



# GMOS Standard Operational Procedure

Method for the determination of total mercury in precipitation

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Annex A      Commercial available precipitation collectors

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## 1. Scope

This Standard Operational Procedure is for the determination of total mercury in precipitation at GMOS monitoring stations using wet-only and/or bulk precipitation collectors. This SOP conforms to existing standards for the measurement of mercury in precipitation set forth by the European Monitoring and Evaluation Programme (EMEP) and the North American Atmospheric Deposition Program (NADP) Mercury Deposition Network (MDN)[1-3]. Furthermore, this GMOS SOP was reviewed and revised during a workshop in Brussels, Belgium on 7-8 April, 2011 in which the participating GMOS partners provided input and suggestions on the procedures described in this document.

This SOP outlines the preparation of sampling materials in the laboratory, the collection of samples in the field, and the analysis of samples following collection. For the majority of GMOS sites, sampling materials will be prepared at designated GMOS laboratories, and precipitation samples collected at GMOS sites will be sent to the same dedicated laboratories for analysis. These laboratories include the CNR Institute of Atmospheric Pollution Research (CNR-IIA), the IVL Swedish Environmental Research Institute, and the Institute “Jozef Stefan” (JSI). Each GMOS site will be assigned to one of these three primary analytical laboratories. Alternatively, samples collected at certain sites in China, Russia, and Germany will be respectively analyzed internally by the Institute of Geochemistry – Chinese Academy of Science (IG-CAS), the Limnological Institute – Siberian Branch of the Russian Academy of Sciences, and the German Environmental Protection Agency, Umweltbundesamt (UBA). Precipitation samples collected at GMOS sites must be analyzed following the analysis method for total mercury given in the EMEP manual [2] or following EPA Method 1631E [4].

This SOP allows for the sampling of deposition using a series of commercially available wet-only and bulk collectors. It is recommended that wet-only collection be employed at all sites where it is feasible (e.g. sufficient power is available, a regular site operator is present, and extreme weather conditions do not prohibit the functionality of the automated wet-only collector). However, at certain sites it may be necessary to employ bulk collection techniques and this is also permissible within the GMOS project. This SOP also requires sample analysis using Cold Vapour Atomic Fluorescence Spectrometry (CVAFS). The standard is applicable for the measurement of mercury in deposition between  $1 \text{ ngm}^{-2}\text{d}^{-1}$  and  $100 \text{ ngm}^{-2}\text{d}^{-1}$ .

It should be noted that in this SOP, requirements and recommendations are both provided where appropriate. Requirements (typically noted by the words “shall” or “must”) are guidelines that must be followed at all sites. Recommendations are suggestions that allow for some flexibility in the procedures based upon the specific characteristics of each site. Careful attention should be paid to these guidelines for GMOS monitoring sites.

## 2. Abbreviations and Definitions

### Mercury Species and Terms:

Hg	Mercury
Wet deposition	Removal of gases and particles from the atmosphere by precipitation-related processes
Dry deposition	Removal of gases and particles from the atmosphere in the absence of precipitation
Total deposition	The sum of wet and dry deposition

### Analytical Terms:

CRM	Certified Reference Material
CVAFS	Cold Vapor Atomic Fluorescence Spectrometry
MDL	Method Detection Limit
QA	Quality Assurance
QC	Quality Control
SRM	Standard Reference Material

### Units:

ng	nanogram; $10^{-9}$ g
pg	picogram; $10^{-12}$ g
L	liters
ml	milliliters
ppt	parts per trillion; ng/L
°C	degrees Celsius
lpm	liters per minute
psi	pounds per square inch
kPa	kilopascals

## 3. Gases and Chemicals

- 3.1 Reagent grade water: ultrapure deionised water with resistivity greater or equal to 18 MΩ cm that originated from a pre-purified (distilled, reverse osmosis, etc.) source. This can be used at the sites for cleaning the collector surfaces, and it is used in the laboratory for cleaning and analysis.

*NOTE: The gases and reagents listed below are used for cleaning the sampling equipment and/or for analysis of precipitation samples. The cleaning is to be performed at the analytical lab prior to shipment to the measurement site; thus, only the analytical laboratories are responsible for having these gases and reagents available. All acids should be tested for Hg concentration before use.*

- 3.2 Grade 4.8 (99.998%) or higher ultra high purity (UHP) Argon for use as a carrier gas for CVAFS that has been further purified by the removal of Hg using a gold-coated sand/bead trap.
- 3.3 Grade 4.5 (standard laboratory grade) nitrogen that has been further purified by the removal of Hg using a gold-coated sand/bead trap.
- 3.4 Concentrated hydrochloric acid, 30 % HCl or 36 to 38 % HCl, with a low mercury blank (< 5 pg/mL, e.g. Suprapur® quality).
- 3.5 Concentrated hydrochloric acid, 37 % HCl (e.g. p.a. quality) for cleaning purposes.

**WARNING** — *concentrated hydrochloric acid is corrosive, and hydrogen chloride fumes are anirritant. Avoid exposure by contact with the skin or eyes, or by inhalation of fumes. Carry out the working laminar flow fume hood. Use suitable personal protective equipment (including suitable gloves, face shield or safety glasses, etc.) when working with the concentrated or dilute hydrochloric acid.*

- 3.6 Concentrated nitric acid, 65% HNO<sub>3</sub>, with a low mercury blank (< 5 pg/mL, e.g. Suprapur quality).
- 3.7 Concentrated nitric acid, 65% HNO<sub>3</sub>, (e.g. p.a. quality) for cleaning purposes.

