly
TE 43c (SO2)	Zero – every 120 minutes Span- every 3 days	Monthly
TE 42c (NO/NOy)	Zero-daily Span-every 3 days	Monthly

Ambient particulate samplers (AIM, sequential dichots, day/night samplers), will be subjected to bi-weekly flow calibrations using a BIOS Defender series primary flow device. The BIOS will be recertified by the manufacturer on an annual basis.

For precipitation samples, at the start of each day of laboratory analysis for mercury, the CVAFS instrument is calibrated using a five-point calibration curve using various amounts of a 1 ng/ml aqueous standard (see Appendix HGpcp-SOP for details). Control standards are analyzed every 6 samples to ensure that the CVAFS instrument has not changed in sensitivity. System and reagent blanks are generated on each day of analysis (Keeler and Landis, 1999).

The SRM for mercury in water (NIST 1641d) will be used as an external SRM in each analytical run. Each laboratory conducting mercury analyses for the project will participate in inter-laboratory comparisons, including FDEP's Hg round-robin inter-laboratory comparisons.

At the start of each day of laboratory analysis for trace elements in precipitation samples, the HR-ICPMS instrument is calibrated using a three-point calibration curve (see Appendix TEpcp-SOP for details). Control standards for specific elements are analyzed to ensure the stability of the HR-ICPMS instrument sensitivity (Landis and Keeler, 1997). If the deviation from expected is greater than 25%, on any single element, the result is flagged. If many of the elements have larger deviations, the samples affected are re-analyzed after re-calibration. In addition to the control standards, a SRM is analyzed each day of sample analysis to evaluate instrument performance. NIST 1640 diluted to 2, 5 and 10% is used for this purpose.

If ED-XRF becomes the analytical method for the filter samples, the QAPP will be updated to include information on calibration procedures and frequency for that instrument.

Meteorological sensors will be calibrated as follows. Sonic anemometers (wind speed and wind direction) and ParoScientific Met4As (T, RH and BP) will be re-certified at the manufacturer on an annual schedule. The ETI electronic rain gauge will be calibrated in the field once a quarter using certified weights to mimic accumulated precipitation. The solar radiation sensor will be calibrated quarterly against a transfer standard. The surface wetness sensor cannot be calibrated, per se, but a response check will be performed weekly by spraying deionized water on the sensor.

2.4 Preventative Maintenance

Maintenance procedures for field and laboratory activities, including spare parts lists and sources of repair and replacement, are included in relevant Standard Operating Procedures in the Appendices of this document. All maintenance or repair to equipment will be documented in a laboratory notebook or electronic site log. Documentation will include instrument identification, a description of the problem(s), work performed, vendor service records, date and analyst's initials.

