UNEP-GEF Project
"Development of a Plan for Global Monitoring of Human Exposure to and Environmental Concentrations of Mercury"
Air monitoring component

UNEP-GEF Project

"Development of a Plan for Global Monitoring of Human Exposure to and Environmental Concentrations of Mercury"

Final Technical Progress Report

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1. Introduction to the Report

This Technical Progress Report is aimed to report on the work made by the CNR-IIA team, during the period December 2014 – June 2018, for the implementation of the Air Component of the GEF-funded project "*Development of a Plan for Global Monitoring of Human Exposure to and Environmental Concentrations of Mercury*" (hereinafter referred to as 'the Project'), agreed between the United Nations Environment Programme (UNEP) and the National Research Council - Institute of Atmospheric Pollution Research (CNR-IIA), through the project Cooperation Agreement (signed by CNR-IIA on 2nd December 2014) and its successive Amendment N. 1 to the Project Cooperation Agreement (signed by CNR-IIA on6th September 2016). The period for the implementation of the last step of the Agreement's activities has been extended by the Small Scale Funding Agreement (signed by CNR-IIA on 24th April 2018) up to the end of July 2018.
The Project has involved the CNR-IIA for the implementation of the Air Component, the World Health Organization (WHO) Europe for the implementation of Human-Bio Monitoring Component and the UNEP Chemicals and Health Branch as executing Agency.
The project is funded through grant 4E59 of the Global Environment Facility (GEF) to UNEP and with co-finance of WHO Europe, CNR-IIA and UNEP.

1.1 Introduction on mercury monitoring and the project

Mercury (Hg) is ubiquitous in the boundary layer, as well as in the free troposphere and stratosphere. It has ground level background concentrations that are nearly constant over hemispheric scales, with southern hemisphere concentrations slightly lower than those in the northern hemisphere. In the troposphere, atmospheric Hg exists predominantly as gaseous elemental mercury (Hg^0; GEM), gaseous oxidized mercury (GOM), and fine particle-bound Hg ($PBM_{2.5}$). Conversions between different Hg forms add complexity to the ability to understand Hg chemistry and transport on the local, regional, and global scales.
Mercury cycling between different environmental compartments depends on the rate of different chemical and physical mechanisms (e.g., dry deposition, wet scavenging) and meteorological conditions, as well as on anthropogenic emissions and atmospheric forcing. Consequently, a complex mixture of chemical, physical and meteorological parameters control the fate of atmospheric Hg, and it is a great challenge to understand the global impact of Hg emissions and deposition. The increase of mercury in the environment over the last hundred years was mostly due to human activity. European Member states are legally obliged to progressively reduce mercury discharges, emissions and losses to zero within the next 20 years.
To prevent global mercury pollution and damage to human and environmental health a new global and legally binding "Minamata Convention on Mercury" has been agreed at the UNEP Diplomatic Conference held in October 2013 in Japan.
The Minamata Convention stresses the importance of mercury monitoring by asking Parties to develop and improve monitoring tools and methods in its Article 19, called "Research, development and monitoring" and by expecting an effectiveness evaluation of the Convention to be conducted six years after its entry into force and periodically afterwards (Article 22).

The Chemicals Branch of UNEP, through the coordination of this Project, aims to strengthen capacity for mercury monitoring at the global level by combining existing mercury monitoring programmes and activities under the UN umbrella and to serve the Minamata Convention, its parties and the global community.

So far, neither air monitoring programmes/projects nor human monitoring programmes/projects have been reviewed ore combined with a view to serve a global chemicals convention. This project is aimed to offer a unique opportunity to create state-of-the-art reports on existing projects, identify key stakeholders, stimulate cooperation of these to meet the requirements in the Minamata Convention on Mercury, assess progress and to close gaps. This UNEP-coordinated project started with the two major players in monitoring environment and humans: GMOS and WHO.

The global goal of the project is to strengthen the capacity for global monitoring of human exposure to and environmental concentration of mercury. The project aims, in particular, to:

a) harmonize approaches for mercury monitoring, and

b) strengthen the capacity for mercury analyses in humans and in the environment.

The project consists of three components:

- **Component 1:** Review of existing information on human exposure to and environmental concentrations of mercury;
- **Component 2:** Development of a monitoring plan on presence of mercury in ambient air;
- **Component 3:** Development of a monitoring plan on human exposure to mercury.

The execution of these components has been supported by UNEP, in close collaboration with WHO Europe and CNR-IIA (with a co-finance by the EU project Global Mercury Observation System – GMOS, www.gmos.eu), local national staff and external international and regional specialists.

CNR-IIA has conducted the activities foreseen in Component 2 described hereafter.

Component 2: Development of the first global monitoring plan on presence of mercury in ambient air.

In Component 2, objectively verifiable indicators include:

the availability of quantitative results from new sampling stations; a GMOS network progress report with air monitoring results that can be integrated into UNEP/GEF report; report/paper characterizing the new sampler; published protocols; report presenting measured data from deployment of PAS in at least three developing country regions; laboratory results; report on comparison of mercury species to total mercury as well as results from active versus passive samplers; and a proposal on global air sampling.

Activities and outputs geared towards the achievement of Outcome 2 have been lead by UNEP in close cooperation with CNR-IIA and GMOS network, and national (site-specific) project partners.

Key activities include:

the development of a suitable sampler to collect gas-phase total mercury; the development of sampling and analysis protocols for PAS sampling sites; PAS sampling by project partners and

analysis of disks; ambient air sampling at UNEP/GMOS superstations; and the drafting of an international air monitoring plan.

Planned activities:
Activity 2.1: Establish a network for atmospheric samples by developing passive air samples to complement the GMOS work

Activity 2.2: Conduct a pilot testing of the atmospheric network for one year

Activity 2.3: draft a proposal for a worldwide air monitoring plan, including interaction between active and passive sampling techniques.

Expected Outcome:
Enhanced understanding of mercury concentrations in ambient air through the strengthening of the Global Monitoring Observation System (GMOS) and the development of the complimentary passive air sampling (PAS) network for ambient air concentrations improves national capacity to analyse mercury in ambient air and to develop and apply sound mercury mitigation plans.

Expected Outputs:

1. Comprehensive network and stations for mercury atmospheric samples established and ready to be used
2. Results of one-year pilot test of the atmospheric network for mercury in ambient air available in a consolidated report
3. Draft proposal for a monitoring plan for mercury on ambient air includes active and passive sampling techniques and short, medium and long term actions.

The project has made use of some GMOS stations, indicated and described in following chapters, which will allow the comparison of sampling and analytical methods.

As stated at the First meeting of the Conference of the Parties to the Minamata Convention on Mercury, held in Geneva, from 24–29 September 2017, the urgent need for a framework for the effectiveness evaluation of the Minamata Convention on Mercury has been recognized worldwide. This framework has to include a strategic and cost-effective approach that provides appropriate and sufficient monitoring data.

The GMOS network, that has supported the Project, and its further development is an important an unique framework to support the Minamata Convention on Mercury, with particular regard to Article 19 on Research, development and monitoring, and article 22 on effectiveness evaluation, because GMOS can provide high quality and coordinated mercury air monitoring activities built on existing monitoring networks.

1.2 GMOS Global Network Infrastructure

The GMOS global network has been established in the framework of the GMOS project, a five-yrs project (2010-2015) funded by the EC within the 7FP with the aim to provide high-quality Hg datasets in the Northern and Southern Hemispheres for a comprehensive assessment of atmospheric Hg concentrations and their dependence on meteorology, long-range atmospheric transport and atmospheric emissions on a global scale.

The GMOS network consists to date of 43 monitoring stations worldwide distributed and located both at sea level (i.e., Mace Head, Ireland; Calhau, Cape Verde; Cape Point, South Africa; Amsterdam Island, southern Indian Ocean) and high altitude locations, such as the Everest K2 Pyramid station (Nepal) at 5050 m. asl and the Mt. Walinguan (China) station at 3816 m. asl, as well as in climatically diverse regions, including polar areas such as Station Nord (Greenland), Pallas (Finland), and in Antarctica, Dome C and Dumont d'Urville. The monitoring sites are classified as Master (M) and Secondary (S) in respect to the Hg measurements performed. In particular, those which are providing Hg speciation data are the Master Stations whereas the Secondary Stations are those that are performing only TGM/GEM measurements (Sprovieri et al., 2016).

Figure 1 shows the map of the GMOS monitoring sites with information on the type of monitoring stations (Master and/or Secondary) established as part of GMOS project as well as already existing monitoring sites as part of European and International monitoring programs and managed by both GMOS partners and External partners who have agreed to share their monitoring data and submit them to the central database following the principles of GEO/GEOSS (Associated GMOS sites). More details about the sites can also be found at the following website: www.gmos.euand, in particular, at www.gmos.eu/sdi/ . Eleven monitoring stations managed by external partners are included within the global network sharing their data to the GMOS central database. These new associated stations follow the “Governance and Data Policy of the Global Mercury Observation System” established for the GMOS network.

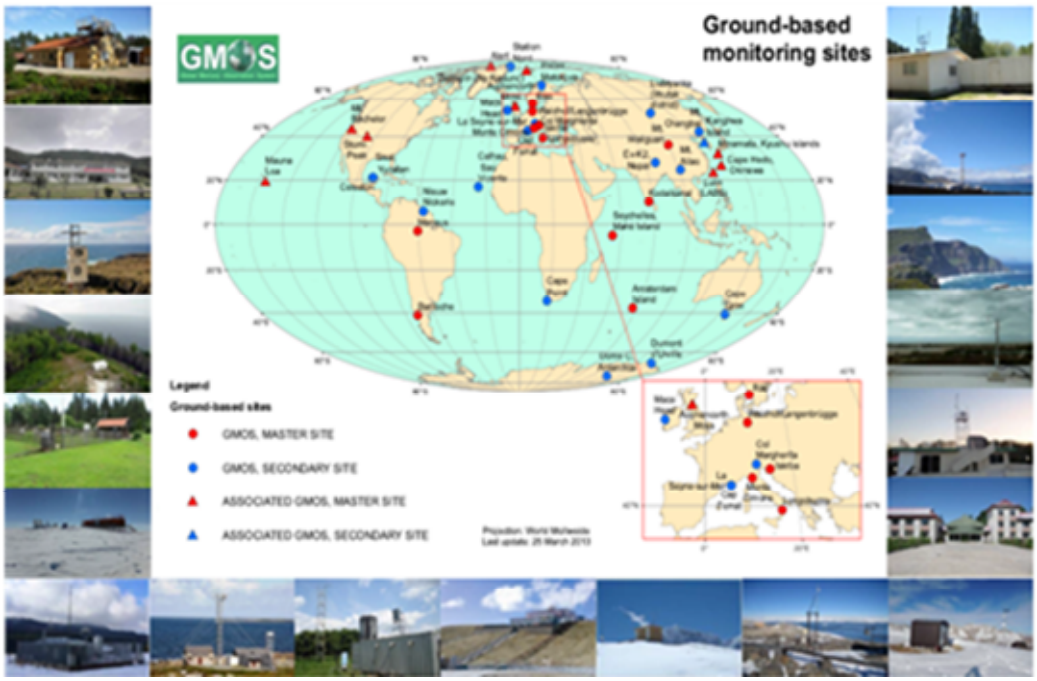


Figure.1 Map of the GMOS monitoring sites

1.3 Integration of GMOS with existing programs and Quality assurance and quality control procedures adopted within the global network.

During the implementation of the GMOS global network, one of the focal point was the integration and harmonization of the GMOS measurement network with external network to allow the exchange and joint evaluation of data. Integration of GMOS with other existing programs included the arrangement of inter-comparisons regarding measurement methods used in GMOS and involved collaboration with external regional networks. Most ambient mercury (Hg) measurements are performed using very similar methods. However one of the overall goal was the development of common protocols regarding how the instruments should be used and maintained in the field necessarily to assure that measurement result from different sites within GMOS and associated networks are comparable. A central part in integrating GMOS with other existing measurement programs was therefore the GMOS Standard Operational Procedures (SOPs).

Harmonized Standard Operating Procedures (SOPs) as well as common Quality Assurance/Quality Control (QA/QC) protocols have been developed according to measurement practices and methods followed within existing regional monitoring networks and based on the most recent literature to achieve a high degree of harmonization (Sprovieri et al., 2016).

In respect to data collection and management, the worldwide configuration of the GMOS network poses a challenge for Hg scientists because traditional approaches to quality assurance and quality control (QA/QC) are no longer practical when compared with the size of datasets coming from different monitoring stations across the globe, also in near-real time way. Moreover, harmonization and comparability of atmospheric Hg measurements worldwide is needful for a global infrastructure in order to secure useful monitoring data for both the scientific and policy communities.

In order to ensure uniformity of Hg measurements across the global network, GMOS developed a centralized quality assurance (QA) and quality control (QC) system (termed GMOS-Data Quality Management, G-DQM) able to acquire atmospheric Hg data in near real-time and, furthermore, to assure and control quality of collected Hg datasets (Sprovieri et al., 2016). G-DQM system is designed to automate the QA process making it available on the web with a user-friendly QC step that ensures the expert supervision. G-DQM is able to verify if the monitoring process adheres to standard procedures in a way that minimizes losses and inaccuracies in data production. G-DQM is part of the GMOS Cyber-Infrastructure (CI), which is a research environment that supports advanced data acquisition, storage, management, integration, mining and visualization, built on an IT infrastructure (Cinnirella et al. 2014).

All datasets collected by GMOS partners respected the same SOPs and the same data lineage. It is possible to match both requirements by plugging the QA/QC process into the CI and providing QA/QC processes as a service. Using this approach it is also possible to define a single automated process for all data collected by the network. Details and definition of each constituting component of the system are reported elsewhere (D'Amore et al., 2015).

2. Sampling and analytical methodologies by conventional instrument: GMOS Standard Operational Procedure (SOP)

Within the GMOS project a state-of-the-art observation system has been developed able to provide the concentration of Hg species in ambient air and precipitation on the global scale in order to provide measurement data bases useful for creating a comprehensive assessment of atmospheric Hg concentrations and their dependence on local meteorology, long-range atmospheric transport and atmospheric emissions as well as for modelling applications on regional and global scale. The assessment of the ongoing effect of mercury on humans and the environment is dependent on accurate measurements of its concentrations and trends. Without accurate, precise measurements of atmospheric Hg species, we cannot understand the chemistry, interpret observed spatial and temporal patterns, as well as improve regional and global models.

The relationship between emission and deposition of atmospheric Hg species is a critical issue also for the regional and global modeling studies to support the development of policies to reduce the Hg levels in the environment.

Hg measurements were carried out using high-quality techniques by harmonizing the chosen measurement techniques with those being performed at existing monitoring stations around the world. Special attention was paid in respect to protocols harmonization, data quality collection and data management in order to assure a full comparability of site specific observational datasets. During the planning and implementation stage of the GMOS global network, harmonized Standard Operating Procedures (SOPs) as well as common Quality Assurance/Quality Control (QA/QC) protocols have been indeed addressed in accordance with the measurement practice adopted in well-established regional monitoring networks and based on the most recent literature.

A great effort was in particular made to implement a centralized system (termed GMOS-Data Quality Management, G-DQM) able to acquire atmospheric Hg data in near real-time and, furthermore, to assure and control quality of collected Hg datasets. This system introduced a big novelty for data control programs, consisting in a service approach that facilitate real-time adaptive monitoring procedures, thus being essential in preventing the production of poor-quality data.

2.1 Methods for the determination of TGM and GEM

The Standard Operational Procedure (SOP) described hereafter is based upon the European standard (NEN-EN 15852 (en) for total gaseous mercury – TGM, and gaseous elemental mercury - GEM) measurements and the Canadian CAMNet/CAPMoN SOP for TGM measurements. It therefore describes methods for determining TGM and GEM in ambient air using the Tekran 2537 or the Lumex RA 915 AM. The Tekran system uses CVAFS to quantify ambient mercury concentrations, while the Lumex system uses Zeeman CVAAS. The proper operation and maintenance of the Tekran and Lumex systems are described below. This operating procedure is designed to support consistent and systematic sampling among the contributing GMOS sites. Results are reported as the average mass of TGM or

GEM per volume of air at 273.15 K and 101.325 kPa, measured over a specified time period. The time should be reported as GMT time and concentrations should be reported as ng m^{-3}. Technical information is provided from the instrument manuals for the Tekran Model 2537 Mercury Vapour Analyser and the corresponding manual for the Lumex RA 915 AM Automatic Mercury Monitor. The SOP also contains quality control protocols to be used in the field when performing TGM and GEM measurements.