**WARNING** — *concentrated nitric acid is corrosive. Avoid exposure by contact with the skin or eyes, or by inhalation of fumes. Carry out the working laminar flow fume hood. Use suitable personal protective equipment (including suitable gloves, face shield or safety glasses, etc.) when working with the concentrated or dilute nitric acid.*

- 3.8 Hydrochloric acid, 3.5 % HCl for cleaning purposes, prepared from concentrated HCl (3.5) by dilution with ultrapure water (3.1).
- 3.9 Nitric acid, 3.5 % HNO<sub>3</sub> for cleaning purposes, prepared from concentrated HNO<sub>3</sub> (3.7) by dilution with ultrapure water (3.1).
- 3.10 Hydrochloric acid, 0.8 % HCl to be added to the sample bottle prior to deployment in the field for preservation of the precipitation samples, prepared from concentrated high purity HCl (3.4) by dilution with ultrapure water (3.1).
- 3.11 Bromine monochloride (BrCl) solution, prepared according to the EMEP manual [2] or according to EPA Method 1631E [4].
- 3.12 Hydroxylammonium hydrochloride solution, prepared according to EMEP manual [2] or according to EPA Method 1631E [4].
- 3.13 Stannous chloride, prepared according to EMEP manual [2] or according to EPA Method 1631E [4].

#### *4. Principles of mercury deposition determination*

Atmospheric deposition is the transfer of pollutants (gases and particles) from the atmosphere to the earth's surface through precipitation-related processes or through the sedimentation of gases and particles in the absence of precipitation. Atmospheric deposition is known to be a primary mechanism by which mercury is introduced to terrestrial and aquatic ecosystems, and therefore it is critical to understand the processes by which mercury enters the atmosphere and is removed to the earth's surface. A primary objective of the GMOS project is to quantify atmospheric mercury deposition on the global scale by deploying unique devices for capturing mercury deposition at a globally distributed network of monitoring sites.

Wet-only collectors are designed to collect only particles and dissolved constituents which are removed from the atmosphere through precipitation-related processes. Wet-only collectors are typically automated with a wetness sensor so that they are only open to the atmosphere during times when precipitation is occurring. There are several commercially available wet-only precipitation collectors (see Annex A). The ability for a particular wet-only collector to effectively capture the wet removal of atmospheric constituents can be affected by a number of factors, including meteorological conditions at the site (e.g. wind speed, type of precipitation (rain or snow etc.)) and the aerodynamic properties of the sampler. As such, it is possible that the wet-only collector may not capture all sedimenting wet particles. Additionally some dry particles, non-sedimenting particles and gases may also be collected when the wet-only collector is open to collect precipitation. However, the collectors presented in Annex A have been thoroughly tested for collection efficiency and are approved for mercury wet deposition collection.

Bulk collectors are designed to collect all sedimenting wet and dry gases and particles. Bulk collectors are open to the atmosphere at all times regardless of whether precipitation is occurring. Bulk collection is a valuable sampling technique when it is of interest to measure the total deposition of mercury from the atmosphere. It is also useful at sites where due to power constraints or operator frequency it is not possible to operate a wet-only collector. However, it is important to note that with bulk collection it is not possible to distinguish whether the collected atmospheric constituents were removed through wet or dry deposition. Additionally, when the collector is open to the atmosphere at all times it is possible that mercury collected during times of precipitation might be volatilized to the atmosphere, while gases and particles might also adsorb to the walls of the funnel during times when there is no precipitation. Ultimately the mercury contained in the sample will be a combination of these various processes. Sample contamination can also occur more easily in bulk samplers due to insects, bird droppings or other material in the sampling vessels, especially when using extended sampling periods.

At the majority of GMOS sites, the deployment of wet-only samplers or the co-location of wet-only and bulk samplers is the preferred sampling method. However, the GMOS Work Package leaders acknowledge that sites may exist within the GMOS project where, given the constraints of the monitoring location (including power availability or the frequency of site access by site personnel), it may not be possible to deploy a wet-only collector. In these particular cases, it is permissible that a bulk collection device be used.

This SOP describes two primary features of mercury deposition sampling:

- 1) sampling of precipitation in the field;
- 2) mercury analysis in the laboratory.

### *5. Siting requirements for mercury deposition determination*

Two types of sites shall exist within the GMOS project:

**Master Sites** will measure continuous speciated ambient mercury (GEM, GOM, and PBM<sub>2.5</sub>) and total mercury in precipitation.

**Secondary Sites** will measure total gaseous mercury (TGM) in the ambient atmosphere and total mercury in precipitation.