2.5 Quality Control Checks

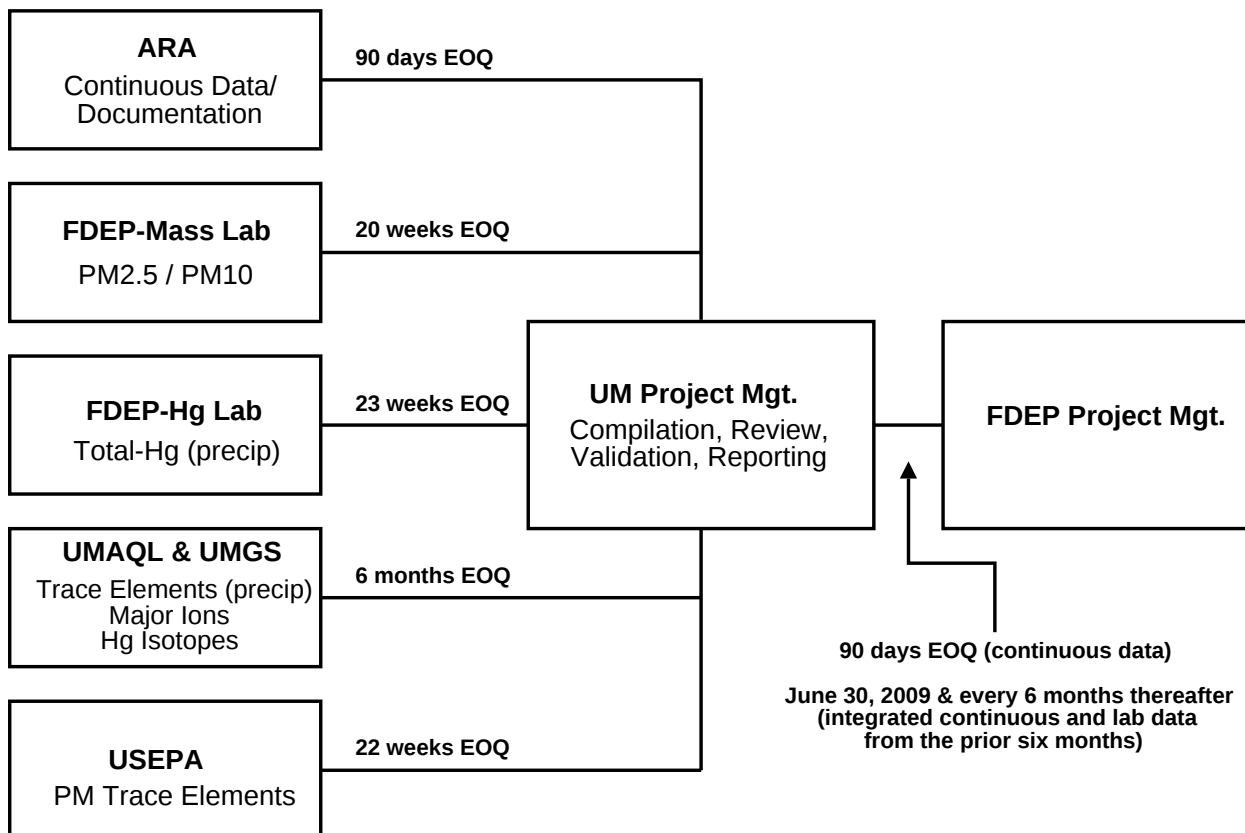
Procedures for field and laboratory internal quality control checks, including protocols for acceptance criteria, frequency of checks, and corrective action are described in the relevant Standard Operating Procedures and Protocols in the Appendices. Summary information has been provided in the following tables in this QAPP:

Table 1.1.	Instrumentation/Measurements for Atmospheric Monitoring
Table 1.2	Data Capture and Analytes Quantified for Atmospheric Monitoring
Table 1.3.	Instrumentation, Accuracy and Detection Limits for Hg in Air
Table 1.4.	Instrumentation, Accuracy and Detection Limits for Trace Gases in Air
Table 1.5.	Instrumentation and Accuracy Specifications for AIM and SHARP Measurements
Table 1.6.	Instrumentation and Accuracy Specifications for Meteorological Measurements
Table 1.7.	Data Quality Objectives for Total Mercury in Precipitation
Table 1.8	Trace Element Method Detection Limits (MDLs)
Table 1.9.	Data Quality Objectives for Trace Elements in Air and Precipitation
Table 1.10.	Laboratory and Field Data Quality Objectives - PM _{2.5} / PM ₁₀
Table 2.1.	Automated and Manual Calibration Schedules for Hg and Trace Gas Analyzers

3.0 DATA MANAGEMENT

An overview of data flow through the Hg TMDL project is shown in Figure 3.1. Data, samples and associated documentation are collected more or less continuously at field sites (not shown) and transferred to ARA and laboratories on set schedules. Continuous data from analyzers (e.g., Tekran and AIM) and flow data from discrete samplers are validated at ARA and submitted to UM-Project Management within 90 days following the end of a calendar quarter (EOQ). The FDEP Mass laboratory receives shipments of sequential Dichot samples on a fixed schedule, weighs and performs internal QA on each sample and submits data to UM within 20 weeks EOQ. The FDEP Hg laboratory reports total-Hg in precipitation samples within 23 weeks EOQ. The UMAQL analyzes a range of sample media, performs internal QA and submits data when finalized to UM. Finally, ED-XRF data may also flow into UM from the EPA XRF laboratory (as well as intensive campaign collaborators) on a schedule that is yet to be determined.