2.1.1 GMOS Standard Operational Procedure.

2.1.1.1 Abbreviations and Definitions

Mercury Species:

Hg	Mercury
TGM	Total Gaseous Mercury: the summary of gas phase species of mercury, including ground state and reactive forms
GEM	Gaseous Elemental Mercury (Hg^0): gas phase mercury in its ground electronic state
GOM	Gaseous Oxidized Mercury: oxidized gas phase mercury compounds
PBM2.5	Particulate Bound Mercury less than 2.5 µm: mercury that is bound to particles with a mean aerosol diameter of 2.5 µm or less.

Analytical Terms:

CVAAS	Cold Vapour Atomic Absorption Spectrometry
CVAFS	Cold Vapour Atomic Fluorescence Spectrometry
Zeeman CVAAS	Zeeman Cold Vapour Atomic Absorption Spectrometry
MFC	Mass flow controller
MFM	Mass flow meter
Zero air	Pre-filtered mercury free air used for calibration
UHP	Ultra High Purity (e.g. for Argon gas used by the Tekran; grade 4.8 (99.998%) or higher)
MDL	Method Detection Limit: the minimum concentration of a substance that can be measured and reported with 99% confidence that the concentration is greater than zero
QA	Quality Assurance
QC	Quality Control

Units:

ng	Nanogram; 10^{-9} g
ng m^{-3}	nanograms per cubic meter

°C	degrees Celsius
cm	centimeters
L	liters
lpm	liters per minute
psi	pounds per square inch
kPa	kilopascals
V	volts.

2.1.1.2 Gases and chemicals

3.1 Grade 4.8 (99.998%) or higher ultra high purity (UHP) Argon for use as a carrier gas for the CVAFS within the Tekran2537.

3.2 Nitrogen, of purity greater than 99.999 %, suitable for use as a carrier gas for CVAAS.

3.3 Air, of class 3.3.3 purity or better according to ISO 8573-1:2010.

3.4 Elemental mercury, of purity 99.9999 %, for preparation of gaseous mercury vapour standard.

WARNING — Mercury is toxic by skin absorption and inhalation of vapour. Use suitable personal protective equipment (including gloves, face shield or safety glasses, etc.) and minimize exposure by using a fume hood.

3.5 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.

3.6 Hydrochloric acid (HCl), concentrated, density ~ 1.18 g/ml, mass fraction 36 % to 38 %.The concentration of mercury shall be less than 0.002 mg/l.

3.7 Hydrochloric acid (3.6), diluted 1:49 with deionised water (3.5) for cleaning of filter housings, and other and sampling components.

WARNING — concentrated hydrochloric acid is corrosive and is also an irritant. Avoid contact with the skin and eyes, or inhalation of the vapour. Use suitable personal protective equipment (including gloves, face shield or safety glasses, etc.) when working with hydrochloric acid. Handle open vessels containing concentrated hydrochloric acid in a fume hood. The vapour pressure of hydrochloric acid is high. Therefore beware of pressure build-upin capped vessels when preparing dilute hydrochloric solutions.

3.8 Laboratory grade methanol: to use for cleaning and drying sampling components.

3.9 Soda lime: soda lime traps are often placed upstream of the detector sample filter to remove free halogens that can shorten the life of the gold trap cartridges. Soda lime should be non-indicating, 4-8 mesh, and free of mercury. Laboratories should contact one of the GMOS work package leaders for information about where and how to purchase acceptable soda lime for the Tekran system.

3.10 Internal permeation source: the 2537 analyzers are equipped with internal permeation sources capable of calibrating the system automatically at a preset time or manually when initiated by the operator.

2.1.1.3 Principle of TGM and GEM measurements

Total gaseous mercury (TGM) is the sum of gaseous elemental mercury (Hg^0; GEM) and gaseous oxidised mercury (GOM), which may constitute from both inorganic and organic gaseous mercury species. Hg^0 is generally the most dominating mercury species in the background atmosphere and constitutes often more than 98% of the total gaseous mercury. Automatic TGM instruments use the amalgamation technique to trap gaseous mercury in the air. Exactly determined air volumes are pulled through a cartridge containing an adsorbent (a gold surface), onto which all gaseous mercury quantitatively is adsorbed. The mercury is then thermally desorbed as GEM (Hg^0) and detected by CVAFS or alternatively by CVAAS. The mass of Hg^0 as a function of the detector response is obtained by calibration using known amounts of Hg^0 vapour. The accuracy of the measurement depends on the accuracy of the calibration and the air volume measurements. Normally mass flow controllers or mass flow meters are used to determine the air volume. The TGM concentration is presented as ng of Hg^0 per m^3, using volumes at standard pressure and temperature. The CVAFS instruments are more sensitive in comparison to CVAAS, but require pure Ar or He gas during the desorption and detection step, whereas CVAAS instruments use mercury free air or nitrogen.

GEM can automatically be measured by pumping ambient air through a long-path optical cell and determining the absorbance of gaseous Hg^0 using Zeeman CVAAS. The absorption signal is calibrated against known concentrations of Hg^0 vapour. With this method the concentration of Hg^0 in the air inside the optical cell is obtained. This technique does not require precise volume measurements. However, the pressure and temperature in the instrument must be measured in order to recalculate the Hg^0 concentration to standard pressure and temperature. The accuracy of the measurement largely depends on the calibration but also on the internal pressure and temperature measurements.

Ambient concentrations of GEM may also be directly measured using cavity ring-down spectroscopy (CRDS) which also is a CVAAS technique that uses a long-path optical cell. Similar requirements as for Zeeman CVAAS apply regarding the accuracy.

Both CVAFS and CVAAS instruments detect mercury as GEM by UV radiation at 253.7 nm. The fluorescence signal (F) obtained with CVAFS is (after base line correction) directly proportional to the excitation intensity (I_e) times the concentration of GEM,

$$F \propto I_e \times C_{Hg^0} \qquad \text{Equation 4.1}$$

Measurement with CVAAS, requires determination of the total UV-intensity in absence of Hg^0 (I_0) and in the presence of Hg^0 (I),

$$A = \ln\left(\frac{I_0}{I}\right) \propto C_{Hg^0} \qquad \text{Equation 4.2}$$

2.1.1.4 Siting requirements for TGM /GEM measurement

Two types of sites shall exist within the GMOS project:

Master Sites will measure continuous speciated ambient mercury (GEM, GOM, and $PBM_{2.5}$) and total mercury in precipitation.

Secondary Sites will measure total gaseous mercury (TGM) or gaseous elemental mercury (GEM) 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).

Parameter	Minimum Distance to Site (km)		Comments
	Regional/Rural Background Stations	*Global/Remote Background Stations*	
SO_2 or NO_x 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

2.1.1.5 General requirements regarding TGM/GEM measurements

Monitoring of TGM and GEM using automatic instruments requires a measurement cabin or house to contain the mercury instrument and additional equipment. The Tekran or Lumex mercury analyzer should be housed in a sheltered, mercury-free, temperature controlled structure with a bench space of ≥ 2 ft x 2 ft (0.6 m x 0.6 m) [2].

Power requirements for the Tekran 2537A/B are 100/120 V, 50-60 Hz and 250 VA max, 100 VA average (CAMNET, 1999). Power requirements for the Lumex RA 915 are220-240 V, 50-60 Hz and 120 VA max (LUMEX, 2007).

The air to be sampled is pulled via a sample inlet and a sample line to the instrument. The inlet should be installed in a free position at least 2 m above the ground so that the air flow around the sampling inlet is unrestricted. Obstructions to the air flow from buildings, trees and other obstacles shall be avoided. The sampling system should be positioned such that the inlet is ≤ 45° from vertical objects and trees, and ≤ 30° from buildings(GAW, 2004; NADP, 2009).Putting the inlet on top of the measurement cabin is often an optimal solution which also may minimize the length of the sample line. The sampling inlet can be made from borosilicate glass or Teflon. The inlet can be made fairly simple, but it shall be well-supported and constructed so that rain or snow cannot enter into the sampling system. Suitable inlets are commercially available. Two simple inlet designs are exemplified in Figure 2.

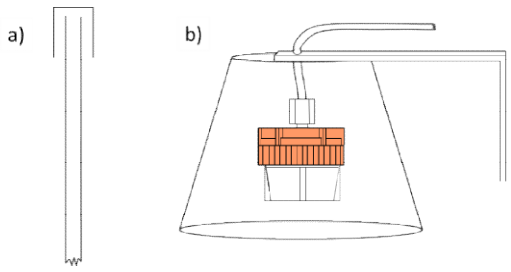


Figure 2. a) Inlet and sampling line consisting of borosilicate quartz glass or fluorocarbon that is protected from rain and snow. This design may require a protecting frame (not shown) which can be made of plastic or metal with coating. **b)** Intake consisting of an open phase filter holder to protect the sample line from particles. 47 mm Teflon filters are recommended for this inlet design. The sample intake is protected from adverse weather conditions by a plastic hood.

The mercury instrument should be installed and connected to the sampling line according to the descriptions given in the user manual provided with the instrument.For the Tekran, a 25 ft heated ¼" Teflon sample line (provided by Tekran) is recommended. A 50 ft heated line is

also available but should only be used if necessary, as the longer sample line can increase flow resistance. Teflon fittings are required for all tubing connections.

Sites may exist in GMOS where due to extreme weather conditions it is necessary to sample ambient air through a high-flow manifold. In these specific cases the use of a manifold and the location of the manifold should be approved by a GMOS Project Coordinator and/or Work Package Leader. The manifold should be high flow and laminar to minimize wall effects. Glass or Teflon manifolds are acceptable. It is advisable that the inlet be positioned ~ 2 m above the shelter height and a 10 µm particulate cut size is suggested. The measurement device (e.g. Tekran or Lumex) should sample from the primary manifold air flow. The measurement device should be connected to the manifold by Teflon tubing. The manifold should be temperature controlled, and the Teflon line from the manifold to the measurement device can be unheated depending on the specific reason for using the manifold at any given site. It is recommended that a filter be installed between the manifold and measurement device to remove any remaining particles from the airstream prior to sampling by the measurement device. Teflon filters (0.2 um pore size, 47 mm) are recommended.

It is recommended that the site operators occasionally (e.g. every 3 months) monitor the GEM concentration inside the monitoring shelter to determine whether there is any risk of contamination or bias from within the shelter. Shelter air should contain < 15 ng/m^3 of Hg.

Trace metal clean techniques must be used at all times in the laboratory and in the field when handling or preparing supplies and performing necessary tasks for ambient mercury sampling. Clean techniques are critical for preventing the contamination of sampling equipment and ensuring the collection of the highest quality data. This includes wearing appropriate clean, non-talc gloves (e.g. nitrile) when handling any component that will come in contact with the sampling stream. In the laboratory, such components should be handled in a clean room, clean bench, or glove box to avoid exposure to contaminated air.

2.1.1.6 Operation and routine maintenance of the Tekran and Lumex systems

Site operators are strongly encouraged to read the Tekran or Lumex operating manuals which accompany their instruments in order to fully understand how the instrument works and what steps are required to maintain the functionality of the instrument. This is especially important for new operators who are using these instruments for the first time. The guidelines below are intended to assist the operator with installing the instrument and maintaining it over time to ensure the collection of the highest quality data within the GMOS project.

Recommended instrument settings for the Tekran model 2537A/B instrument

The parameter settings recommended at a typical background site are listed below. The Autocal feature should beset to “Yes”to indicate that the internal permeation source used for automatic calibrations is chosen (See section 7.5 below). Note that the sample timing in Table

2could be optimized for more remote sites where it is difficult to obtain Argon (e.g. longer sampling time to reduce the frequency of Argon usage). However, more frequent heating is better for the gold cartridges and as such Tekran recommends a 5-minute sampling interval. As such, 5-minute sampling is recommended for the majority of GMOS sites.

Table 2: Recommended parameter settings for the Tekran model 2537A/B instrument

Method. Edit. Timing-1

Sample:	300 s	FlushHi:	40 s
Calib:	300 s	Meas-dly:	5 s
Zero-sub:	No [(a)]	BL-Time:	20 s

Method. Edit. Timing-2

Intg-Dly:	15 s	Pk-Time:	35 s
HtADur:	32 s	Cool-Dn:	80 s
HtBDur:	32 s	Round:	5min

Method. Edit. other

Car-Meas:	80 ml/ min	SmplRate:	1.00 l/min
Car-Idle:	5 ml/ min	WarmA:	3 %
CarFlush:	100 ml/ min	Warm B:	3 %

Method. Edit. Perm-Src

Autocal:	No/Yes	PermTime:	120sec
Cal-Conc:	Instrument specific	CalibInt:	71.0 hr

(a) Zero-sub should be set to "No". During normal performance the zero values (BlArea) should be very low(< 1500). If high zero values persist it might indicate problems with leaking or contamination. Consult the Tekran manual for appropriate maintenance

Maintenance procedures for the Tekran model 2537A/B instrument

To assure collection of the highest quality data, the instrument must be inspected and maintained on a regular basis. A trained operator must visit the measurement site weekly. In addition, remote monitoring of the data is recommended where possible, as it allows for observing the performance of the instrument in between visits to the measurement site. A weekly site checklist to be used by the field operator is given in following paragraphs. The operator should bring this document to the site each week and appropriately note the maintenance performed. A brief summary of the primary features of the Tekran 2537 that

require regular attention are provided here, and the specific maintenance procedures are described in following paragraphs:
Lamp voltage – the intensity of the mercury lamp inside the 2537 analyzer should be checked regularly to ensure that it maintains a relatively constant value. The lamp voltage can be checked on the lamp circuit board and a red light on the front panel indicates when an adjustment is required.

Baseline and baseline deviation – the baseline voltage and deviation indicate the performance of the instrument electronics, and these values are displayed on the front instrument panel as well as in the output data. The baseline should maintain a consistent small positive value. A large baseline deviation or noisy baseline could indicate problems with the lamp or other electronics.
Gold trap performance – ambient mercury is continuously analyzed on alternating A and B gold bead traps. Mercury is released from the traps when they are heated by the trap heating coils. It is important that the A and B traps demonstrate consistent concentration measurements. Oscillating concentrations values could indicate a problem with one of the traps or heating coils.

Flow rate – the 2537 pump will be set to a constant flow rate. The actual flow rate should be monitored to ensure that the pump is functioning correctly and the correct amount of ambient air is being sampled.

Argon tank pressure – mercury is carried from the gold traps to the analyzer using Argon gas. The 2537 will cease sampling and go into Idle mode if the Argon pressure decreases to less than 200 psi (1400 kPa). Therefore, the tank pressure should be monitored regularly and the tank should be replaced before it is empty.

Calibration – the instrument is regularly calibrated by an internal permeation source to ensure that the traps and analyzer are operating consistently. The calibration consists of a zero and span (known amount of mercury released from the permeation source) for each trap. Each calibration result must be examined to assure that it can be used to determine TGM values of high analytical quality.

Weekly maintenance (Each visit)
Each week the operator is responsible for the following primary tasks to maintain the performance of the Tekran 2537:

- Complete weekly site report
- Examine instrument data and parameters (e.g. sample volume, baseline voltage, zero air flush values, peak status, argon tank, temperatures, error lights, etc.) and note on checklist
- Confirm that the 2537 baseline level is between 0.100-0.250V
- Confirm that the standard deviation of the baseline is< 0.100 mV
- Check the 2537 lamp voltage

- Examine a recent period of consistent data collection without any obvious disturbances (e.g. sudden peaks in concentration). Compute the average of 5 consecutive A trap concentrations and 5 consecutive B trap concentrations. Confirm that the average concentrations of the 5 consecutive the A/B trap measurements are different by < 10%.