The following siting requirements shall be followed when establishing new GMOS sites:

1. It is recommended that the GMOS monitoring sites be located in background areas which are not directly impacted by anthropogenic emissions of mercury or other airborne pollutants. The sites shall be representative of a large area, i.e. the concentration(s) of mercury obtained at the site shall be representative for the region where the measurements are performed. Measurement sites close to natural mercury emission sources, such as active volcanoes, are not recommended unless the measured ambient mercury is actually representative for a large area.
2. GMOS sites shall be chosen based on existing sites that can provide available ancillary measurements. Examples include EMEP and GAW sites. In this way, the site will have the necessary existing infrastructure for atmospheric mercury monitoring, including available power, shelter, and site personnel.
3. It is recommended that GMOS sites be selected based upon the criteria set forth by GAW with respect to distances from major natural and anthropogenic sources. Stations within the GAW framework are categorized as either global or regional with respect to the remote nature of the sites and the relative impact of sources and pollutants. Within GMOS, it is strongly recommended that sites satisfy the minimum-distance guidelines of global background stations; however, regional background stations may be permitted depending on the specific site characteristics (Table 1).
4. The monitoring sites shall be as exposed as possible without influence from surrounding topography or other obstacles within a 2 km radius around the site. Naturally vegetated areas with level ground are recommended [5]. Vegetation surrounding the site should be maintained at < 0.5 m and not higher than half the height of the measurement device (e.g. precipitation collector) [5].

5. The sites must have sufficient power available to support the operation of desired sampling equipment. Responsible personnel must review the instrument specifications to determine whether the site has the necessary capabilities.
6. All activities near the site shall be recorded on a regular basis. This includes active natural and anthropogenic sources, motor vehicle traffic, distance to population centers, activity of major wildlife, and frequency of people visiting the monitoring site. This is critical for understanding variability in the measurement data.

Table 1: Minimum-Distance Guidelines for GMOS Stations. (GAW, 2004) [5]

Parameter	Minimum Distance to Site (km)		Comments
	<i>Regional/Rural Background Stations</i>	<i>Global/Remote Background Stations</i>	
SO <sub>2</sub> or NO <sub>x</sub> Point Source			If emission sources (such as power plants, refineries, chemical plants, smelters or other major industrial facilities) are located in the general upwind direction from the collector, then the regional distances indicated should be doubled
>100 tonnes per year	20	50	
>1000 tonnes per year	50	100	
Major Industrial Complex	50	150	
Town, population 1,000-10,000	10	25	Future population growth and associated land development should be considered carefully, especially for towns and villages near a station. If population centres are located in the general upwind direction from the collector, then the regional distances indicated should be doubled
Town, population 10,000-25,000	20	50	
City, population 25,000-100,000	50	100	
City, population >100,000	100	200	
Parking lot or large paved area	0.2	0.5	On-site parking lots and maintenance yards also need to be kept at least 300 meters from the collector
Secondary road, lightly travelled	0.5	1	The local road network around the site is of particular concern. Traffic volume and type as well as road surface will largely determine the impact at the site
Secondary road, heavily travelled	1	5	
Major highway, airport, railway, shipping lane, harbour	5	25	Moving sources of pollution, such as air, ground, or water traffic or the medium on which they traverse (e.g. runway, taxiway, road, tracks, or navigable river), should not be within 500 metres of the collector
Feedlot operations	2	50	Acceptable distances will vary greatly depending on size of the operation. Even small concentrations of animals should be housed no closer than 500 metres. If the feedlot, dairy barn or animal waste pile can be smelled at the collector, it is too close
Intensive agricultural activities	2	10	Surface storage of agricultural products, fuels, vehicles or other source materials should be kept at least 500 metres from the collector
Limited agricultural activities	0.4	1	Storage of small amounts of agricultural products, fuels, or other source materials should be kept at least 500 metres from the collector
Sewage treatment plant	2	20	
Active volcano, fumarole, etc.	20	100	Geothermal sites including geysers and springs may have significant emissions and should be avoided
Natural salt, dust, alkali sources	2	2	Windswept materials from salt and alkali flats as well as sea spray from coastlines can contaminate samples
Vertical objects (Includes towers, wires, fences, trees), angle of projection from instrumentation	≤ 45° from top of instrument		For an angle of 45° from horizontal, the object must be a distance equal to the object's height away from the instrument
Buildings, angle of projection from instrumentation	≤ 30° from top of instrument		For an angle of 30° from horizontal, the object must be a distance equal to twice the object's height away from the instrument

## 6. Sampling equipment – General requirements

Mercury deposition for the GMOS project will be collected using wet-only precipitation samplers (or bulk samplers at sites where wet-only collection is not possible) which are designed specifically for mercury deposition determination (see Annex A for suitable commercially available samplers). It is required that all materials used in the sampling trains of these precipitation collectors be made from borosilicate glass or fluorocarbon polymers which are approved for mercury collection and analysis. These materials must be cleaned following acceptable protocols for mercury determination, as described in Section 8.

In general, the precipitation collector should consist of a cylindrical funnel with a circular horizontal opening of at least 8 – 10 cm inner diameter. The funnel is connected through a capillary or vapor lock to a bottle that stores the precipitation sample during the sampling period. In order for the sample not to be contaminated during heavy rain, the rim of the funnel shall be positioned >1.5 m above the ground level. The sampling equipment must be housed in a suitable container or cabinet that protects the sample from sunlight and moderates the temperature of the sample so that it is not susceptible to evaporation under high temperatures or to freezing during low temperatures. As such the temperature of the sample container should be kept between 5° C and 35° C and can be monitored using a standard thermometer. The basic principle of the sample train assembly is illustrated in Figure 1.