Figure 3.1 Data Flow Chart for TMDL Project



All data will be subjected to a final review and data sets will be prepared for submittal to FDEP. Continuous data (atmospheric Hg, trace gases, meteorology, continuous PM) will be submitted to FDEP within 90 days EOQ, and interim data reports integrating continuous data and all laboratory data will be submitted to FDEP every 6 months, starting June 30, 2009. The initial interim data report will include all data collected through December 31, 2008. Subsequent interim data reports will include the next 6 months of data collection (i.e., December 31, 2009 report to include data collected through June 30, 2009). A fully QA/QC'd database for the 1st year and complete 2 years of project monitoring will be provided to FDEP by June 30, 2010 and March 31, 2011, respectively.

3.1 Data Reduction, Validation, and Reporting

3.1.1 Data Reduction

Data management for continuous variables begins on-site with acquisition of 1-minute data and associated diagnostic variables by the data acquisition system via digital or analog connection to each piece of equipment. Note that Tekran data are generated in 5-minute intervals while AIM and Sunset Carbon Analyzer data are generated in 60-minute intervals. The 1-minute data are then pushed each morning to the ARA data management center in Plano, TX and loaded into a SQL server master database. From this point onward, all data are managed using FirstLight, a series of custom software programs for reviewing, screening, adjusting, validating and reporting air quality data (for additional information on FirstLight, see FL-DOC). As the 1-minute data flow into FirstLight, they are subjected to a series of range checks designed to screen out data points that are clearly invalid. After screening, data flags are read and embedded calibration data are extracted and analyzed. Response factors derived from calibration data are then applied to 1-minute values, and the adjusted 1-minute data are then used to calculate 5-minute averages and summary statistics (max., min., standard deviation, median and count).

Data handling and reporting for samples processed and analyzed at FDEP Laboratories are detailed in 2 Appendices, Data-SOP and Report-SOP.

Field data for discrete samples are recorded on electronic or pre-printed forms that provide space for operator comments and suggestions and pertinent observations. In addition, the acceptability of each sample is recorded and judged by the field operator. Pertinent sampling information is entered into a computer database. Analytical results from laboratory procedures are recorded in bound laboratory notebooks and later entered into a computer database. Analyzer outputs are collected on various electronic media including fixed drives and diskettes. All databases are backed up to network drives and removable high volume disk media (e.g. DVD). These raw data are stored and will be archived for a minimum of 5 years after the completion of the project.

Continuous data are collected at each Supersite by various electronic data acquisition systems, downloaded to the ARA data management center in Plano, TX, written to a computer hard drive and a networked database daily. All databases are backed up to removable high volume disk media (e.g., DVD). These raw data are stored on-site and offsite and will be archived for a minimum of 5 years after the completion of the project.

During the course of this project, a clear record will be kept by each group allowing any final data point to be traced back to their original raw data.

3.1.2 Data Integrity and QC Validation

The 5-minute and 60-minute averages are then subjected to another round of automated screening. At this stage, data screening includes not only the adjusted 5-minute averages, but summary statistics and diagnostic variables, as well. For example, 5-minute standard deviations are used to determine if an analyzer is off-line (s.d.=0) or if data are unreasonably noisy (s.d. > predefined threshold). Similarly, diagnostic data, such as flows and temperatures, are used to determine whether or not an analyzer is operating under the proper conditions and to flag associated data accordingly. FirstLight then recalculates 60-minute averages and summary statistics (based on valid 5-minute averages) and 24-hour averages and summary statistics (based on valid 60-minute averages).

Following the automated screening process, all data are subjected to manual review using the FirstLight graphical interface. This step includes review of 5-minute averages and associated statistics, calibration data, diagnostic data and associated documentation. It also includes inter-parameter consistency checks, another round of range checks and nearest neighbor comparisons. 60-minute and 24-hour averages are automatically recalculated if any 5-minute average is flagged invalid. After these steps, continuous data are at Level 1 validation and ready for submittal to UM. Data submissions will include 5-minute and 60-minute averages. Each reporting interval will also include standard deviation, minimum, maximum and count. Raw unprocessed data will also be made available to UM to facilitate validation and provide a fully traceable record.

For laboratory measurements, each analyst and/or technician is responsible for determining that the results of each analytical determination have all associated QC measurements and that the acceptance criteria are met and documented according to protocol. All records are generated in accordance with previously established protocols developed for UMAQL projects. This records management system employs validation by the field manager, laboratory manager, or PI, as appropriate. Hand written records are entered into computer databases and all data are stored on hard disk in a central computer. The electronic filing directory system to be used is described in the following section.