For example:
mean (A)= Average (A1, A2, A3, A4, A5)
mean (B) = Average (B1, B2, B3, B4, B5)
APD=[mean(A) –mean(B)]/Average{[mean(A)+mean(B)]}
Where "APD" = Average Percent Difference

- Examine the every 71-hourinternal automaticcalibrations – confirm that the calibration zeros are 0.000 and that the A and B trap spans are different by ≤ 5%
  - *NOTE*: If the trap spans differ by 5-10%, the operator does not necessarily need to take action but he/she should note this difference in the event that the traps continue to differ by a greater percentage or in the event that there is a sudden change in trap performance. If the trap spans differ by more than 10% then the operator may need to take corrective action and should consult the Tekran 2537 manual for guidance.
- Examine the argon tank and regulator pressures
- Confirm that all error lights are off, the Perm light is blinking, and all switches are in the correct position

Bi-weekly Maintenance

Bi-weekly the operator is responsible for the following tasks in addition to the weekly tasks:

- Replace soda lime trap
- Replace sample inlet particulate filter (0.2 um pore size, 47 mm diameter)
- Confirm that the instrument meets all specifications

NOTE: Sites with high humidity (e.g. coastal and marine sites) may require the soda lime trap to be changed weekly instead of bi-weekly. All new sites should initially follow the guidelines above, but consider adjusting the frequency of soda lime change once initial data is collected and site-specific procedures can be determined.

Quarterly maintenance

The operator is responsible for the following tasks on a quarterly basis in addition to the weekly and bi-weekly tasks described in following paragraphs. Note that not all tasks listed below are performed every quarter so it is important that the operator pay attention to when these procedures are required:

Each Quarter:

- Check sample line for recovery and leaks (see section 10.20 of the Tekran 2537 manual or Tekran Technical Note TN2537_210).

- Perform elemental injections on gold trap cartridges A and B (see section 7.5 for explanation; see Annex A for instructions on the use of the mercury vapour source for elemental injections)
- Examine gold cartridge heating coils and confirm that they are bright orange when heating
- Confirm that instrument shelter air contains ≤ 15 ng/m^3 of mercury
- Install new 2537sample filter
- Clean Teflon line from 2537 to soda lime trap
- Perform leak check of the 2537 analyzer. This can be done by disconnecting the sample line from the back of the instrument (where the filter housing is located) and physically blocking the filter inlet with a Teflon cap. The pump flow should drop to zero (pump will begin to race). At that time the Teflon cap can be removed and sample line can be reattached.

2nd Quarter only:
- Measure, verify, and calculate % difference of the 2537 flow rate
- Verify 2537 scalefactor

4th Quarter only:
- Change 2537 heater coils, zero air canister, DFU filter
- Measure, verify, and calculate % difference of the 2537 flow rate
- Verify 2537 scalefactor
- Calibrate flow meter
- Rinseheatedsampleline
- Verify standard addition performance
- Site audit

As-needed maintenance

The following tasks should be performed by the operator as needed:
- Reset or replace2537lamp
- Install new matched pair of gold cartridges
- Clean or replace 2537 Teflon valves
- Clean or replacecuvette
- Service or repair the 2537 pump (e.g. replace pump brushes)
- Replace septum
- Check perm source temperature and perm vent flow
- Replace filter holders and fittings
- Replace Argon gas cylinder when pressure is < 200psi (<1400 kPa)
- Swap equipment (record new serial number)

Calibration

The Tekran 2537 should be regularly calibrated by the following method involving the internal permeation source:

- An automatic internal calibration using the internal permeation source, which utilizes known amounts of mercury vapour. It is recommended that this calibration be performed automatically by the instrument at least every 72 hours with a permeation time of 120 seconds (ICS, 2010). The operator should keep a record of these calibrations (spans and blanks) in order to observe patterns in instrument behaviour over time (ICS, 2010).

Occasionally, it is also necessary to perform Manual injections or Standard Additions of known amounts of mercury vapour obtained from a temperature controlled mercury vapour source (e.g. Tekran model 2505). This procedure is used to verify the permeation source and confirm that it is stable. This procedure is not recommended as a means to regularly calibrate the 2537 instrument. This should be performed quarterly by a trained technician or field operator (ICS, 2010). The procedure is described in the Tekran 2537 manual. Information on the characteristics of the mercury vapour source and how it should be used with the Tekran 2537 are also presented in following paragraphs.

Instrument settings for the Lumex RA 915 AM instrument

The Lumex RA 915 AM instrument is designed for monitoring of gaseous elemental mercury (GEM) in ambient background air. The instrument is fully automated and performs zero drift correction and calibration with programmable time intervals. During calibration a narrow cell, containing mercury vapour in equilibrium with pure liquid mercury, is moved into the light path of the spectrometer. The temperature inside the cell is measured and the concentration of gaseous Hg^0 is calculated from the mercury vapour pressure equation. As part of the calibration a zero air signal is obtained by feeding the instrument with purified air from a zero air filter. The recommended parameter settings for the Lumex RA 915 AM instrument are shown in Table 3.

Table 3. Recommended parameter settings for the Lumex RA 915 AM instrument

Parameter	**Setting**	**Comment**
Averaging time	2 s	The average time of each individual measurement
Meas. duration	240 s	The period between zero drift correction. An average (240 s) zero drift corrected GEM value is stored in the instrument memory.
ZC num	72	Automatic calibration is performed at each 48th zero drift correction, that is every 6 hour.
P0	101 kPa	Reference pressure*
T0	273.15 K	Reference temperature*

*The reference pressure and temperature used to calculate standard concentration values.

Routine checks and maintenance of the Lumex RA 915 AM instrument

To assure high quality the instrument must be checked and maintained on a regular basis. A monthly visit to the measurement site is required. In addition the performance of the instrument should be checked one or two times per week by remote monitoring. A check and maintenance protocol is given following paragraphs. This document is intended as a check-list. It also serves as a form in which control and maintenance work can be documented. It should be brought with to the site and filled in during the work.
The instrument is performing self-tests with regular intervals. In case of failure the monitor transmits an error code to the process control system, see Table 4, and the instrument stops the measurement. If this happens one may try to restart the instrument. If the problem continues a Lumex authorised service engineer must be consulted. The instrument should regularly be served with 6 month intervals.

Table 4: Error codes

Code		**Description**
BIN	DEC (Shown at display)	
11111110	254	Lamp failure
11111101	253	Calibration cell failure
11111011	251	Valve failure
11110111	247	Ambient air temperature out of range
11101111	239	Calibration cell temperature out of range
11011111	223	Flow out of range
10111111	191	Pressure sensor failure
0111111	127	Concentration out of range

Note.
If two or more failures occur, the error codes will be different. For example, if "Analytical cell temperature out of range" and "Calibration cell temperature out of range" occurs at the same time, the BIN code will be 11100111 and the DEC code 231.

The Lumex RA 915 AM instrument may be calibrated by exposing to air containing Hg^0, generated from a constant mercury source, or using cells with saturated Hg^0 vapour.

2.1.1.7 Data download, storage, and management

Data from the Tekran speciation system should be captured using a desktop computer, laptop computer, or data logger at the monitoring site.

The GMOS sites are free to quality assure and use their data in their own manner, but all GMOS data should be processed by GMOS project managers in the same way.

The most important process related to data management within the GMOS project is the transfer of collected data to a central database. As such, GMOS will provide an Interoperable System (ICT) to all the partners which allow the sharing of:

(1) information and data from historical databases,

(2) measurements collected at GMOS ground-based sites and measurement campaigns,

(3) model output.

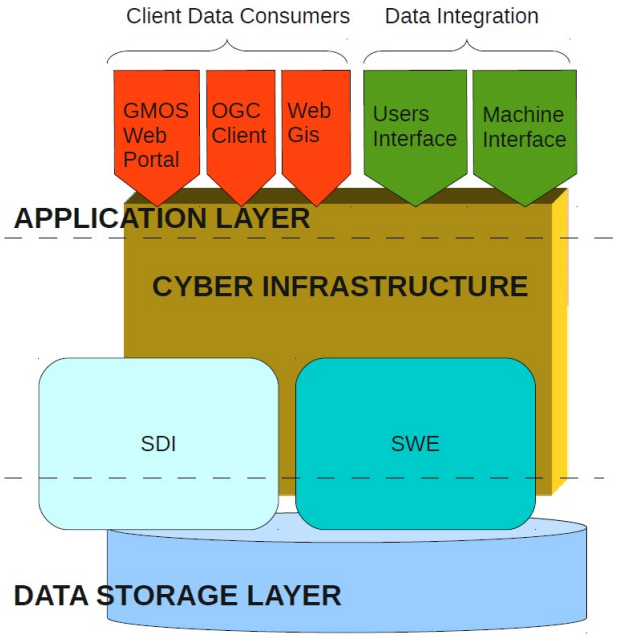
The development of the ICT system will consider a range of data formats given that data will be provided from in-situ or mobile sensors, from oceanographic or aircraft measurement campaigns, or from numeric models.

The GMOS ICT System will be based on a Spatial Data Infrastructure (SDI), which contains two central databases:

I) a Database Management System (DBMS) for most of the data; and

II) a *Sensor Web Enablement* (SWE) system for data coming from monitoring stations.

This Data Storage Layer (see Figure 3) will be managed by Cyber Infrastructure, which will serve as an integration system for data coming from GMOS partners' activities. Administrators will have an account in the Cyber Infrastructure in order to manage data process and integration.



Data stored in the Data Storage Layer and managed by the Cyber Infrastructure will be provided to users by means of different devices contained in an Application Layer. Each device represents a different view of the data managed by the Cyber Infrastructure. The GMOS web site can be used as device where data will be provided to users as simple link for data link, or by a Web visualization system to visualize information (Human to Machine process, H2M). Additional devices will be oriented to a machine access (Machine to Machine process, M2M) like Web Services OGC compliant.

How to upload data in the GMOS ICT System

The Cyber Infrastructure will have a simple Web Interface through which users can produce metadata (following an INSPIRE scheme), upload data, and assign rights to their data.
Two main methods will be used for uploading data to the GMOS ICT System:

1. Directly upload data using the Web User Interface. In this case a user will access a dedicated web page through a username and a password. He/she will fill in a few mandatory fields to construct the metadata and upload the file. The Cyber Infrastructure will manage and store the data.

2. Upload data through an automatic connection (by using common communication protocols like FTP, HTTP, etc.). The system can be configured in a *data-pull* event (in which the system will periodically call dedicated computers and folders to retrieve data) or in a *data-push* event (in which the users can notify the system by an e-mail that new data have been loaded in a folder).

Under two of the Deliverables from the WP9, GMOS will report in detail the SDI architecture and the metadata requirements.

2.1.1.8 Quality control and quality assurance

Laboratories involved in preparing supplies for operation of the TGM/GEM monitoring instruments must demonstrate adherence to quality control and assurance procedures.Site operators should also be thoroughly trained by a technician or GMOS project coordinator who is familiar with the operation of the instrumentation. The operator is responsible for reviewing all Standard Operating Procedures, troubleshooting guides, and site maintenance documents provided.

The analyzer must also be calibrated regularly, as described previously. The site operator is responsible for evaluating the raw instrument data on a weekly basis. Any abnormalities should be noted on the weekly field sheet, and as necessary the site operator should troubleshoot and perform instrument maintenance to resolve any persistent problems.

Regular Site Audits

Regular site audits by a trained technician are recommended in order to ensure continued instrument performance and the collection of high quality data. The following procedures are recommended during regular (e.g. annual or bi-annual) site audits [2]:

General site inspection:

- Verify overall operation of the equipment
- Inspect area around the station and confirm compliance with siting criteria
- Determine height of sample inlet
- Identify location of sample inlet with respect to the laboratory building

- Identify type and size of inlet hood
- Identify type and length of sample line
- Observe movement of people and vehicles near site

Instrument inspection:

- Determine sample volume
- Check for contamination of sample line and sample filter
- Inspect sample line integrity

The following checks apply to the Tekran 2537 only:

- Leak test on each gold cartridge
- Determine difference between cartridges (expect difference within 10%)
- Permeation source check
- Cartridge integrity and interference
- Verify performance of the Standard Addition Unit (calibration unit should stabilize overnight before injections are performed)
- Compare performance of syringes
- Compare calibration set-ups

The GMOS team will regularly and systematically perform QA/QC procedures on the speciated ambient Hg measurements collected at all sites. The QA/QC procedure will be designed to generate error flags for problematic data. This systematic examination of the data over time will allow for determining the benchmarks for high quality data within the GMOS project. Through frequent and systematic examination of the data it will also be possible to ensure that the site operators are operating the instrumentation correctly and collecting consistent high quality data. The quality of performance at each site will be in part determined by the percentage of complete data that is collected, which will be determined by the presence of complete sampling cycles free of instrument or measurement error. Throughout the course of the project, GMOS will work with other networks such as AMNet to determine appropriate detection limits for measurement parameters as well as acceptable limits of precision and uncertainty, because widely accepted values have not currently been established for measurements with the Tekran speciation system.

3. Passive Sampling and sample handling

3.1 Introduction

Several strategies were planned by CNR-IIA to get novel passive sampling systems of mercury based on nanostructured materials and keeping in mind the main features of a passive sampler. Indeed the peculiarity of the passive samplers relies on the unassisted molecular diffusion of gaseous agents (i.e. volatile vapours of elemental mercury) through a diffusive surface onto an adsorbent scaffolding. Unlike active (pumped) sampling, passive samplers require no electricity (expensive pumps), have no moving parts, and are simple to use (no pump operation or calibration). After sampling, the adsorbed mercury should be desorbed off the adsorbent by solvent (chemical procedure)or thermal desorption (physical procedure). Passive samplers have to be commonly compact, portable, unobtrusive, and inexpensive. They are able to give information about the average pollution levels over time periods of 8hours to weeks/months. They have not to require supervision and can be used in hazardous environments. The low cost of the materials allows the sampling at multiple locations (e.g., for highlighting pollution "hotspots"; or determining long term data trends in a specific geographical area). The passive sampler, designed and fabricated within CNR, comprised a nanostructured adsorbing membrane coating a porous quartz slice, a glass vessel and a cap with a protective grid for the exposure to the environment. More specifically, it consisted of an adsorbent membrane made of titania nanoparticles (≤25nm diameter) that after a suspension in an aqueous solution of PVP/HAuCl4 and UV-irradiation changed the colour from white to blue-violet, resulting from a fine decoration with gold nanoparticles (6-20 nm). Such a functionalization occurred for the photocatalytic properties of TiO_2 (anatase). The nanostructured suspension was deposited on a thin quartz slices (450 μm thick, 20 mm length), dried to 550°C and then incorporated into an axial diffusive sampler in order to be exposed firstly to air polluted with well-known amounts of Hg^0 for calibration and characterization and secondly to the atmosphere.

3.2 Materials, methods and PAS membrane characterization

All chemicals were purchased from Sigma-Aldrich and used without further purification: polyvinylpyrrolidone (PVP, Mn 1,300,000), Titanium (IV) oxide (anatase, ≤25nm diameter, Sigma Aldrich, CAS 1317-70-0) and gold(III)chloride hydrate (HAuCl4, 99.999%). Ultrapure water ($5{\cdot}5\ 10^{-8}$ S cm^{-1}) was produced by MilliQ-EMD Millipore. Quartz slice filters (Whatman) were 450 mm thick with a porosity of about 2 mm. Therefore, Titanium (IV)oxide (anatase) (Sigma Aldrich, CAS 1317-70-0) were suspended in an aqueous solution of PVP/HAuCl4 for the preliminary investigations. Such a suspension was UV-irradiated for 1 h, thus changing the colour from yellow to blue-violet (shown in Figure 4) and subsequently centrifuged to remove PVP. The suspension was vortexed and deposited on the quartz slices, then dried to 80°C, and before being placed and sealed into the analyst sampler, it was subject to a thermal desorption at 550°C within a customized oven under a clean air flow in order to remove any trace of mercury absorbed during preparation.