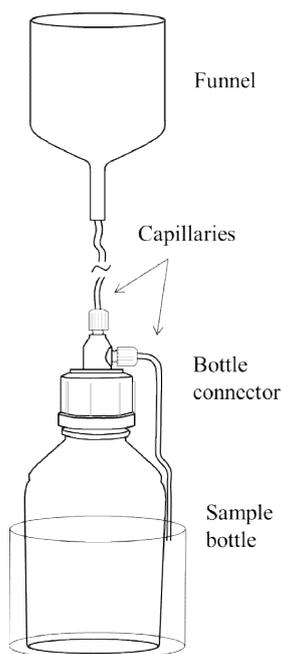


Figure 1. Example of a precipitation collector.

The funnel shall have a cylindrical vertical section of sufficient height to avoid sampling losses resulting from splashing. The funnel and the sample bottle are connected via a glass capillary or, alternatively, a narrow tube made from fluorocarbon polymer. The second capillary allows the air to exit during sampling and serves as a drain in case of overflow. The use of capillaries prevents evaporation of the sample and diffusive uptake of elemental mercury from the surrounding air.

The dimensions of the funnel and the sample bottle shall be selected with respect to the expected precipitation collected during the actual sampling period. The funnel area shall be large enough to collect a minimum precipitation depth of 1 mm per week.

The sampling efficiency of funnel/bottle collectors must be verified by comparing the precipitation collected by the sampling device with the precipitation determined using a standard meteorological rain gauge. The rain gauge should be positioned horizontally  $\geq 5\text{m}$  and  $< 30\text{m}$  from the collector, and vertically there should be  $\leq 0.3\text{m}$  between collector and rain gauge orifices [5, 6]. At certain sites, where more than 20% of annual precipitation is in the form of snow, the rain gauge should also be equipped with a wind shield [5]. The difference in precipitation between the standard rain gauge and the sample collector shall not be greater than 20% for precipitation depths between 1 mm to 2.5 mm, and not greater than 10 % for precipitation depths larger than 2.5 mm of precipitation [5]. Checking sampling efficiency is especially important if a wet-only collector is used.

### 7. Analytical Laboratories Responsible for GMOS Sites

The majority of monitoring sites within GMOS will be assigned to one of the designated analytical laboratories (CNR-IIA, JSI, and IVL). These analytical laboratories will be responsible for cleaning precipitation supplies (e.g. bottles, funnels, and capillaries), sending clean supplies to the monitoring sites, receiving samples and used supplies from the monitoring sites, and analyzing collected precipitation samples. The sites will be distributed evenly among the laboratories, as shown in Table 2. The GMOS monitoring sites in China and Russia are an exception, because due to shipping restrictions it is more practical to analyze precipitation samples at laboratories within these respective countries (Table 2). The designated laboratories for these samples are the Institute of Geochemistry – Chinese Academy of Science (IG-CAS) and the Limnological Institute – Siberian Branch of the Russian Academy of Sciences (SB RAS) (Table 3). Furthermore, samples collected at the German sites will also be analyzed internally by the German Environmental Protection Agency, Umweltbundesamt (UBA) (Table 3).

**Table 2.** Distribution of GMOS monitoring sites among the primary analytical laboratories.

CNR-IIA	JSI	IVL
Amsterdam Island	Bariloche, Argentina	Cape Grim, Australia
Cape Point, South Africa	Cape Verde	Mace Head, Ireland
Celestun and Mexico	Ferrat, France	NyAlesund, Norway
Col Margherita, Italy	Iskrba, Slovenia	Pallas, Finland
Ev-K2, Nepal	La Seyne, France	Rao, Sweden
Monte Curcio, Italy	Paramarimbo, Suriname	Station Nord, Greenland
Longobucco, Italy	Rondonia, Brazil	

**Table 3.** List of monitoring sites in China and Russia for which samples will be analyzed in local laboratories.

IG-CAS	SB RAS	UBA
Mt. Waliguan – Zhuzhang	Lystvyanka, Irkutsk	Waldhof, Germany
Mt. Waliguan - Changbaishan		
Mt. Waliguan		

## 8. *Preparation of sampling materials for precipitation collectors*

All sampling materials shall be prepared and handled using trace metal-free ultra clean techniques in Class-100 clean rooms or Class-100 clean benches and with approved reagents. All parts of the precipitation collector that are in contact with the sample shall be cleaned extensively before use, following the cleaning procedure described here. Powder-free plastic or nitrile gloves shall be used during all steps of the cleaning procedure and while handling clean sampling train components. Cleaned sampling materials must be stored in double plastic zip-lock type bags until they are used in the field (the use of triple bags is recommended).

All sampling materials must be cleaned following either the procedure defined in the EMEP manual [2] or a modified version of the procedure defined by EPA Method 1631 (Revision E) [4]. GMOS has consulted the modified versions of the EPA 1631 Method (Revision E) outlined by the U.S. MDN [7] and by Landis and Keeler, 1997 [8]. These methods are summarized here, but the analytical laboratories should consult the respective analytical manuals for the procedure they will be following.