FDEP Mercury and Gravimetric Laboratory data validation procedures are documented in Data-SOP in the Appendices.

3.1.3 Data Storage

All database files are identified by the filename and subdirectory structure. Final data records are retained on the computer drive until reports and publications are written and accepted, or for a minimum of 5 years after completion of the project (per requirements of Contract SP673 with FDEP), whichever is longer. After completion of the project and a final review by the Project Manager, all electronic data will be duplicated on DVD and stored in replicate for a minimum of five years after conclusion of the project contract at FDEP, UM and ARA. Written data shall be stored for a period of five years after conclusion of the project contract at UM.

Data handling and reporting for samples processed and analyzed at FDEP Laboratories are detailed in 2 Appendices, Data-SOP and Report-SOP.

3.2 Data Assessment

All data will be evaluated to determine if they meet the criteria outlined previously for precision, accuracy, completeness, and blank values. Samples not meeting criteria will be re-analyzed, where possible, or flagged as previously described. Flagged data will alert the user that they did not meet QA criteria, and why, and will be clearly documented in the final report and data sheets.

Data from samples processed and analyzed at FDEP Laboratories will be assessed in accordance with guidelines detailed in Appendices Data-SOP and Report-SOP.

3.3 Data Distribution

Data from each entity participating in the project (e.g., FDEP labs, ARA, EPA, UMAQL, UMGS) will be sent to the UM Project Management in keeping with the schedules described previously for merging, validation and reporting to FDEP. Interim data deliverables submitted to FDEP Project Management for the purposes of demonstrating progress, facilitating scientific discussion or presentation will be considered DRAFT data. A final database from Year 1 of monitoring will be provided to FDEP by June 30, 2010. A Project final database for all monitoring for the project will be provided to FDEP by March 31, 2011. Data in the Year 1 and Project final databases will have been fully merged and validated by the UM Project Management team and suitable for public distribution.

3.4 Data Audits

All data are subject to project auditing by or on behalf of FDEP at any time during the project and clear records will be kept by each entity participating in the project allowing any processed data points to be traced back to the original raw data.

4.0 PROJECT ASSESSMENT AND OVERSIGHT

4.1 QA Responsibilities

The personnel structure of the UMAQL and ARA make it impossible to provide complete separation of quality assurance oversight and assessment from the efforts to collect and process project data. The scope of this project and most of the work require the combined specializations of all key group members, leaving no separate individual to serve exclusively in a QA capacity. However, each individual on this project is professionally vested in maintaining high standards in order to maximize the value of the research products. Within these contractor groups, E. Edgerton will be responsible for the direction, oversight and QA/QC of the continuous measurements at the 4 Supersites. J. Barres will be responsible for QA related activities associated with precipitation supply preparation, sample collection, transport, preservation, analysis and data processing. FDEP Laboratory QA Officer, A. Tintle, will be responsible for QA related activities associated with the FDEP Mercury and Gravimetric Laboratories. M. Landis will be responsible for deployment, technical support and QA activities for the automated particulate collector, speciated mercury technical support, and for QA activities for the trace element analyses of the sequential particulate filters by USEPA ORD-NERL.

4.2 Performance and System Audits

Regular checks and calibrations of the field instruments will be performed by the site operator. Internal audits will be performed by ARA on at least an annual schedule, with initial audits within the first month of sampling at each site. The Tekran and AIM analyzers require a higher level of oversight and will be audited twice a year by ARA. EPA Region 4 SEDS personnel (G.. Noah) will also conduct external audits of TMDL equipment and operation, at project startup and periodically thereafter. The UMAQL may request an external audit by other auditors, as well. The results of audits will be provided in the quality assurance reports described under Section 4.4 .

4.3 Corrective Action

As mentioned earlier in the Quality Assurance section of this document, there are procedures that are followed to identify any major source of error should it occur. The data are flagged and the appropriate procedures are followed (as outlined in the relevant standard operating procedures and protocols in the appendices).

4.4 Quality Assurance Reports

For the duration of the project, Quarterly Reports will be submitted to FDEP Project Management. A Project Final Report will be submitted to FDEP at the completion of the project. The required contents of the final report will be determined by FDEP Project Management and the participating contract groups.