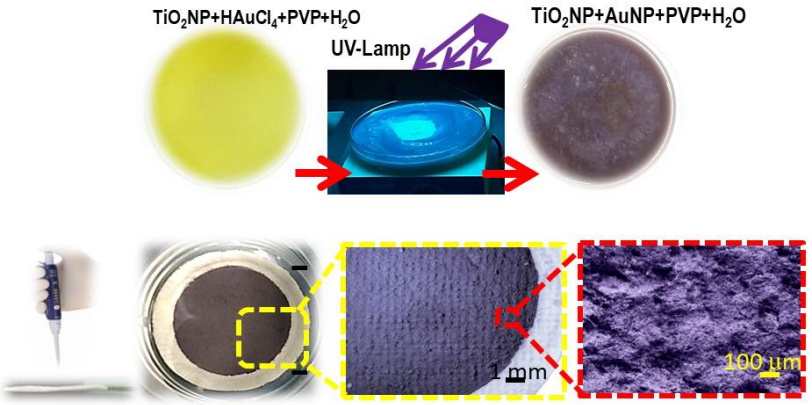


Figure 4. Preparation of the nanostructured material and deposition of it to get a thin layer onto a porous quartz slice

The nanostructured layers looked well attached to the substrates and nanoparticles were analyzed by UV-Vis spectrophotometry (Spectrophotometer UV-2600, Shimadzu, UV-Vis-NIR Mini-Spectrometer Hamamtsu) before and after gold nano-functionalization confirming the gold reduction and adhesion on the surface of the titania NPs, thus suggesting, according to literature results, a very small diameter (under 20 nm) of AuNPs (Figure 5). These novel structures have been considered as very attractive passive sampling system due to both the strong affinity between mercury and gold and a wide adsorbing surface due to the nano-size of the materials (expected high efficiency and lifetime). The absorption (and reflectivity) band at 550 nm was blue-shifted (up to 546 nm) when exposed to Hg mercury vapours. Scanning Electron Microscopy micrographs confirmed that gold nanoparticles were spherical but with different size in diameter, however smaller than TiO_2NPs' one. Gold nanoparticles resulted strictly linked to the NPs, creating a series of gold multi-decorated particles, thus suggesting a huge receipting surface.

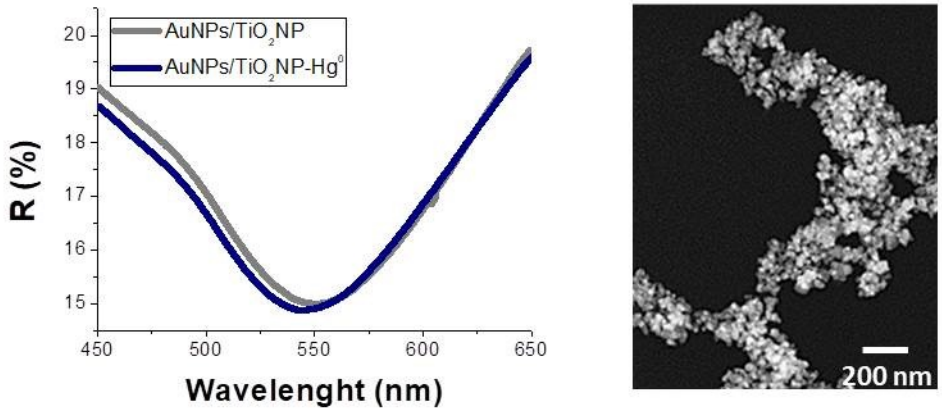


Figure 5. UV-VIS spectra (%R) of a thin layer of AuNPs/TiO2NPs coating a silicon wafer and exposed to Hg vapors for 15 min (on the left) and SEM micrograph (dark field) of the nanostructured aggregation of nanoparticles (on the right).

A prototype of thermal desorption system was also planned in CNR-IIA and developed (Spaziani, Italy) in order to be connected to the most commons analytical systems of mercury. The prototype was manufactured in quartz and housed in a heater system (De Marco Forneria) to allow the fast desorption of the Hg adsorbed on the thin layer of the nanostructured material, flowing dry air throughout the desorption chamber. A picture of the prototype is reported in Figure 6**.**

Figure 6. A prototype system for Hg-PAS thermal desorbing developed in CNR-IIA

In order to calibrate the adsorbing membrane to GEM, increasing amounts of Hg^0 (Tekran Model 2505, Mercury Vapour Concentrator) were injected by a gas-tight syringe into a suitable sealed chamber hosting the membrane at r.t. (20°C).

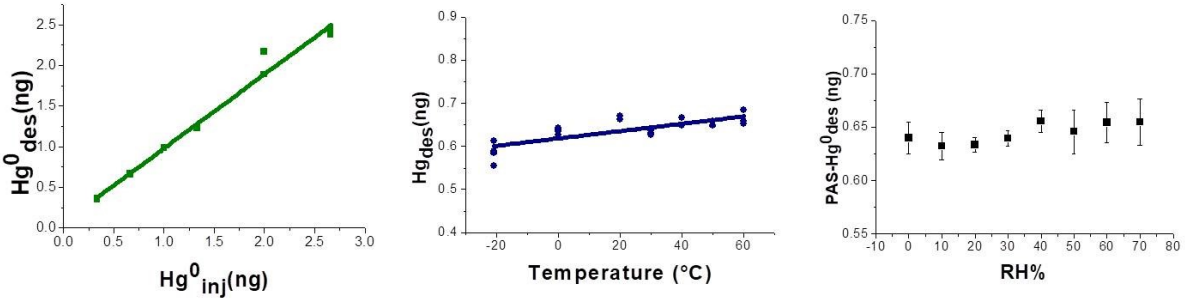


Figure 7. Plots depicting the desorbed GEM from AuNP/TiO_2membrane upon exposure, within a sealed glass vessel similar to a PAS container, to: Hg^0vapor increasing mass values (on the left), a known mass of Hg^0vapor (about 652 pg) when temperature of the sampler changed (ranging between -20°C and 60°C) (in the middle), a known mass of Hg^0vapor (Mean Value: 645± 0.01 pg) when %RH in the sampler changed (ranging between 5% and 70% relative humidity).

In laboratory the potentials and the limitations of the nanostructured membrane were investigated in several environmental conditions and at different Hg^0vapor concentration. Experimental results reported that the membrane was able to adsorb up to 92% of the injected mass. The adsorption curve shape was linear up to 2.7 ng of Hg^0. A slight increasing of the adsorbed mass was reported when relative humidity increased within the measurement chamber, and specifically the membrane was able to entrap an additional amount of 0.4 ± 0.01 pg of the analyte per %RH unit. By the way, when %RH was ranging between 50-70%, the desorbed values oscillated between 0.632 ng and 0.656 ng. Similarly, temperature

affected the analyte adsorption onto the PAS-membrane since the curve slope increased in 0.62 pg per Celsius degree in a thermal range of -20-60°C when about Hg^0 mass of 645 pg was injected. Finally, interesting result was the complete restoration of the PAS membrane after tens cycles of measurements, suggesting the potential to use the same passive sampler for many exposures.

3.3 Experimental calculation of the sampling rate.

The functioning of the diffusive samplers is based on the movement of the contaminant molecules across a concentration gradient. In the collecting device (the case of the passive sampler) the contaminants diffuse from an area of higher concentration towards an area of lower concentration.
According to the first Fick Law, the rate at which chemicals diffuse is represented by the following formula:

$$Q = D\left(A/L\right)C\,T$$

where Q is the amount collected (ng), D is the diffusion coefficient (cm^2/min), A is the cross-sectional area of the diffusion path (cm^2), L is the diffusive path length (cm) C is the airborne concentration (mg/m^3) and T is the sampling time (min). Each contaminant has its own diffusion coefficient determined by its unique chemical and physical properties. The *A/L* parameter is determined by the sampler's geometry; the product of *D (A/L)* is the theoretical sampling rate of a diffusive sampler for a specific compound (e.g. elementary mercury).

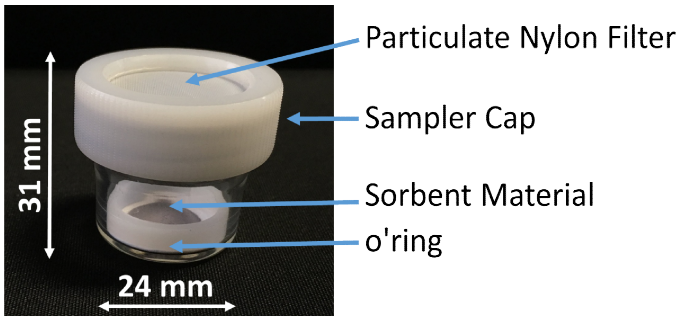


Figure 8. Prototype of mercury passive sampler

In order to calculate the sampling rate of the developed passive sampler, several measurements have been performed. Below some experimental results obtained under two different environmental conditions are reported.
The first experiment consisted in testing a set of passive samplers in a "measurement chamber" filled with air where a certain mercury concentration was fixed by means of a suitable controlled mercury vapour source (Fig.9). The second one consisted of an actual monitoring campaign outside the CNR laboratories, whereas it was possible to monitor (at fixed times) the mercury, the temperature, relative humidity and wind speed(Fig. 9).

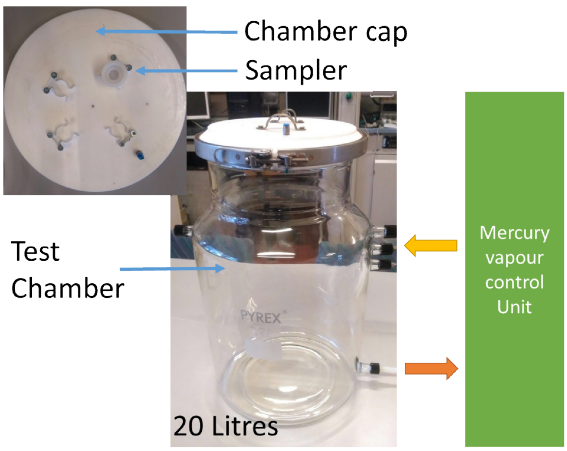


Fig.9 Experimental measurement chamber

The samplers were tested at different concentration of mercury and at different exposure time. During the experiment the parameters as mercury concentration, relative humidity and temperature were monitored by TEKRAN 2537A. Mercury Vapour Analyzer, Vaisl a humidity and temperature transmitter, respectively. Three different samplers (PAS) were placed in the chamber and were exposed to three concentration values of ≈1.2, 3.5 and 4.5 (ng/m^3) in different time of exposure (3,7 and 15 days, respectively). Each sampler was completely desorbed from Hg^0 before and after each exposure to Hg^0 vapour in air. From each experimental run we have got two significant data: the total adsorbed mercury mass (ng) and the exposure time (days). Using these data, we have been able to calculate the sampling rate value by the Fick law, and the results were reported in Table5.

Table 5

Sampler	**Hg^0vapor concentration (ng/m^3)**	**Adsorbed Hg^0vapor concentration raw data (ng/m^3)***	**Hg^0 adsorbed mass (ng)**	**Exposure time (days)**	**Sampling rate (m^3/days)**
Sampler SL1	1.220	24.8	0.124	7	0.0145
Sampler SL2	1.200	24.8	0.124	7	0.0148
Sampler SL3	1.210	23.12	0.116	7	0.0136
Sampler SL1	1.256	55.8	0.279	15	0.0148
Sampler SL2	1.240	54.4	0.272	15	0.0146
Sampler SL3	1.260	53.89	0.269	15	0.0143
Sampler SL1	3.420	28.04	0.140	3	0.0137
Sampler SL2	3.440	28.567	0.143	3	0.0138
Sampler SL3	3.400	28.845	0.144	3	0.0141
Sampler SL1	3.510	71.334	0.357	7	0.0145
Sampler SL2	3.490	70.9	0.355	7	0.0145
Sampler SL3	3.540	71.84	0.359	7	0.0145
Sampler SL1	3.600	145.4	0.727	15	0.0135
Sampler SL2	3.550	147.23	0.736	15	0.0138
Sampler SL3	3.460	144.09	0.720	15	0.0139

Sampler SL1	4.560	92.54	0.463	7	0.0145
Sampler SL2	4.526	94.23	0.471	7	0.0149
Sampler SL3	4.490	90.45	0.452	7	0.0144
Sampler SL1	4.749	195.52	0.978	15	0.0137
Sampler SL2	4.399	192.45	0.962	15	0.0146
Sampler SL3	4.510	190.2	0.951	15	0.0141

*measured by TEKRAN 2537A unit, the temperature was 24 °C (with a fluctuation of 1 °C) and RH% was 40% (with a fluctuation of 2 %) over the whole experiment.

From the experiment results we have calculated the medium value of sampling rate that was 0.0142 (m^3/day) with a very low standard deviation (SD) of 0.000429.

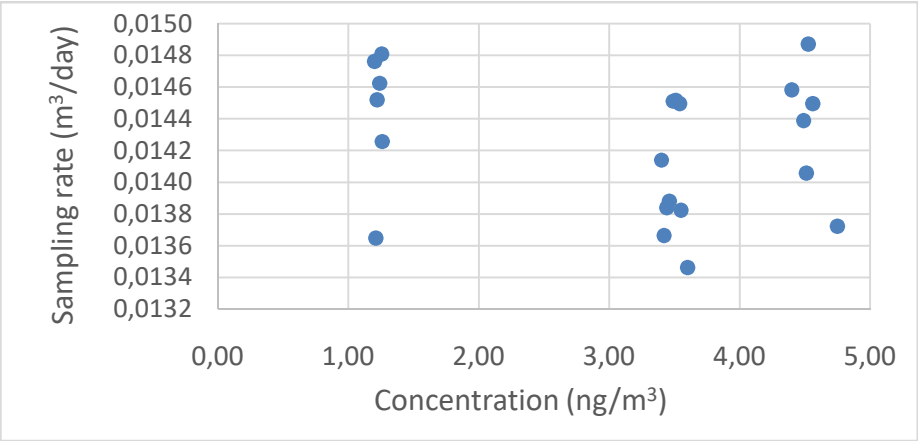


Figure 10. Estimated sampling rate vs concentration (ranging from 1.2 to 4.5).

In Figure 10 we have plotted the calculated sampling rate data for each exposed concentration (class of experiment) showing a low inter classes dispersion coefficient. The comparison between the estimated concentration, calculated using the experimental sampling rate and the measured value by TEKRAN has been reported in Figure 11.

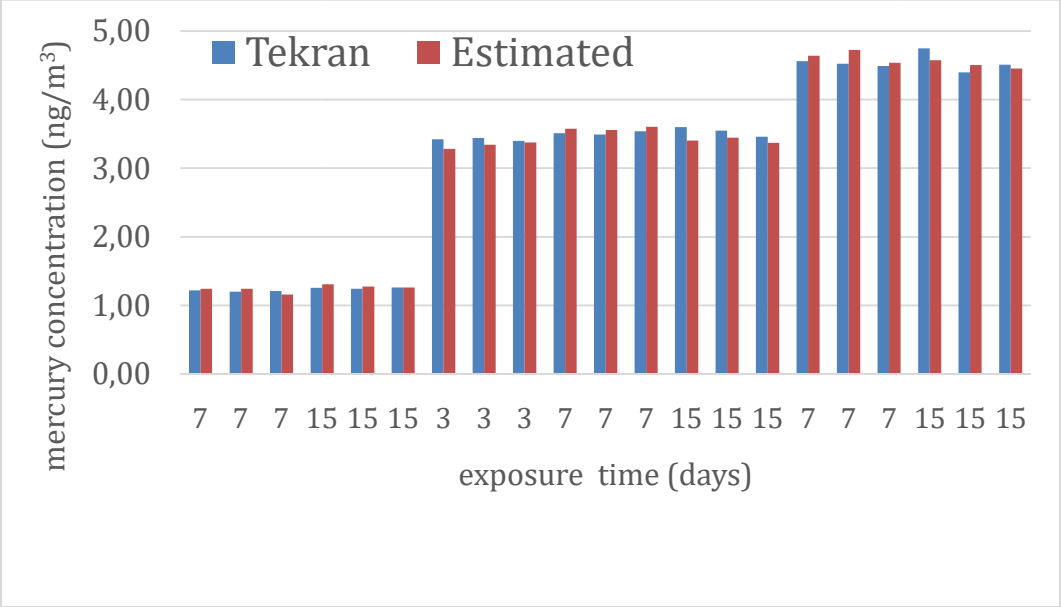


Figure 11. Comparison between the estimated concentration using the experimental sampling rate and the measured value by TEKRAN analyzer

In order to estimate the sampling rate of the developed PAS outside the laboratory, we have exposed a set of PASs in the area close to our laboratory in Monterotondo (RM). During the exposure we have monitored (at fixed times) the mercury concentration in the air by TEKRAN 2537A and some environmental parameters such as wind, relative humidity and temperature.

Figure 12. PAS setup used during the outside exposure comprising a shelter and N°. 8 housings for PASs.