The EMEP method for cleaning precipitation sampling supplies is as follows:

- 1) Leach in an alkaline detergent for 24 hours. Rinse thoroughly with de-ionized water.
- 2) Leach in a solution of HNO<sub>3</sub> (Puriss) (3.7) diluted 1:3 with de-ionized water for 7 days. This should be done in a polyethylene tank placed under a fume hood. Rinse thoroughly (3-5 times) with de-ionized water.
- 3) Leach in a 0.1 M solution of HNO<sub>3</sub> (P.A.) (3.7) in high-purity water (3.1) for 7 days. Rinse thoroughly (3-5 times) with de-ionized water.
- 4) Fill bottles with high purity water (3.1). Add 5 ml/l BrCl(3.11) solution. Leave to stand for at least 24 h.
- 5) Add 5 ml/l 12% NH<sub>2</sub>OH·HCl (3.12). Leave to stand for 1 hour.
- 6) Pour out the above solution. Rinse with large amounts of high-purity water (3.1). Allow materials to dry in a clean area (e.g. laminar flow hood or cabinet)
- 7) Bottles that are believed to be contaminated are baked at 500°C for 5 hours and then washed according to the procedure above, but excluding step 1.

A modified version of the EPA 1631 (Revision E) method for cleaning Teflon or glass precipitation sampling bottles is as follows:

- 1) In a fume hood, wash all surfaces of the bottle and cap with laboratory grade acetone. Then wash all surfaces of the bottle and cap with an alkaline detergent and de-ionized water. Wash the bottle and cap separately and rinse each five times with de-ionized water to remove all of the detergent.
- 2) Heat new bottles in 3.5 % HNO<sub>3</sub>(3.9) for 48 h at 65-75 °C. Used bottles known not to have contained high concentrations of mercury (> 100 ng/L) can be heated in 3.5%

HNO<sub>3</sub>(3.9) for 6 hours at 65-75 °C. To do this, fill the bottle to the neck with 3.5% HNO<sub>3</sub> and place the cap loosely on top. Alternatively submerge the bottle and caps in separate polyethylene tanks containing 3.5% HNO<sub>3</sub> as long as all the inner surfaces of the bottle and caps are in contact with the HNO<sub>3</sub> solution. Place bottles or polyethylene tanks in a heated water bath inside a fume hood. After heating is complete, rinse all surfaces of the bottle and cap five times with ultrapure water (3.1).

- 3) Fill the bottle to the top of the neck with a 1% solution of BrCl(3.11) in ultrapure water (3.1). Leave to stand for at least 24 h. Rinse the bottle and cap five times with ultrapure water (3.1).

After either the EMEP or the EPA cleaning method has been completed, 20 mL/L of 0.8% high purity HCl (3.10) must be added to the bottle. This is used to preserve the sample while it is in the field. Seal the bottle and place it inside a minimum of two new plastic or polyethylene zip-lock type bags (the use of triple bags is recommended). Store as such until the bottle is taken to the field for sampling.

A modified version of the EPA 1631 (Revision E) method for cleaning glass funnels and capillaries is as follows:

- 1) Wash all surfaces of the funnel and capillary with laboratory grade acetone inside a fume hood. Then wash all surfaces thoroughly with an alkaline detergent. Rinse each component five times with de-ionised water.
- 2) Heat in 3.5 % HNO<sub>3</sub>(3.9) for 6hrs at 65-75 °C. This can be done by submerging the bottle in a polyethylene tank containing the HNO<sub>3</sub> solution. Ensure that all the inner surfaces of the funnel or capillary are in contact with the HNO<sub>3</sub> solution. This procedure should be performed in a fume hood. After heating is complete, rinse all surfaces five times with ultrapure water (3.1). Allow the components to dry in a clean cabinet or laminar flow hood.
- 3) Place the funnel and capillary in separate double plastic or polyethylene zip-lock type bags (the use of triple bags is recommended). Store as such until they are taken to the field for sampling.

## *9. Sample retrieval in the field*

For the initial stages of the GMOS project, it is required that samples be collected at a minimum on a bi-weekly basis. However, samples which are collected more frequently will provide higher resolution data. As such, it is strongly recommended that precipitation samples be collected on a weekly or event basis. This should be possible at sites with frequent operator availability and ease of shipping supplies between the site and analytical laboratory. New sites which begin by collecting samples biweekly are encouraged to change to weekly sample collection once the site is well established and the operator and shipping protocols are in place.

Biweekly or weekly samples shall be collected on Tuesday mornings at 8:00AM Local Standard Time. Should a site choose to collect samples on an event basis, the operator should retrieve the sample bottle at 8:00AM Local Standard Time on the morning following the conclusion of the precipitation event.

The description below is valid for both bulk and wet-only precipitation collectors. All samples and replacement sample bottles shall be handled with care using clean techniques in order to avoid contamination during transport and storage. Sample bottles shall only be handled using powder-free plastic or nitrile gloves and all bottles shall be kept in double or triple plastic zip-lock type bags during transport and storage.