In addition, beginning on or before June 30, 2009, UMAQL will provide an interim data report to FDEP which will include data files from both the field data and the data from laboratory analyses. The interim data reports and files will provide documentation/integration of the data measurements with respect to common site/date identification, and will provide an initial QA/QC assessment by ARA Inc. and UMAQL. The interim data reports will serve as the basis for discussion between UMAQL and FDEP regarding an understanding of data formatting and content, and any known QA/QC issues regarding the data. The initial interim data report will include all data collected through the end of the 1st calendar quarter of Task 04 (established as through December 31, 2008). Subsequent interim data reporting from UMAQL to FDEP will occur every 6 months, to include the next 6 months of data collection (i.e., December 31, 2009 report to include data collected through June 30, 2009).

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APPENDICES

Filename	Title [originator]
SpecHG-SOP	<i>Field Standard Operating Procedures for Measurement of Ambient Gaseous and Particulate Mercury [ARA]</i>
AIM-MAN	<i>Ambient Ion Monitor (AIM) Pre-Installation Requirements Checklist and Confirmation [URG]</i>
SHARP-MAN	<i>Synchronized Hybrid Ambient Real-time Particulate Monitor Model 5030: Instruction Manual [THERMO]</i>
ACtable-SOP	<i>Acid Cleaning Groups – Standard Operating Procedure [UMAQL]</i>
ASPS2-SOP	<i>Mercury and Trace Elements in Precipitation Samples using the Automated Sequential Precipitation Sampler II: Standard Operating Procedures for Field Operators [UMAQL]</i>
TEpcp-SOP	<i>Determination of Trace Elements in Precipitation, Dry Deposition, Ambient Aerosols, and Other Samples using Inductively Coupled Plasma – Mass Spectrometry: Standard Operating Procedure [UMAQL]</i>
HGpcp-SOP	<i>Trace-level Total Mercury in Water by Purge and Trap (Dual Gold Traps) and Cold Vapor Atomic Fluorescence Detection (CVAFD) [FDEP]</i>
HGisotopes-SOP	<i>Determination of Mercury Isotopic Composition in Precipitation [UMGS]</i>
IONSpcp-SOP	<i>Analysis of Precipitation, Acid Aerosols, and Other Samples by Ion Chromatography – Standard Operating Procedure [UMAQL]</i>
ADS-SOP	<i>Compendium Method IO-4.2 Determination of Reactive Acidic and Basic Gases and Strong Acidity of Atmospheric Fine Particles [EPA]</i>
PMdichot-MAN	<i>R & P 2025 Dichotomous Partisol®-Plus Model 2025 Sequential Air Sampler: Operating Manual [R&P]</i>
PMmass-SOP	<i>Determination of PM_{2.5} in Ambient Air by Gravimetric Analysis [FDEP]</i>
FL-DOC	<i>Description of FirstLight Data Management Software [ARA]</i>
Met4A-MAN	<i>User's Manual for MET4 and MET4A Meteorological Measurement Systems [Paroscientific]</i>
OCEC-SOP	<i>Standard Operating Procedure (SOP) for the Analysis of Organic and Elemental Carbon (OC/ED) Using the Sunset Laboratory Semi-Continuous Carbon Aerosol Analyzer [Sunset Laboratory]</i>
AMBGAS-SOP	<i>Automated collection of trace gas and flow data [ARA]</i>

APPENDICES, cont'

Filename	<i>Title [originator]</i>
SRsensor-MAN	<i>LI-COR Terrestrial Radiation Sensors - Instruction Manual [LI-COR]</i>
LWS-MAN	<i>Model 237 Leaf Wetness Sensor - Instruction Manual [CSI]</i>
Sonic-MAN	<i>Model 81000 Ultrasonic Anemometer - Operating Instructions [R.M.Young]</i>
Rainfall-MAN	<i>NOAH IV Total Precipitation Gauge - Technical Manual [ETI]</i>
Data-SOP	<i>Standard Operating Procedure for Records Maintenance and Storage [FDEP]</i>
Report-SOP	<i>Standard Operating Procedure for Reporting Qualified Data [FDEP]</i>
Curriculum Vitae	



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