The PASs installation is shown in Figure 12. Upon the monitoring campaign the PASs were exposed to wind speed of about 8 Km/h ± 5, a temperature vale of 25 °C with excursion

values of ± 15 °C (day/night) and a relative humidity value of 45 RH% with max excursion values of ± 25%.

In the table 4.2 we have reported the data collected during the experiments with the estimation of the sampling rate for each run. The samplers were exposed for 4, 11, 15 days and the outdoor mercury concentration was in the range of 1.45-1.63 (ng/m^3).

Table 6: PAS data from outside experiment

Sampler	Exposed Mercury concentration (ng/m3)	Mercury absorbed concentration (data raw) (ng/m^3)*	Mercury absorbed mass (ng)	Exposure time (days)	Sampling rate (m^3/days)
Sampler SL1	1.63	77.107	0.386	15	0.0158
Sampler SL2	1.60	73.418	0.367	15	0.0153
Sampler SL3	1.61	72.735	0.364	15	0.0151
Sampler SL1	1.65	72.55	0.363	15	0.0147
Sampler SL2	1.54	67.883	0.339	15	0.0147
Sampler SL3	1.60	68.314	0.342	15	0.0142
Sampler SL1	1.60	54.557	0.273	11	0.0155
Sampler SL2	1.48	49.416	0.247	11	0.0152
Sampler SL3	1.53	52.501	0.263	11	0.0156
Sampler SL1	1.50	51.747	0.259	11	0.0157
Sampler SL2	1.56	47.029	0.235	11	0.0137
Sampler SL3	1.56	53.2	0.266	11	0.0155
Sampler SL1	1.45	16.939	0.085	4	0.0146
Sampler SL2	1.48	15.751	0.079	4	0.0133
Sampler SL3	1.53	17.951	0.090	4	0.0147

In Figure 13 we have plotted the evaluated sampling rate data for each concentration measured during the outside monitoring “campaign”. From these collected data we have calculated the mean value of the sampling rate that was 0.0149 m^3/day with a very low standard deviation of 0.000732.

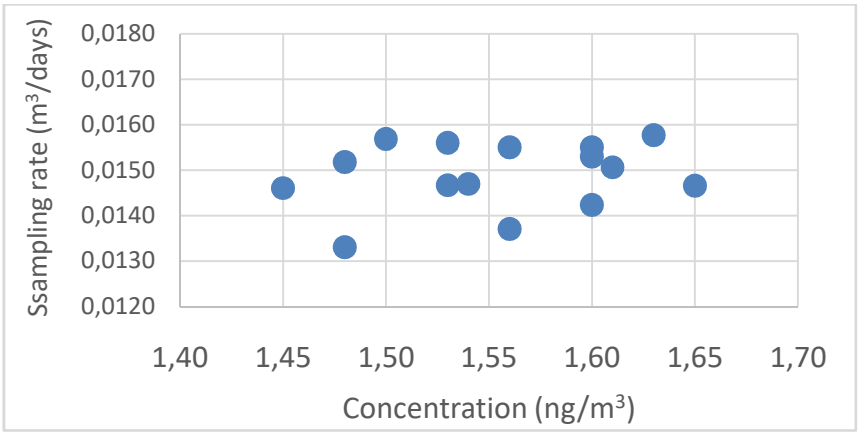


Figure 13. Estimated sampling rate vs outdoor concentration.

Figure 14 reports the comparison between the estimated mercury concentration, calculated using the evaluated sampling rate and the measured value by TEKRAN unit.

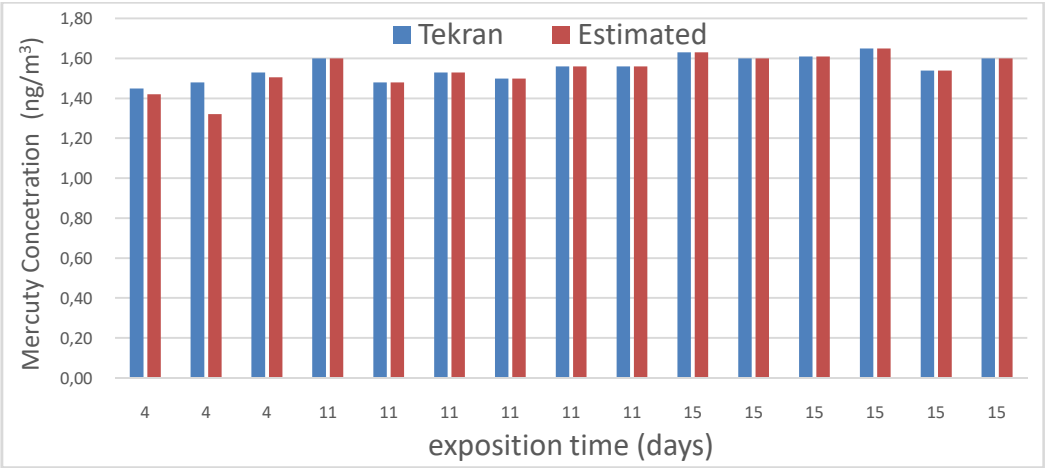


Figure 14. Comparison between the outdoor estimated concentration using the experimental evaluated sampling rate and the measured value by TEKRAN unit.

4. Experimental design for sampling (analysis of types of stations)

4.1 Monitoring sites located in different countries

The CNR-IIA has a big experience gained through the GMOS project, that provides consistent and high-quality mercury measurements worldwide and validate models for policy scenarios analysis.
The novel Hg passive samplers have been firstly tested in the CNR-IIA labs and a plan to share them among the selected GMOS (for ambient monitoring) and WHO sites (for ambient and human-biomonitoring) in different environmental and meteorological conditions was developed.

During the reporting period, the CNR-IIA has involved many GMOS experts asking to GMOS managers of ground-based monitoring sites around the world that perform mercury measurements by conventional instruments to be agreed for performing Hg measurements using the new sensor device developed by the CNR across the GMOS monitoring sites. Then a detailed plan of sampling campaigns using the passive samplers have been developed for all GMOS and WHO sites involved (Tables n. 7and n. 8).

As first exercise, CNR-IIA proposed a selection of 4 monitoring stations established within the GMOS network, mostly background sites, to undertake passive sampling and analysis of Hg in ambient air in order to strengthen capacity to provide globally comparable data. Then, as further task, a list of polluted sites was selected in coordination with WHO national coordinators.

The list of the sites of the first pilot survey, including also those highly impacted where ambient and biomonitoring measurements has been performed in collaboration with WHO, were agreed with UNEP and WHO teams. The complete map of all sites is reported in the following Figure.

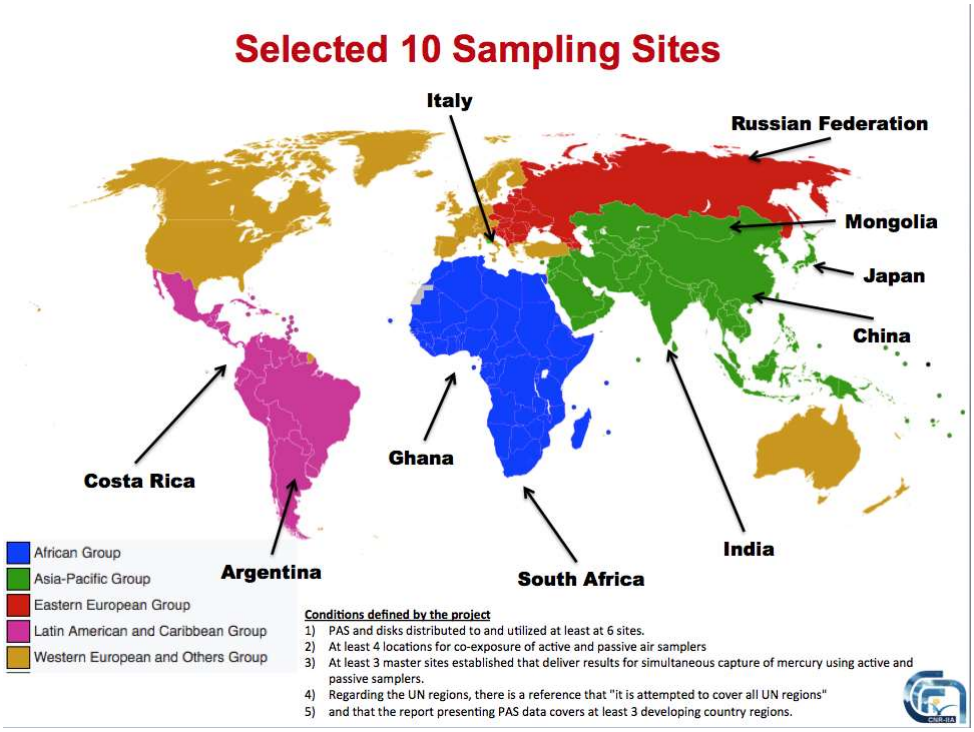


Figure 15. UNEP-GEF monitoring sites worldwide distributed

As specified in the project document, 3 Master sites and 1Secondary Site (GMOS stations) have been proposed by CNR-IIA within GMOS and included into the air sampling-scheme. These stations have delivered results for simultaneous exposure of mercury using active and passive air samplers.
Furthermore for the development of the air sampling scheme, 6 new sampling sites (named WHO sites), that are not part of the GMOS network, have been proposed by CNR-IIA within the choice made by WHO national coordinators (as regions were mercury Human Bio-Monitoring campaigns- HBM were carried out). Despite different invitations to take part in the campaigns, the Kyrgyz Republic and the Russian Federation belonging to the WHO network, did not accept the invitation to take part to mercury air sampling campaigns.

The CNR-IIA defined therefore a set of final air monitoring stations composed by two groups:

a. the first, at GMOS stations, mostly background/rural sites - for co-exposure of active and passive air samplers;
b. the second, defined in the region where WHO carried out its human-biomonitoring, at highly polluted sites, for exposure of passive air samplers.

The ‘Group of GMOS stations’ includes the following countries:

1. Italy - Monte Curcio, and Japan
2. Argentina - Bariloche
3. South Africa – Cape Point
4. Japan - Cape Hedo.

This set of stations, consists of 4 locations (phrased in the project as "> 3") including 3 GMOS master sites (Italy-Monte Curcio, Argentina-Bariloche, and Japan-Cape Hedo); and 1 Secondary site (South Africa – Cape Point).
Japan substituted the Chinese station of Mountain Changbai, previously included in the initial proposal.

The 'Group of WHOsites' included, in its first proposal, six sites used amongst for HBM activities. One site in the Russian Federation was then substituted by one GMOS station because the WHO national coordinator in Russia could not take part to the campaigns. The Chinese site was substituted by the GMOS station at Mt. Ailao, under specific request made by chinese experts. The 'Group of WHO sites' includes:

5. Mongolia
6. Ghana
7. India
8. Costa Rica
9. China - Mt. Ailao / GMOS station
10. Russian Federation - Listvyanka/ GMOS station.

The final list of the monitoring sites located in different countries is as following:

1. Argentina – Bariloche,EMMA station / **GMOS station**, **BAR**
2. China - Mount Ailao/ **GMOS station**, **MAL**
3. Costa Rica
4. Ghana
5. India
6. Italy - Mount Curcio/ **GMOS station**, **MCU**
7. Japan - Cape Hedo / **GMOS station**, **CHE**
8. Mongolia
9. Russian Federation - Listvyanka/ **GMOS Station**, **LIS**
10. South Africa - Cape Point Station / **GMOSstation CPO**

It was attempted to cover all UN regionsand most of them were covered(Asia, Africa, Grulac, Europe). Moreover the present report presenting Passive Air Samplers data covers at least 3 developing country (Ghana, India, Costa Rica).

4.2 Configuration and characteristics of the selected GMOS ground-based sites

This section provides a brief review of principal characteristics of the selected GMOS monitoring sites distributed in the Northern and Southern Hemispheres in framework of the global network. In particular, Table**7**shows the characteristics of the GMOS ground-based sites reported as "Master stations (M)" where Gaseous Elemental Mercury (GEM), Gaseous Oxidized Mercury (GOM), and mercury associated to suspended particulate matter ($PBM_{2.5}$)

are continuously measured, and the "Secondary stations (S)" are those where only Total Gaseous Mercury (TGM) is continuously measured.

Table 7: Location, elevation, type* of stations (M= Master, S=Secondary), and affiliation of GMOS monitoring sites.

STATIONS	LAT	LON	Elevation (m asl)	Country	TYPE*	INSTITUTE	AFFILIATION
Listvyanka	51,85	104,89	560	Russia	S	SPBSU	GAW
M.te Curcio	39,31	16,42	1780	Italy	M	CNR-IIA	GAW
M.te Ailao	24,53	101,03	2503	China	M	IGCAS	
Cape Point	-34,35	18,49	230	South Africa	S	SAWS	GAW
Bariloche	-40,40	-71,42	840	Argentina	M	INIBIOMA	GAW
Cape Hedo			60	Japan	M	MoE-NIMD	GAW

Listvyanka (LIS): This site is situated at the coastal hill (near Lake Baikal), at the Astrophysical Observatory, about 1 km from the outskirts of the Lystvyanka settlement and 70 km from Irkutsk city. All surrounded hills are covered by forest (mostly pine). At the site there is rocky soil with a thin grass. The site has been part of the East Asia Network for Acid Deposition Monitoring (EANET) since 2000.

Mount Curcio (MCU): The site is a GAW Climatic-Environmental Observatory located in a strategic and isolated position within the Sila massif, one of the main three areas making-up the Sila National Park, in the South of Italy. It is characterized by no local sources of contamination and no access by road and it is 200 m from a ski resort and from the cable car arrival point of the surrounding ski area. The operative station is situated at 1780 m a.s.l. on a southern Appenine mountain peak with completely free horizon, thus allowing to gain atmospheric monitoring measurements with a large spatial representativeness. It is interestingly placed on the middle of the Mediterranean basin, around 30 and 60 km far from the Tyrrenian and the Ionian Sea, respectively. Due to its elevation and position, Mt. Curcio station is even able to intercept dust plumes from the Saharan desert as well as volcanic ashes and gases from Stromboli and Mt. Etna volcanoes, located at around 120 km south-easterly and 220 km south-south easterly from the atmospheric monitoring site, respectively.

Mount Ailao (MAL): is located at a summit of the northern edge of the Ailao Mountain National Nature Reserve in central Yunnan province, southwestern China. The reserve has an area of 677 km2 and is predominantly (> 80 %) covered by evergreen broadleaf primary forests. This site is frequently influenced by long-range transport of Hg released from anthropogenic sources and biomass burning in southwestern China, the Indochinese Peninsula, and South Asia.

Cape Point (CPO): The station is located at the tip of the Cape Peninsula (210 m above sea level) within a nature reserve. It is surrounded by the ocean. The area has a rocky terrain and is sparsely vegetated. The site experiences moderate temperatures, dry summers with occasional biomass burning episodes in the surrounding area and increased precipitation during austral winter.

Bariloche (BAR): This station is located near the laboratory of photobiology on the shore of the Gutierrez River. The area is a natural forest (mixed Andean forest, Nothofagus spp. and several species of bushes and grasses) and close to the station there is riparian endemic vegetation (max. 4-5 m height) as wells as a few planted pine trees (> 20 M Height).
Cape Hedo (CHE): Okinawa is an optimum location in Japan from which to monitor the atmospheric conditions in East Asia as air masses from Japan, Korea, China, and Southeast Asia, can all be captured there, depending on the season. An operator visit the Cape Hedo Atmosphere and Aerosol Monitoring Station once a month. There is a supporting staff at the station who visits there 3 times a week.

4.3 Field Seasonal sampling Campaigns

During the Project the AIR SAMPLING PLAN (See Tables below) has been developed and the strategies to get novel passive air sampling systems for mercury were further planned and implemented.
The project was aimed to perform a global scale validation of sampling devices (PAS) and gather ambient mercury data for exposure assessment along with WHO HBM campaigns in the same regions.
Therefore the sampling campaigns have been structured using a much higher number of samplers that have been co-located and have been exposed for 1, 2 and 3 weeks in parallel (as reported in column I of the air sampling scheme – Tables 8 -9); this has allowed to cross check the following key parameters for the QA/QC:

- linearity over time,
- reproducibility
- behaviour of samplers at different climate conditions.