Below is a list of equipment needed for retrieval of the sample, cleaning the precipitation collector and installation of a new replacement sample bottle. The following items should be transported in a durable box or rubber bin to the sampling site:

- Powder-free plastic or nitrile gloves
- New sample bottle acidified with HCl (double or triple bagged)
- Rinsing bottle (500 ml) with ultrapure de-ionised water (3.1)
- 100 ml graduated cylinder
- Clean particle-free paper towels(e.g. Crew wipes)
- Zip-lock type plastic bags
- Field sample sheet, pencil and mark pen
- Spare parts: Acid cleaned funnel, capillary/tube and bottle connector stored in double zip bags

## **Procedure**

1. Upon arrival at the site, inspect the area around the collector for any disturbances or unusual activity. Inspect the precipitation collector and rain gauge. Note whether all instrumentation is functioning properly.
2. Stand downwind of the precipitation collector before opening it to retrieve the sample. This will prevent any particles on your person from being transported into the sample.
3. Record the minimum and maximum temperature of the precipitation collector cabinet. In the case of an automated collector, if the cabinet temperature is not between 5° C and 35° C, adjust the thermostat to obtain a temperature that is within the acceptable range.
4. While wearing new gloves release the sample bottle from the connector and bring it out from the precipitation collector.
5. Put the lid on the bottle, tighten and examine the sample regarding particles, colour etc. Make notes in the field sample sheet accordingly.
6. Place the sample in double or triple zip-type bags and mark with date and sample number.

7. Note the time and date of sample retrieval on the field sample sheet.
8. In the case of overflow, measure the volume in the overflow container by pouring it into a 100mL graduated cylinder. Record the overflow volume on the field sample sheet. The excess water should be poured out on the ground, not into the sample bottle.
9. Carefully examine the funnel, capillary/tube and bottle connector regarding dust, insects and bird droppings, etc. Note any observations on the field sheet.
10. For wet-only collectors, clean the automatic lid using de-ionised water (3.1) and a clean particle-free paper towel. Test the lid to confirm that it is opening/closing properly by lightly wetting the precipitation sensor. Clean the precipitation sensor by rinsing with de-ionised water and if necessary gently wipe with a clean paper towel.
11. Install the new bottle into the collector. Keep the cap on the bottle until the new funnel and capillary are in place. Note the date and time on the new field sample sheet.
12. Install a new funnel/capillary by holding each inside their zip-lock bag until they are in place in the collector. Remove the bags and ensure that the funnel and capillary are properly attached.
13. Remove the cap from the bottle and attach the bottle to the new capillary.
14. Close the precipitation collector and make a final check of the old field sample sheet to verify that it is complete.
15. The precipitation sample, used funnel and capillary, and the field sample sheet should be shipped to the designated analytical laboratory for analysis. If it is not possible to ship the sample and supplies immediately upon collection, alternatively the sample may be stored in a refrigerator at the site or nearby laboratory for up to one month before sending to the designated analytical laboratory.
16. If necessary, download the rain gauge data.

An example field sampling sheet is shown in Annex B.

The site operator is responsible for maintaining the collector, as well as identifying and trouble-shooting problems with the collector. If problems with the collector cannot be resolved immediately by the operator or replacement parts are needed, the operator should contact the analytical laboratory which has been assigned to them. The analytical laboratories will be able to assist with more advanced trouble-shooting, acquiring necessary parts for the collector, etc.

## *10. Sample retrieval and handling of sampling materials at the sampling site; An alternative method, using disposable bottles*

At sites equipped by a laboratory or similar facilities, simplified procedures for handling samples and cleaning of the sampling equipment can be used. The use of disposable bottles that can be used as is directly from the provider, together with a cleaning procedure at the site or at a nearby laboratory is cost efficient. This is especially useful if the distance between the measurement site and the analysing laboratory is long and when transportation possibilities are limited.

The properties of a fluorinated high density polyethylene bottle with 1000 ml volume (FLPE, product No: 2097-0032, manufactured by Nalgene) has been tested in terms of its blanks and holding capacity in respect to mercury, see reference [9]. The tests show that the Hg blanks obtained after storing deionised water samples (with the normal HCl addition) are sufficiently low. The holding tests also show that this bottle is suitable for sampling of mercury in precipitation.

All sampling equipment must first be cleaned using the thorough procedures as described in Chapter 8 before it can be used. The cleaning should be performed at the laboratory analysing the precipitation samples. As an alternative to send the sampling equipment to the analysing laboratory for cleaning after each sampling period it may be cleaned at the sampling site, provided that laboratory facilities are available. At least one time per year all sampling equipment should be sent to the analysing lab to be cleaned according to the procedures described in Chapter 8.

For instruction on collecting precipitation samples and start new sampling, see chapter 9. The sampling funnel and additional equipment are cleaned according to the instructions below.

### ***Cleaning routine at the sampling site***

1. Wash the equipment carefully normal tap water using an alkaline detergent.
2. Rinse thoroughly with tap water and finally with deionised water.
3. The sampling equipment is leached in a leaching bath with diluted hydrochloric acid.
4. Keep the equipment in the leaching bath (lid on) all the time when not in use.
5. Before use, put new disposal gloves on and pick up the equipment from the leaching bath.
6. Rinse with deionised water and shake of the water and let dry.
7. Put the equipment into double plastic bags and bring it to the sampling site.

## ***Leaching tank***

The leaching bath consists of a box made from polypropylene, according to Figure 2. Before use it should be acid cleaned at the analysing lab, following the procedures in Chapter 8.



Figure 2. Plastic box made from polypropylene.

The leaching bath is prepared by filling the box with deionised water, to a level of about 15 cm from the bottom. Then 20 ml of concentrated hydrochloric acid (3.4) per litre deionised water is added (use gloves and glasses). The leaching bath should be renewed once a year.