The sampling campaigns have been performed over two campaigns, in summer and winter seasons, at WHO sites and over three seasons at GMOS stations (as reported in column K).
The data are then representative of seasonal mercury concentrations at all site.
The air sampling campaigns have been scheduled over one month and half during two seasons.
This data will be a good basis to complement the WHO HBM data for exposure assessment.

Furthermore an instructive Video on Practical instructions for Mercury Air Passive Samplers (PAS) has been realized and shared with UNEP and WHO trough the following link:

- https://drive.google.com/open?id=0B-ireFSFTkqKS2c0ckNDdXJ4OVk .

Practical instructions and criteria to use mercury Passive Air Samplers (PASs) for air monitoring campaigns together with specific forms to be filled in, were developed by CNR-IIA and sent to all partners involved in the campaigns.
This manual is reported in ANNEX G.

Shipments of technical-scientific material started between en of October 2016 and November 2016 due to delay from administrative headquarters on the second instalment of the project.

GMOS stations delivered their results for simultaneous exposure of Hg using active and passive air samplers.

The ***first air sampling campaign*** was carried out ***between February and March 2017***, on the following specific dates:

- ARGENTINA, from 1 February to 15 March 2017
- CHINA, from 10 February to 24 March 2017
- GHANA, from 15 February to 29 March 2017
- INDIA, from 1 February to 15 March 2017
- ITALY, from 1 February to 15 March 2017
- JAPAN from 24 February to 28 April 2017
- MONGOLIA, from 1 February to 15 March 2017
- RUSSIAN FEDERATION, from 6 February to 20 March 2017
- SOUTH AFRICA from 1 February to 15 March 2017.

The ***second air sampling campaign*** was carried out between ***end of May and beginning of August 2017***, on the following specific dates:

- ARGENTINA, from 31 May to 12 July 2017
- ITALY, from 31 May to 7 July 2017
- JAPAN, from 31 May to 2 August 2017
- SOUTH AFRICA, from 1 June to 13 July 2017.

The ***third air sampling campaign*** was carried out between end of ***August and November 2017*** at the following specific dates:

- ARGENTINA, from 15 September to 27 October 2017
- CHINA, from 31 August to 12 October 2017
- GHANA, from 18 September to 30 October 2017
- INDIA, from 13 September to 25 October 2017
- ITALY, from 13 September to 25 October 2017
- JAPAN, from 11 September to 20 October 2017
- MONGOLIA, from 22 September to 3November 2017
- RUSSIAN FEDERATION, from 13 September to 25 October 2017
- SOUTH AFRICA, from 11 September to 24 October 2017.

COSTA RICA started its first campaign by 25 October 2017 with a big delay compared to other involved countries to logistics problems linked to custom clearance of scientific material.

Name of Site/Country (and type of sampling periods)	Type of station	Type of Network	UNEP Regions	Master Site / Secondary Site	Sampling Points	N. of shelters	N. of Exposure Periods	Passive samplers (duplicates per shelter)	Total exposed passive samplers	Number of campaigns
Kyrgyz Republic	Complex - Mining & Industrial	WHO	**ASIA**		1	1	1w, 2w, 3w for 1,5 month for 2 seasons			
Mongolia	ASGM	WHO	**ASIA**		1	1	1w, 2w, 3w for 1,5 month for 2 seasons			
1w							6	2	12	2
2w							3	2	6	2
3w							2	2	4	2
Blank Field (exposed for 6 weeks)							1	2	2	2
Sub total									24	
Ghana	Waste management and food consumption	WHO	**AFRICA**		1	1	1w, 2w, 3w for 1,5 month for 2 seasons			
1w							6	2	12	2
2w							3	2	6	2
3w							2	2	4	2
Blank Field (exposed for 6 weeks)							1	2	2	2
Sub total									24	
India	Complex - Industrial, Waste, Food cons.	WHO	**ASIA**		1	1	1w, 2w, 3w for 1,5 month for 2 seasons			
1w							6	2	12	2
2w							3	2	6	2
3w							2	2	4	2
Blank Field (exposed for 6 weeks)							1	2	2	2
Sub total									24	
Costa Rica	Complex - ASGM & Food (fish)	WHO	**GRULAC**		1	1	1w, 2w, 3w for 1,5 month for 2 seasons			
1w							6	2	12	2
2w							3	2	6	2
3w							2	2	4	2
Blank Field (exposed for 6 weeks)							1	2	2	2
Sub total									24	
China - ***Mt Ailao (GMOS station) as substituted site***	Food consumption and air pollution	WHO	**ASIA**		1	1	1w, 2w, 3w for 1,5 month for 2 seasons			
1w							6	2	12	2
2w							3	2	6	2
3w							2	2	4	2
Blank Field (exposed for 6 weeks)							1	2	2	2
Sub total									24	
Russian Federation - ***Listvanka (N. Mashanov - GMOS station) as substituted site***	Food (local fish cons.)	WHO / GMOS	**EUROPE**				1w, 2w, 3w for 1,5 month for 2 seasons			
1w							6	2	12	2
2w							3	2	6	2
3w							2	2	4	2
Blank Field (exposed for 6 weeks)							1	2	2	2
Sub total									24	
TOTALS					6	6			144	

Table 8. Air sampling Scheme PART 1

SITES TYPE 2 (GMOS) - for co-exposure of active and passive air samplers

Name of station (and type of sampling periods)	Type of station	Type of Network	UNEP Region	Master Site / Secondary Site	Sampling Points	N. of shelters	N. and types of Exposure Periods	Passive samplers: duplicates per shelter	Total exposed passive samplers	Number of campaigns
Monte Curcio (Italy)	Rural station	GMOS	**EUROPE**	**MASTER SITE**	1	1	2w, 3w for 1,5 month for 3 seasons			
~~NO 1w~~										
2w							3	2	6	3
3w							2	2	4	3
Blank Field (exposed for 6 weeks)							1	2	2	3
Sub total									12	
Bariloche (Argentina)	Rural station	GMOS	**GRULAC**	**MASTER SITE**	1	1	2w, 3w for 1,5 month for 3 seasons			
~~NO 1w~~										
2w							3	2	6	3
3w							2	2	4	3
Blank Field (exposed for 6 weeks)							1	2	2	3
Sub total									12	
Cape Point (South Africa)	Rural station	GMOS	**AFRICA**	**SECONDARY SITE**	1	1	2w, 3w for 1,5 month for 3 seasons			
~~NO 1w~~										
2w							3	2	6	3
3w							2	2	4	3
Blank Field (exposed for 6 weeks)							1	2	2	3
Sub total									12	
~~**M. Changbai (Cina)**~~ **** Cape Hedo, Japan *as substituted site***	Rural station	GMOS	**ASIA**	**MASTER SITE**	1	1	2w, 3w for 1,5 month for 3 seasons			
~~NO 1w~~										
2w							3	2	6	3
3w							2	2	4	3
Blank Field (exposed for 6 weeks)							1	2	2	3
Sub total									12	
TOTALS					**4**	**4**			**48**	

Table 9. Air sampling Scheme PART 2

An alphanumeric code was reported onto each passive sampler for identifying, according to the following scheme:
S2-C2-0316
Specifically, **S2** is a tag related to the sampling site (named as S0, S1, S2, S3, S4, S5, S5, S6, S7, S8, S9 respectively).
C is a tag related to the exposure time:

- all the samples named as **A** have been exposed to the air for **1 week**;
- all the samples named as **B** have been exposed for **2 weeks** and finally
- all the samples named as **C** have been exposed for **3 weeks**.
- The samples named as Blank (1 and 2, respectively) have been kept exposed throughout the sampling campaign, but tightly closed.

In the following Figure 16is reported the sampling scheme with information related to the codes of PASs and the time of exposure of each group (i.e., two weeks, three weeks etc.).

SAMPLING SCHEME FOR 'GMOS STATIONS' Group

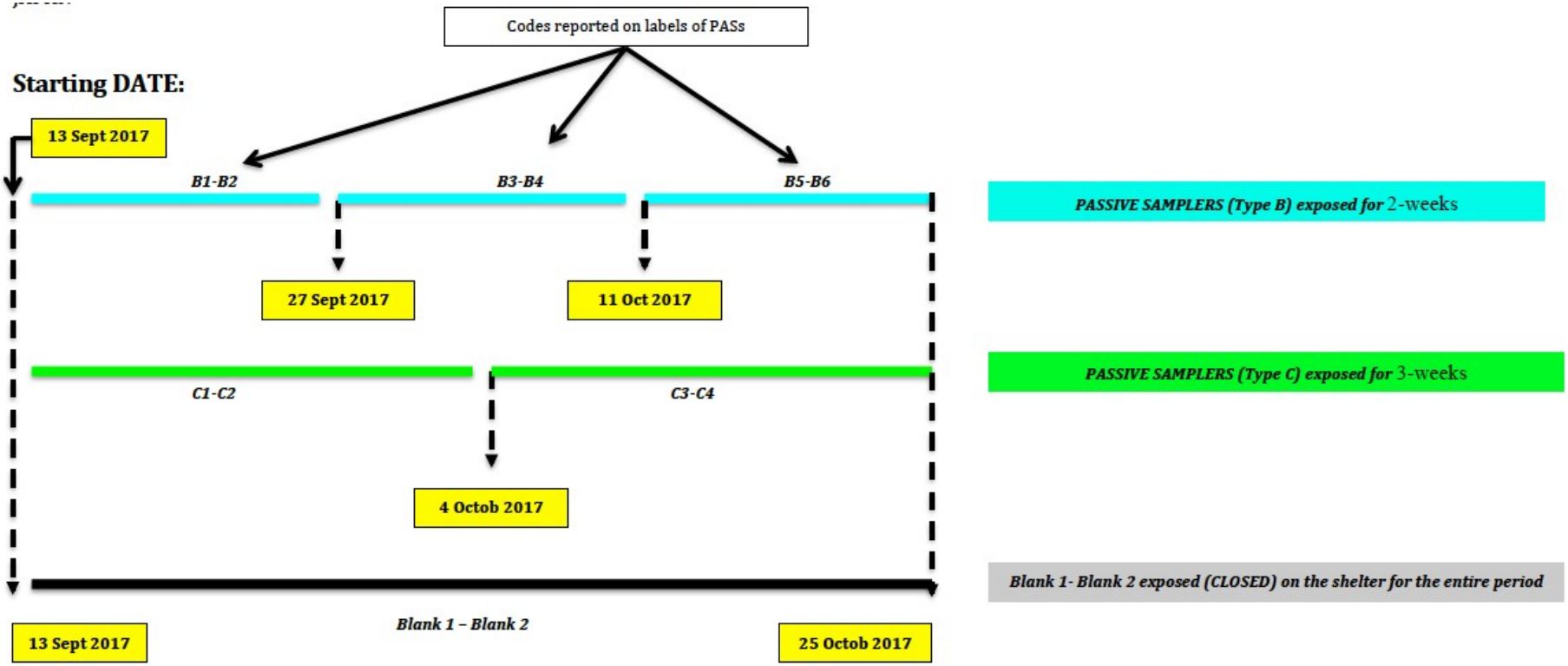


Figure 16. Sampling scheme with information related to the codes of PASs and the time of exposure (i.e., two weeks, three weeks etc.) for 'GMOS STATIONS'.

SAMPLING SCHEME FOR 'WHO SITES' (polluted sites)

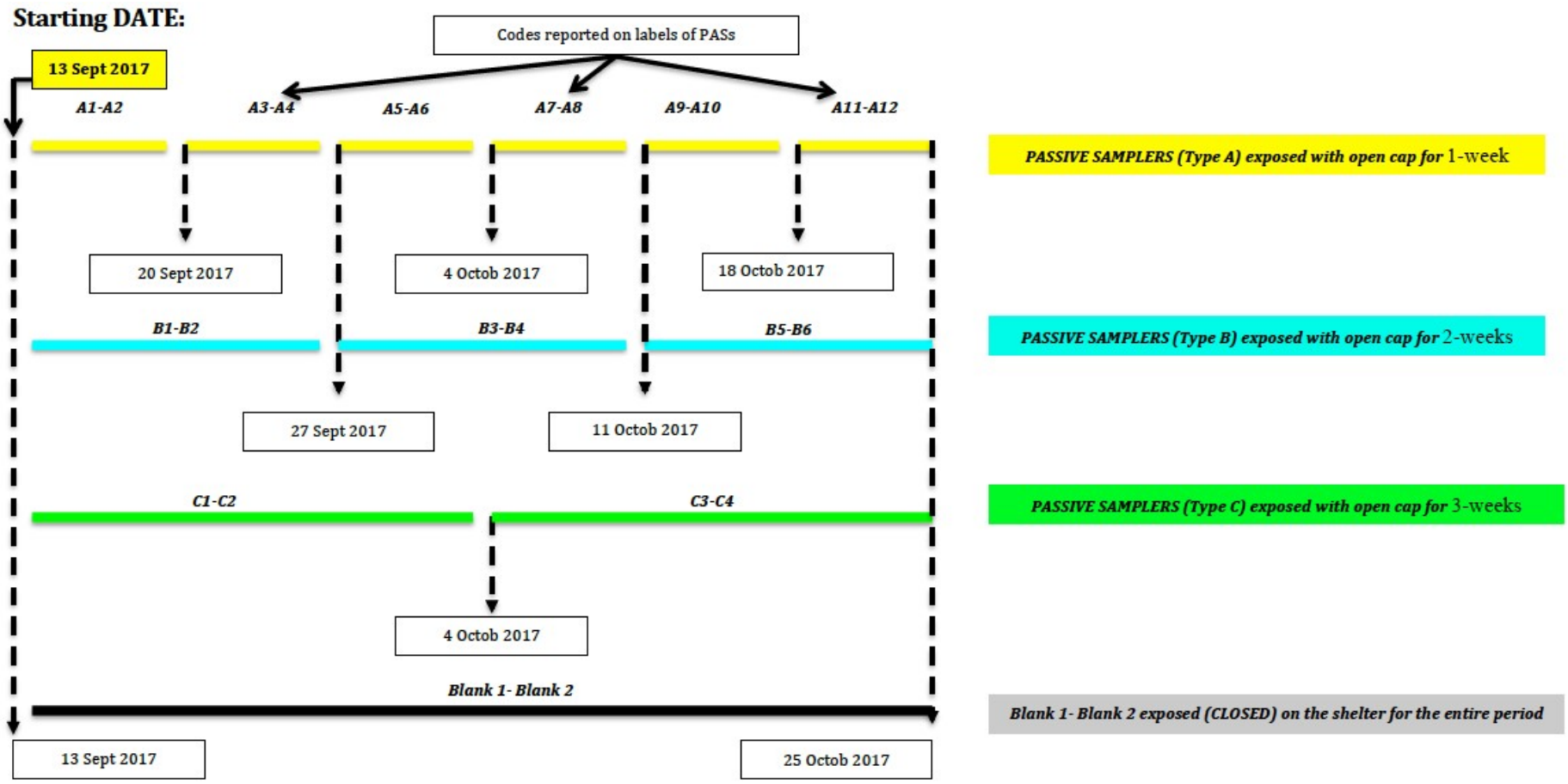


Figure 17. Sampling scheme with information related to the codes of PASs and the time of exposure (i.e., two weeks, three weeks etc.) for 'WHO SITES.

5. Data evaluation (including QA/QC and Data Treatment, Comparisons with automatic analyzers)

5.1 Hg Tekran/Lumex Measurements and on-going GMOS ground-based mercury measurements

Most of the on-going GMOS stations measure concentrations of atmospheric mercury fractions by using an automated and continuous mercury speciation system: the Tekran Mercury Vapour Analyzer Model 2537 coupled with the speciation models 1130 for GOM, and 1135 for PBM (Tekran Instruments Corp., Toronto, Ontario Canada). This equipment meets the GMOS requirements and is commonly available. Measurements are obtained through a multi-step procedure as described elsewhere using an impactor inlet (2.5 µm cut-off aerodynamic diameter at 10 L min^{-1}), a KCl-coated quartz annular denuder in the 1130 unit, and a quartz regenerable particulate filter (RPF) in the 1135 unit. TGM measurements in air can also be performed by using a monitoring system from Lumex, which does not employ trap-and- desorb technology (Lumex, St. Petersburg, Russia). Among the on-going GMOS stations there are actually two ones that are measuring TGM/GEM levels by using the Lumex Analyzer. In this experiment, in particular, only the site in Russia, LIS, use the Lumex analyser. Data coming from the on-going ground-based sites have been acquired by the GMOS Cyber-(e)-Infrastructure (GMOS-CI). The GMOS-CI collects raw data on mercury observations and ancillary parameters from the GMOS network. Each monitoring site measures mercury and associated parameters followed Standard Operating Procedures (SOPs) established by the GMOS Consortium. SOPs were developed and defined at the beginning of the project, and adopted within the global network. The GMOS-CI was designed to integrate data from different data sources using different network protocols and data formats. In order to comply with this vision, different strategies were needed to match the requirements of each GMOS site, which are served by ICT infrastructures with different architectures and capabilities. In some cases, monitoring sites are reached by an Internet connection, while others are not. GMOS-CI offers two options in order to integrate data:

- Data Upload through the GMOS GeoPortal, for those stations without Internet connection, by using a Human to Machine (H2M) approach; or
- Data Integration, using the System Integration capabilities of GMOS-CI, for those stations connected to Internet, by using a Machine to Machine (M2M) approach.

In order to gain data reliability and comparability raw data are screened with an ad-hoc validation process the "*GMOS-Data Quality Management System – G-DQM*" aimed to Quality Assure and Quality Control all datasets coming from the on-going GMOS sites. Once validation process has been completely done all resulting data files, reporting only valid data, are also arranged and harmonized and stored within the GMOS central database.

Data Quality Management in GMOS (QA/QC)

Within the GMOS network, in order to gain data reliability and comparability a great effort was also made to construct a centralized system based on a unique and separate QA/QC methodology able to assure and control the quality of mercury datasets coming from the GMOS network. This system, namely G-DQM (GMOS-Data Quality Management), is aimed to process raw data by integrating information coming from station e-logbooks (i.e. centralized electronic logbooks) and from automated Quality Assurance (QA) scripts (used as flagging criteria) related to specific procedures for the measurement of atmospheric mercury speciation data. Actually, there are only other two programs, RDMQ^{TM} and AMQC, independently developed by Environment Canada and the National Atmospheric Deposition Network (NADP), respectively, whose aim is to Quality Control (QC) atmospheric mercury speciation data related and restricted to North American monitoring sites. The big novelty introduced by G-DQM system consists in the service approach that facilitate real-time adaptive monitoring and ultimately support real-time decisions based on the Standard Operating Procedures (SOPs) adopted in GMOS. In this way, the G-DQM system can prevent the production of poor-quality data as well as can provide a thorough consistency of globally-based data that can be thus effectively used for international negotiations and global models of atmospheric mercury.

Sampling Methods

The collection quartz coated surface (passive membrane) is the key factor of the passive sampling system which can be thermally regenerated and reused for further measurements after the desorbing phase. The average concentration at the measurement site over the time period that the sampler is exposed to ambient conditions is determined by thermal desorption analysis of the passive membrane. Passive samplers were desorbed at 550°C and directly analyzed by CVAFS (Cold Vapor Atomic Fluorescence Spectrometry) using a Tekran 2537 analyser. The analytical technique is based on 5 min thermal desorption at 500° C of the passive membrane under argon or nitrogen of purity greater than 99,999 %, suitable for use as a carrier gas for CVAAS and CVAFS. Figure 18 shows examples of couples of PASs desorption step, and both graphics reported in the figure highlight the peak concentration obtained exactly after 5 min of the desorption time.

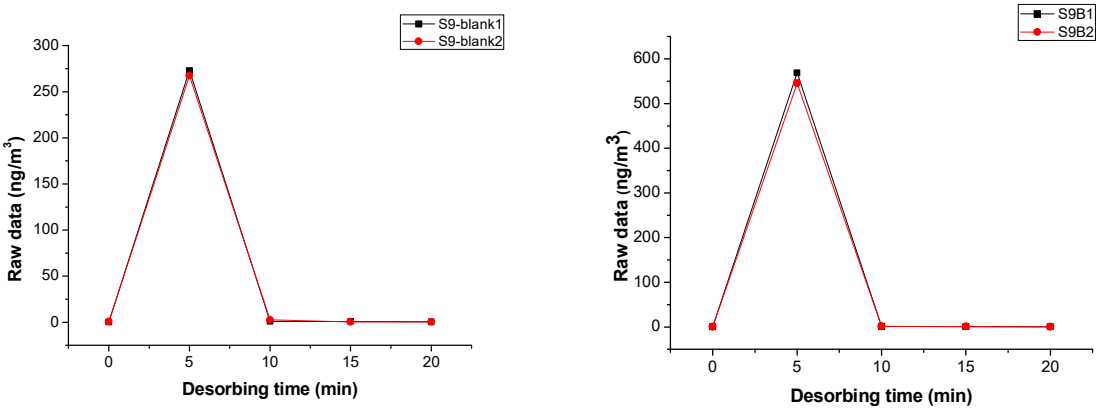


Figure 18. Examples of couples of PASs desorption step.

The lower detection limit of the samplers is determined by the use of blanks. The field blanks are kept in their containers and accompany the samplers to the field. Then, they are returned after the passive samplers were exposed, and are analyzed along with the exposed samples. The concentrations determined from the exposed filters are then corrected using the blanks. The lower detection limit is commonly defined as 2 to 3 times the standard deviation of the blanks. The repeatability of the results is quantified and checked by use of duplicate samples.
TGM/GEM was measured from the start of the intercomparison exercise using both the methods, conventional measurements by Tekran/Lumex systems and Hg passive samplers. Only one of the sites (LIS) used a Lumex instrument as reported in Table 2. As has been demonstrated in earlier intercomparisons, the Tekran and Lumex methods yield comparable results (Brown et al., 2010; Sprovieri et al., 2016). The Lumex instrument was run at a 5 min sampling frequency as well as the Tekran analysers at BAR and MCU, whereas the Tekran at CPO was run at 15 min sampling frequency according to the GMOS-SOPs for remote and rural monitoring sites. The manual PASs method was run for 2 weeks and 3 weeks sampling times. All reported Tekran/Lumex concentrations were therefore converted to bi-weekly/three weekly averages to allow comparison between the measurements and methods.

5.2 Comparison between the PAS devices and conventional Tekran/Lumex analysers Hg results

Table 10shows the statistical summary of TGM/GEM concentrations at the selected GMOS monitoring sites during the first and second campaigns obtained by conventional instruments (Tekran and Lumex). The GMOS sites located in the Southern Hemisphere, CPO and BAR, recorded mean concentrations of 0.92 ± 0.07 and 0.87 ± 0.17 ngm-3, respectively during the first campaign (see Table 2), and 0.97 ± 0.08 and 0.66 ± 0.13 ngm-3during the second campaign according to the annual mean concentration values normally observed in the Southern Hemisphere which are lower than those observed in the Northern Hemisphere (Sprovieri et al., 2016).
The other two sites, MCU and LIS, in fact recorded mean values of 1.16 ± 0.16 and 1.39 ± 0.25ngm-3, respectively, during the first campaign, and 1.15 ± 0.12 ngm-3 at MCU during the second campaign which are in good agreement with the overall mean concentrations observed at the multiple sites of the network distributed in the Northern Hemisphere (see Table 10).
The last site, MAL, showed several technical problems of the Tekrananalyzer, hence the QA/QC system recorded as "invalid" most of data, resulting in a final data covering for just the first two weeks. However, the mean concentration for MAL was of 1.40 ± 0.31 ngm-3 during the first campaign in good agreement with the Hg background in the Northern Hemisphere. During the second campaign MAL, due these technical problems on the Tekran system was not involved.
As Table 10 shows, also LIS site was not involved during the second campaign due to a period of technical maintenance of the Lumex instrument, therefore, the co-exposure of active and passive sampling devices was performed during the second campaign only at three

sites, one in the Northern Hemisphere, MCU, and two in the Southern Hemisphere, BAR and CPO. While from winter to spring/summer MCU did not show significant variations of concentrations, BAR and CPO stations recorded higher Hg concentration during the summer and lower during the cold season (see Table 10).

Table 10: Hg statistical summary at GMOS monitoring sites during the first and second campaigns by conventional instruments (Tekran/Lumex analysers).

1st Campaign	**BAR**	**MCU**	**CPO**	**LIS**	**MAL**
Sampling Time	Tekran 5'	Tekran 5'	Tekran 15'	Lumex 5'	Tekran 5'
n	*6843*	*7302*	*3828*	*11500*	*1498*
Min (ngm^{-3})	0.39	0.70	0.63	0.59	0.64
Mean ± SD (ngm^{-3})	**0.87±0.17**	**1.16±0.16**	**0.92±0.07**	**1.39±0.25**	**1.40±0.31**
MAX (ngm^{-3})	1.25	2.30	1.06	2.60	3.46
2nd Campaign	**BAR**	**MCU**	**CPO**	--	--
n	*7348*	*7949*	*3821*	--	--
Min (ngm^{-3})	0.20	0.70	0.65	--	--
Mean ± SD (ngm^{-3})	**0.66 ± 0.13**	**1.15 ± 0.12**	**0.97 ± 0.08**	--	--
MAX (ngm^{-3})	1.47	1.45	1.60	--	--

The Table 11shows statistical summary of Tekran/Lumex and PASs data at GMOS sites during the considered sampling periods whereas in Figure 3 are reported the Hg mean concentrations obtained by both sampling systems at all GMOS sites during the two sampling periods.

A preliminary analysis showed that the comparison between the mean concentrations obtained by both PASs and Tekran/Lumex analyzers produced acceptable results with the exception of CPO site where the PASs system recorded not typical Hg concentrations observed in South Africa and extraordinary higher than those of the Tekran [(TK: 0.92 ± 0.07 and 0.97 ± 0.08) (PASs: 1.74 ± 0.20 and 3.72 ± 0.6)] during both campaigns and above all during the second sampling period (see Table 11).

Table 11. Statistical summary of Tekran/Lumex and PASs data at GMOS sites during the first and second campaigns *(calculated only for the first two weeks).

ngm^{-3}	BAR	MCU	CPO	LIS	MAL
1st Campaign	Tekran	Tekran	Tekran	Lumex	Tekran
Mean ± SD	0.87 ± 0.17	1.16 ± 0.16	0.92 ± 0.07	1.39 ± 0.25	1.40±0.31*
1st Campaign	PASs	PASs	PASs	PASs	PASs
Mean ± SD	0.95 ± 0.17	1.37 ± 0.28	1.74 ± 0.20	0.98 ± 0.18	1.32 ± 0.04*
ngm^{-3}	BAR	MCU	CPO	--	--
2nd Campaign	Tekran	Tekran	Tekran	--	--
Mean ± SD	0.66 ± 0.13	1.15 ± 0.12	0.97 ± 0.08	--	--
2nd Campaign	PASs	PASs	PASs	--	--
Mean ± SD	0.44 ± 0.03	1.02 ± 0.12	3.72 ± 0.64	--	--

The higher and variable PASs results at CPO probably were due to uncorrected management and closure of the samplers exposed as well as incorrect storage and shipping of them as scheduled within the method (i.e., triple Ziplock bags). In addition, it is important taken into account that these results could be also influenced by the local conditions (i.e., dust, high wind speed, etc.) along with other parameters and factors occurred at the sampling site. Several samplers returned from the South Africa, in fact, showed the presence of dust inside the passive vials. A more detailed analysis has been reported within the subsequent paragraph.

The best results were recorded at the MCU station, where the PASs results were in agreement with the Tekran concentration for both the campaigns. The comparison results obtained at LIS and MAL also showed acceptable results compared to the active systems used. Also at MAL, it is important to point out that the comparison between Tekran and PAS data have been performed only on the first two weeks, as reported above, due to the overlap of some technical problems with the Tekran system. Figure 20reports the comparison between Hg Tekran mean values and PASs results for the first two weeks, showing a good agreement over the only single available data.

Most of the Tekran data recorded at this site during the sampling period, after the QA/QC process by the G-DQM system, has been in fact invalidated and only two weeks of them were of high quality, therefore, not enough for comparison with the PASs data recorded over the whole period. This is also the reason for that MAL has not been involved during the second sampling campaign.

At BAR, the PASs values resulted better for the first campaign, while the second campaign recorded values lower than Tekran concentrations. From the Figure 19it is possible to highlight that the PASs concentrations sometime resulted overestimated and underestimated compared to the Tekran values.

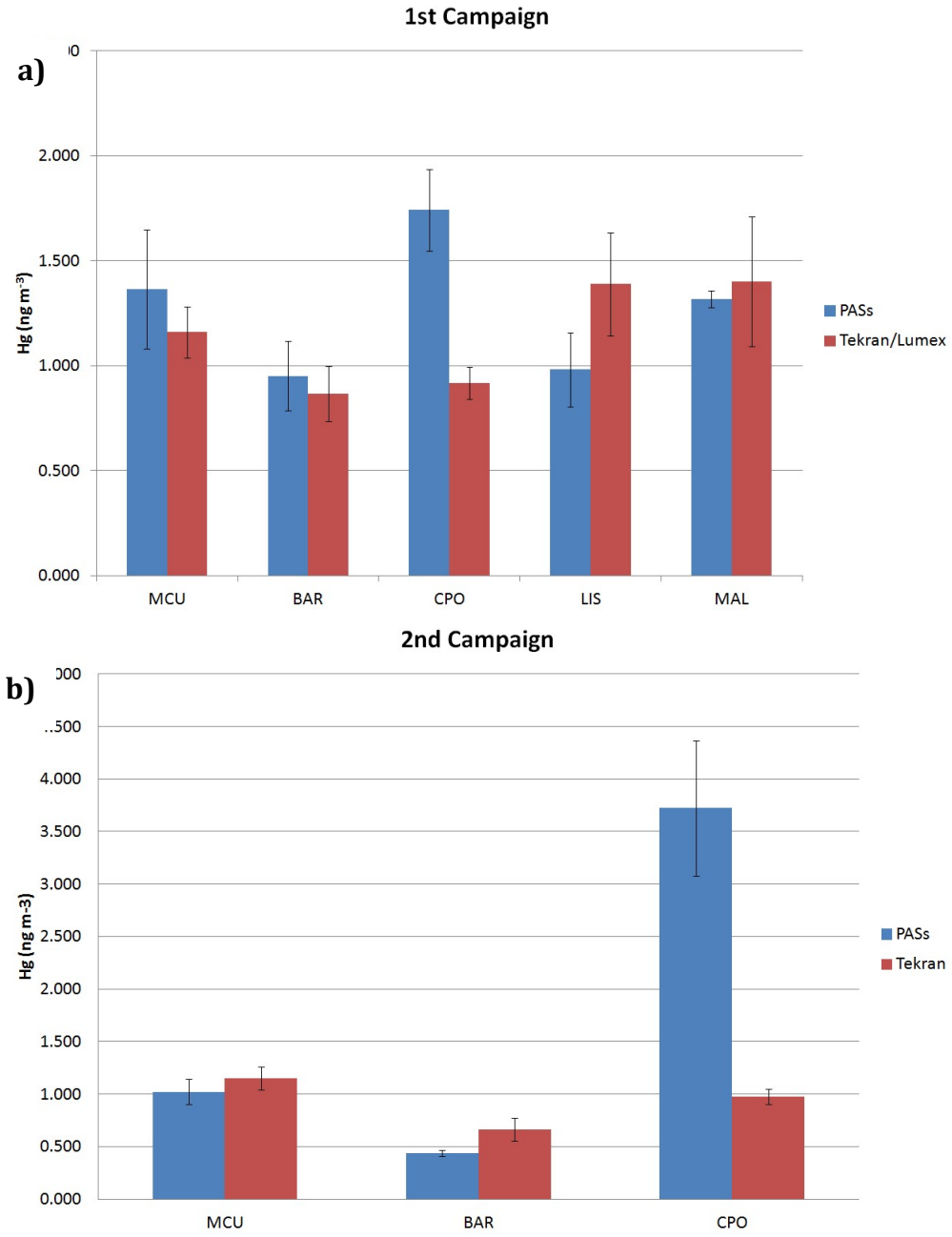


Figure 19. Comparison between Hg Tekran mean values and PASs results for the 1st (a) and 2nd (b) campaign at all GMOS sites.