## ***11. Analysis***

Following collection the precipitation samples should be sent to the designated GMOS laboratory for analysis. The analysis methods for total mercury given in the EMEP manual [2] or EPA Method 1631E [4] are both approved methods for the GMOS project. Given that the two analytical methods are very similar, only the EPA 1631E Method is outlined here. Analytical laboratories should see the corresponding EMEP and EPA documentation for further details on analytical protocols. Given that samples are preserved in the field using 5 ml/l of HCl, samples should be stable for up to 90 days after the date of collection [4] and as such should be analyzed within this time period.

In summary, an example of the EPA Method 1631 Revision E is as follows:

When samples arrive at the designated analytical laboratory, BrCl in HCl (3.11) should be added to the sample to give a BrCl concentration of 1% (v/v). The bottle should be capped and stored for at least 24 hours prior to analysis.

Prior to analysis, a weighed sample aliquot of 50-100 mL should be taken from each sample and transferred to acid cleaned 125 mL Teflon bottles or sampling vials. Add 200  $\mu$ L of 20% hydroxylammonium hydrochloride (3.12) to the aliquot and pour immediately into a purge vessel. Add 300  $\mu$ L of 25% SnCl<sub>2</sub>(3.13) to the sample and purge using ultra-pure argon onto

a gold trap. Analyze the sample for mercury concentration using thermal desorption and dual gold trap amalgamation with CVAFS.

An average blank value should be determined for each analytical session. This value should be subtracted from the total concentration to determine the sample mercury concentration for each sample.

The detection limit for this method is expected to be ~0.1 ng/L (3 times the standard deviation of the reagent blanks).

This method is described in further detail in EPA Method 1631E.

## 12. QA/QC

### **Field QA/QC:**

*Field blank:* Field blanks should be taken at least four times each year. Two extra sampling bottles should be brought to the site; one containing diluted HCl, prepared by adding 1 ml diluted HCl (3.10) per 1000 ml ultrapure de-ionised water (3.1) and one empty. After removing the regular sample bottle the empty bottle should be installed and the dilute HCl poured through the sampling device (e.g. funnel and capillary). The bottle should be stoppered, double bagged and immediately brought to the laboratory for analysis. The mercury content of the dilute HCl should be compared to that of samples stored in a clean laboratory environment. If the blank values exceed 20% of the concentrations normally measured at the site, measures should be taken to reduce the blanks (for example, by exchanging or by cleaning the sampling devices). The yearly average blank value is used to determine the detection limit.

### **Laboratory QA/QC:**

The following QA/QC techniques are recommended based upon the NADP analytical QA/QC protocol [7].

*Analytical Blank:* An average blank value should be determined for each analytical session. This value should be subtracted from the total concentration to determine the sample mercury concentration for each sample.

*Certified reference materials:* Certified reference materials should be tested regularly to verify that standards are acceptable. Weekly, a standard reference material with a concentration representative of precipitation samples collected during this project should be analysed. The NADP recommends a standard concentration of 4.64 ng/L be used. Laboratory spike recovery tests should also be analysed weekly.

*Reagents:* New reagents should be tested before use to confirm they are acceptable for use.

*Analytical precision:* Sample duplicates and reference materials should be regularly tested. Regular blank testing of sample bottles (laboratory and field blanks) should also be performed. Quality control samples should also be analyzed (see below).

*Quality Control (QC) samples:* The following should be analyzed regularly in the same manner as samples [7].

*Field blank:* described above

*Laboratory bottle blank:* after bottle is cleaned, 20mL of 1% HCl is added. Two bottles are randomly selected and analyzed each week

*Preparation blank:* 1% (v/v) 0.2N BrCl, 0.2mL 20% hydroxylamine HCl, and 0.3mL 20% SnCl<sub>2</sub> in 100mL of reagent water.

*Ongoing calibration standards:* continually analyzed during sample analysis, typically after a suite of 10 samples and at the end of the analytical session. 1.0ng Hg standard is used.

*Ongoing calibration blanks:* continually analyzed during sample analysis, typically after a suite of 10 samples and at the end of the analytical session.

*Matrix duplicates:* sample is split into two portions to be compared analytically

*Matrix spikes:* MDN sample with known Hg content in supplemented with 1.0ng Hg standard

*Certified reference material:* commercially available material with known quantity of analyte in specific matrix. NIST 1641d is used.

*Blank spikes:* reagent water or analytical reagents with predetermined quantities of analyte added. Undergoes same preparation and analysis as corresponding samples.

*Method Detection Limit (MDL):* seven or more low-level matrix-specific spikes are processed according to preparation and analytical method protocols.  $MDL = t \cdot SD$  of replicates ( $t$  is Student's T-value for the number of replicates minus one degree of freedom and SD is the standard deviation) [7].

*Control charts:* track QC results over time and detect unfavorable analytical trends.

*Laboratory performance:* Laboratory personnel must verify instrument performance routinely. A certified technician should calibrate analytical instruments once per year. Internal laboratory audits should be performed quarterly.

### **External QA/QC**

Laboratories that perform analysis of mercury in precipitation samples collected within GMOS shall participate in a relevant external quality assessment scheme or proficiency testing scheme such as participating in laboratory and field intercomparison. External laboratory audits should be performed once every three years. Laboratory inter-comparisons will also be performed among the GMOS designated analytical laboratories as well as with the analytical laboratories of external partners. GMOS laboratories may also participate in the Brooks-Rand laboratory inter-comparison which takes place every spring. Furthermore, GMOS laboratories may also perform inter-comparisons with other large-scale networks, such as the U.S. Mercury Deposition Network (MDN) and the Canadian Air and Precipitation Monitoring Network (CAPMoN)

### 13. *Data Management*

Each site will submit a weekly form with information about the sample collected, including sampling period, sample condition, precipitation information, and site operation (see Annex B). The rain gauge data should also be provided.

The analytical laboratory is responsible for verifying and validating the weekly site data and performing initial data assessment.

Results will also be compared with the site operator's notes, to see if untypical results are due to special activities or conditions at the site. If it is decided to reject or to correct data, the reason for the correction should be stated, and the data should be flagged.

Reported sample volumes will also be compared with daily precipitation amounts from the standard meteorological rain gauge at the site to give an independent control of the sample collection.

The laboratory analyst is responsible for reviewing the analytical data. The analytical laboratories participating will perform an overall data review.

### 14. *References*

- [1] NEN-EN 15853 (en). Ambient air quality - Standard method for the determination of mercury deposition. ICS 13.040.20, June 2010.
- [2] EMEP manual for sampling and analysis, CEN/TC 264 rev, NILU, Kjeller, Norway: <http://www.nilu.no/projects/ccc/manual/index.html>
- [3] NADP MDN Project Specific SOP. FGS-MDN-01. Revised March 17, 2003.
- [4] Method 1631, Revision E: Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry.
- [5] Manual for the GAW precipitation programme. Guidelines, Data Quality Objectives and Standard Operating Procedures. WMO TD No. 1251. WMO/GAW Report nr 160. WMO, 2004.
- [6] NADP Site Selection and Installation Manual. September 2009.
- [7] NADP MDN Quality Assurance Plan, Mercury Analytical Laboratory. November 10, 2006.
- [8] Landis, M.S. and Keeler, G.J., 1997. Critical Evaluation of a Modified Automatic Wet-Only Precipitation Collector for Mercury and Trace Element Determinations. *Environmental Science and Technology* 31, 2610-2615.
- [9] Wängberg I, Horvat M. and Sprovieri F. Blank and holding tests with PETG and FLPE bottles. Internal GMOS report.

## Annex A

### Commercially available wet-only and bulk samplers for mercury

<p>Loda Electronics Co</p> <p>Wet-only collector</p> <p>Model 2001 precipitation samplers for the Mercury Deposition Network (MDN). Price: XXX US \$</p> <p><a href="http://www.lodaelectronics.com">http://www.lodaelectronics.com</a></p>	
<p>N-CON Systems Mercury Deposition Network sampler</p> <p>Wet-only collector Funnel diameter: 124 mm (120.8 cm<sup>2</sup>) Martha Beach Jack Beach</p> <p><a href="mailto:nconsystems@gmail.com">nconsystems@gmail.com</a></p> <p>Price: ≈4100 US \$</p>	
<p>Eigenbrodt Environmental Measurement systems</p> <p>Wet-only collector Equipped with heating and cooling (-25 – +35 °C)</p> <p>NSA 181/KE 490 cm<sup>2</sup> collection area glass funnel Price ≈ 18000 EUR</p> <p><a href="http://www.eigenbrodt.de">http://www.eigenbrodt.de</a></p>	

## Annex B: GMOS Mercury Wet Deposition Tracking Form

<b>Site Name:</b>	<b>Country:</b>
<b>Sample ID:</b>	<b>Funnel ID:</b>
<b>Date Samples Shipped:</b>	<b>Operator:</b>

<b>Date of Setup (dd/mm/yyyy)</b>		<b>Date of Collection (dd/mm/yyyy)</b>	
<b>Time of Setup (UTC)</b>		<b>Time of Collection (UTC)</b>	
<b>Sampler Type</b>	<b>Type of Precipitation</b>		<b>Overflow (ml)</b>
Wet-Only <input type="checkbox"/> Bulk <input type="checkbox"/> <b>Model:</b>	Rain <input type="checkbox"/> Snow <input type="checkbox"/> Mix <input type="checkbox"/>		
<b>Operator Comments:</b>			

*Only For Use in the Analytical Laboratories*

<b>Laboratory Name:</b>	<b>Date Received:</b>
<b>Comments:</b>	<b>Received by:</b>

Oxidation of Mercury Precipitation samples with 1% BrCl.

<b>1. Total Bottle Weight</b>	
<b>2. Original Bottle Weight</b>	
<b>3. Precipitation Volume (subtract #2 from #1)</b>	
a) Record HCl batch number: _____ b) Add the original HCl amount (20 mL/L, determined by the bottle size) to the <b>Precipitation Volume</b> to determine the <b>Sample Volume</b> .	
<b>4. Sample Volume</b>	
a) Multiply <b>Sample Volume</b> by 0.01 to determine <b>BrCl Volume to Add</b> .	
<b>5. Volume to Add</b>	BrCl:
<b>6. BrCl Batch Number</b>	BrCl:
<b>Date Sample Processed, Initials</b>	
<b>Date Sample Analyzed, Initials</b>	