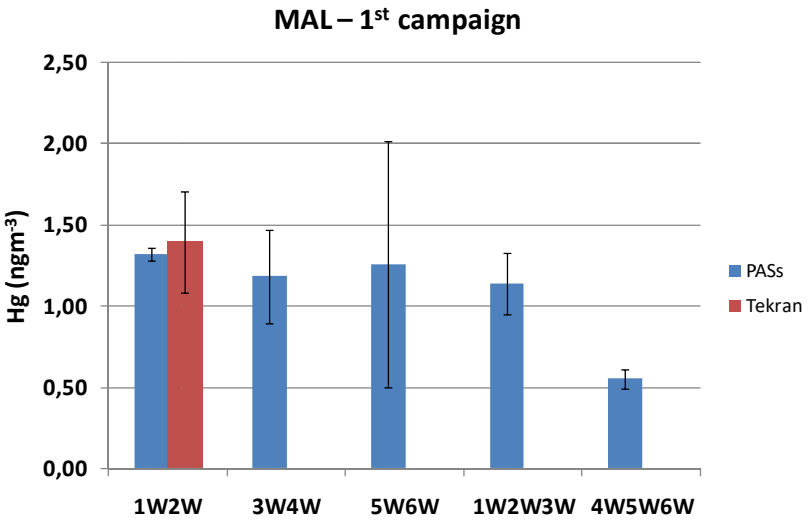


Figure 20. Comparison between Hg Tekran mean values and PASs results for the first two weeks at MAL and PASs results observed for the whole sampling period related to the 1st sampling campaign.

To obtain a synthetic characterization on the operation of the passive devices,for each observed sampling period, a comparison between the mean value of Tekran/Lumex Hg levels and the mean value of the two simultaneous passive samplers had been carried out.

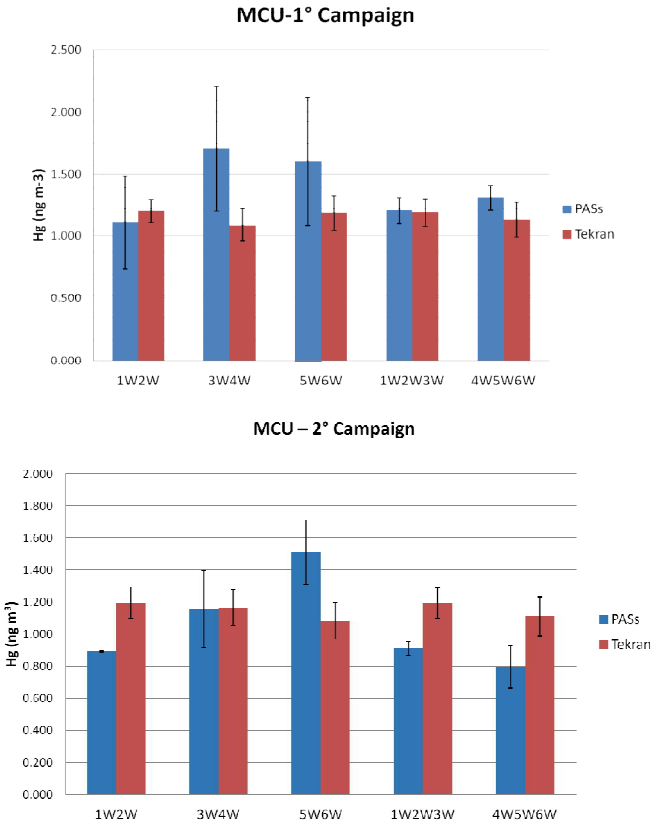


Figure 21. Comparison between Hg Tekran mean values and PASs results for the 1st and 2nd campaign at Mt. Curcio.

The comparison analysis for the Mt. Curcio station showed good results especially for the 1st campaign, where PASs values (mean ± sd) were always in agreement with Tekran data. On the other hand, the 2nd campaign showed mainly PASs values lower than Tekran mean (1W2W, 1W2W3W, 4W5W6W) (Fig. 21).

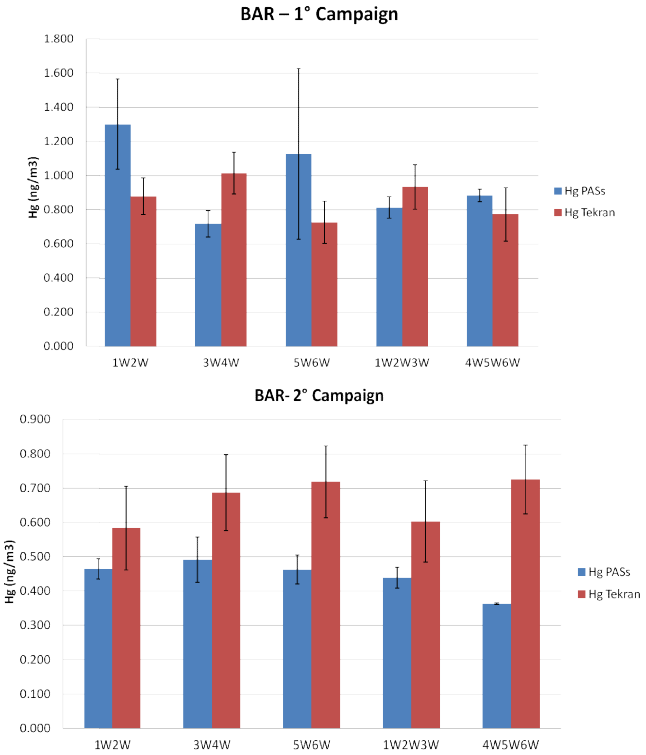


Figure 22. Comparison between Hg Tekran mean values and PASs results for the 1st and 2nd campaign at Bariloche.

The 1st Campaign performed at Bariloche, recorded good results especially for the three-weeks samples, while, by the comparison of the 2nd Campaign the Passives underestimated the Tekran values (Fig. 22).

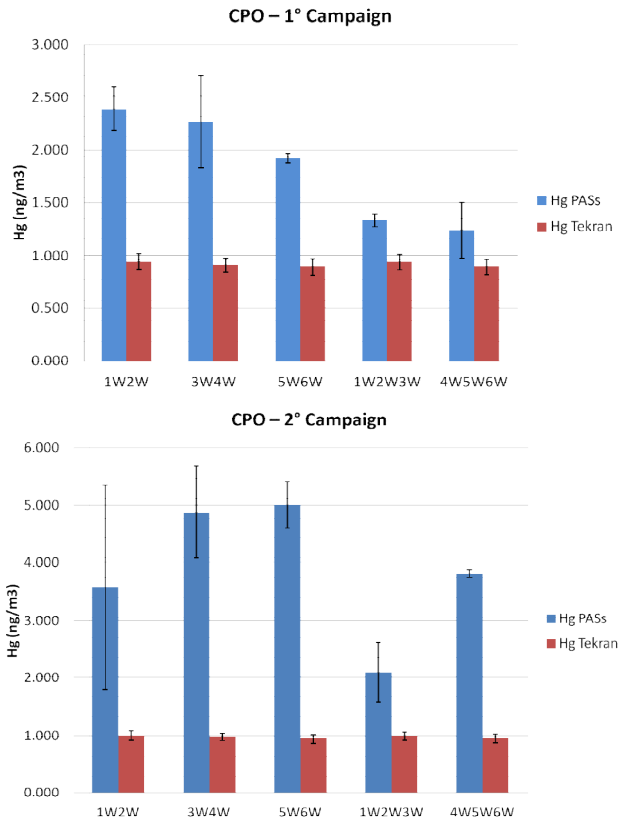


Figure 23. Comparison between Hg Tekran mean values and PASs results for the 1st and 2nd campaign at Cape Point.

As already mentioned, the Cape Point campaigns showed several problems, like as, the dust into vials of passives or errors of storage, which caused invalid results, mainly with values very high (until 5 times the right value) (Fig. 23).

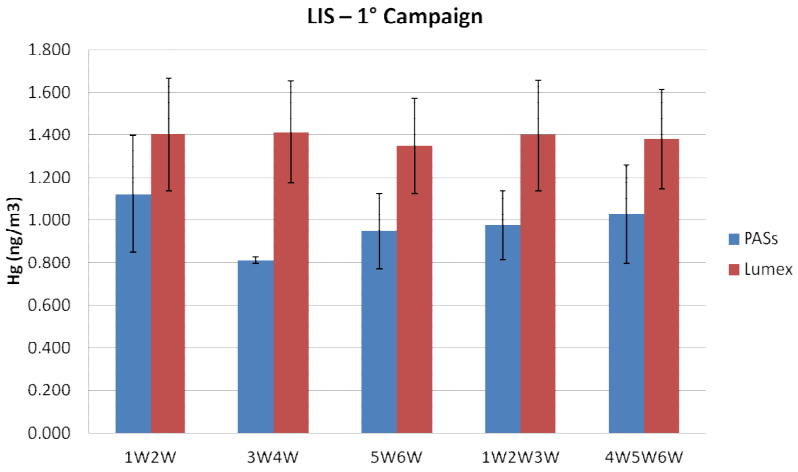


Figure 24. Comparison between Hg Tekran mean values and PASs results for the 1st campaign in Listvyanka.

The results of comparison campaign at LIS was acceptable, with PASs values in agreement with the mean values of Tekran, with the only exception of the 3W4W sample (Fig. 24).

In Table 12, a synthetic statistical comparison between the results obtained by passive samplers and conventional analyzers was carried out to evaluate the difference (in %) calculated between the two systems over the sampling time considered.
In particular, mean values over two-weeks and three-weeks for both Tekran/Lumex and PASs are reported in Table 12, as well as the difference between the systems. It is clearly observed that the overall variability in terms of percentage (%) between the methods decreases during the first sampling campaign, highlighting that the correlation between the PASs and the tekran/Lumex instruments improved continuously during the measurement period reaching acceptable difference values over three weeks. This results could be a clear consequence of the two simultaneous passives divergence over two weeks observed throughout the preliminary analysis performed by the boxplots of Hg data by PASs and Tekran/Lumex values, reported in the following paragraph.

Table 12. Synthetic statistical comparison between the results obtained during the first campaign by passive samplers and conventional analyzers carried out to evaluate the difference (in %) calculated between the two systems.

		Mean	Hg Tek (ng m^{-3})	Sd ± Tek (ng m^{-3})	Hg PASs (ng m^{-3})	Sd ± PASs (ng m^{-3})	Difference (%) systems
1° Campaign	MCU	Bi-weeks	1.16	0.14	1.47	0.46	-27%
		Three-weeks	1.16	0.15	1.26	0.10	-8%
		Bi-Three-weeks	**1.16**	**0.14**	**1.37**	**0.28**	**-18%**
	BAR	Bi-weeks	0.87	0.13	1.05	0.28	-20%
		Three-weeks	0.85	0.15	0.85	0.05	0%
		Bi-Threei-weeks	**0.86**	**0.14**	**0.95**	**0.17**	**-10%**
	CPO	Bi-weeks	0.92	0.07	2.20	0.23	-139%
		Three-weeks	0.92	0.07	1.29	0.16	-40%
		Bi-Three-weeks	**0.92**	**0.07**	**1.74**	**0.20**	**-90%**
	LIS	Bi-weeks	1.39	0.24	0.96	0.16	31%
		Three-weeks	1.39	0.25	1.00	0.20	28%
		Bi-Three-weeks	**1.39**	**0.24**	**0.98**	**0.18**	**29%**

In summary, excluding CPO station due to the discussed dataset, the difference (in %) between both systems for the first campaign ranged from 10% to 29% (in absolute value).

Table 13. Synthetic statistical comparison between the results obtained during the second campaign by passive samplers and conventional analyzers carried out to evaluate the difference (in %) calculated between the two systems.

		Mean	Hg Tek (ng m^{-3})	Sd ± Tek (ng m^{-3})	Hg PASs (ng m^{-3})	Sd ± PASs (ng m^{-3})	Difference (%) systems
2° Campaign	MCU	Bi-weeks	1.15	0.11	0.80	0.10	31%
		Three-weeks	1.15	0.11	0.46	0.05	60%
		Bi-Three-weeks	**1.15**	**0.11**	**0.63**	**0.07**	**45%**
	BAR	Bi-weeks	0.66	0.11	0.28	0.03	58%
		Three-weeks	0.66	0.11	0.21	0.01	69%
		Bi-Three-weeks	**0.66**	**0.11**	**0.24**	**0.02**	**63%**
	CPO	Bi-weeks	0.97	0.07	3.83	0.83	-294%
		Three-weeks	0.97	0.08	2.30	0.21	-136%
		Bi-Three-weeks	**0.97**	**0.07**	**3.07**	**0.52**	**-215%**

Table 13 reports the same information related to the second sampling campaign. It is important to point out that the improvement of the difference between the methods did not occur in this case. In fact, has not been observed a decrease of the difference (in %) between systems over a longer sampling time. In this case, the difference (in %) between systems ranged from 11% to 34%.

Box Plots analysis

In order to test the comparability of the methods a detailed data analysis have been performed considering Hg distributions and values observed at the selected sites by automated (Tekran/Lumex) and manual PASs instruments, respectively. In particular, the correct operation of the Hg passive devices was tested by exposing simultaneously two passive samplers for each selected measuring periods (varying from two or three weeks) and by comparing their results with those obtained, over the same observing period, from Hg standard reference instruments. According to the proposed development method, the mean value of the concentrations revealed by each passive device should be considered as the representative measure for their simultaneous exposure. The idea of this method is to guarantee stronger results considering possible statistical fluctuations of values. However, a preliminary analysis was herein carried out to evaluate the measurement precision of each single passive device, and the potential occurrence of specific working anomalies as well as the influence of erroneous procedures of handling and storage.

The Hg data distribution observed during each sampling campaign and at each selected monitoring station by the reference active instrumentation has been plotted by boxplots, where the central line of the boxplot shows the median value, the whiskers extend to the most extreme data points which are no more than range times the interquartile range from the box, and finally, the points besides the whiskers are outliers. Each obtained boxplot was then overlapped with both the single values of the corresponding Hg levels measured by the two

co-exposed passive samplers, to establish how much the latest ones fit within the Hg Tekran/Lumex distribution.

Hereafter, for each involved monitoring stations, specific graphs are reported and discussed for both the 1st and the 2nd campaigns and with respect to the planned measuring periods: 3 bi-weekly periods (1W2W, 2W4W, 5W6W) and 2 three-weekly periods (1W2W3W, 4W5W6W). At MCU station, the statistical distribution of Hg levels recorded by Tekran was quite steady for both the 1st and the 2nd campaigns, with whisker values ranging in any case from 0.8 to 1.5 ngm^{-3} (See Figure 25). Otherwise, the Hg concentrations measured by each single co-exposed device (Passive 1 in red and Passive 2 in blue) showed in general a more variable response, either for each single exposition, either over time. Going in details, as Fig. 9a shows, it is possible to observe that during the 1st campaign the difference of each single measurement from the two co-exposed devices was larger over all the 3 bi-weekly periods (1W2W, 2W4W, 5W6W) with a divergence between values (Passive1 - Passive 2) around 0.7 ngm^{-3}. Anyway, over both the 2 three-weekly periods (1W2W3W, 4W5W6W), the precision was better, with a difference in values of only 0.1 ngm^{-3}. Further, in terms of accuracy it is possible to notice that the response of the passive devices was better over the 2 longer sampling periods (1W2W3W, 4W5W6W), with Hg concentrations levels resulting included within the whiskers of the Tekran Hg data distribution. During the 2nd campaign better results were obtained, in terms of both precision and accuracy (see Fig. 25b). Also in this 2nd campaign the divergence of measurements from the two co-exposed devices was larger over the bi-weekly periods in respect to the three-weekly ones but, in this case, with a narrow difference in values (around 0.3 ngm^{-3}). Over both the three-weekly periods the difference in values was almost null and thus showing a very good result. In terms of accuracy it is possible to notice that during the 2nd campaign, with the 5W6W as the only exception, the values recorded with the passive systems were close to the lower whisker value of the Tekran data distribution, thus resulting in a general underestimation by PASs in respect to the reference Hg values. Differently, during the 1st campaign there was a general overestimation. This difference in the device response over the two observing campaigns could suggest a potential influence of some meteorological factors. For this reason and for the MCU station as a case study, an in depth analysis was done, where the main meteorological parameters have been also taken in consideration in evaluating their possible influence on the PASs correct operation (see the following section).

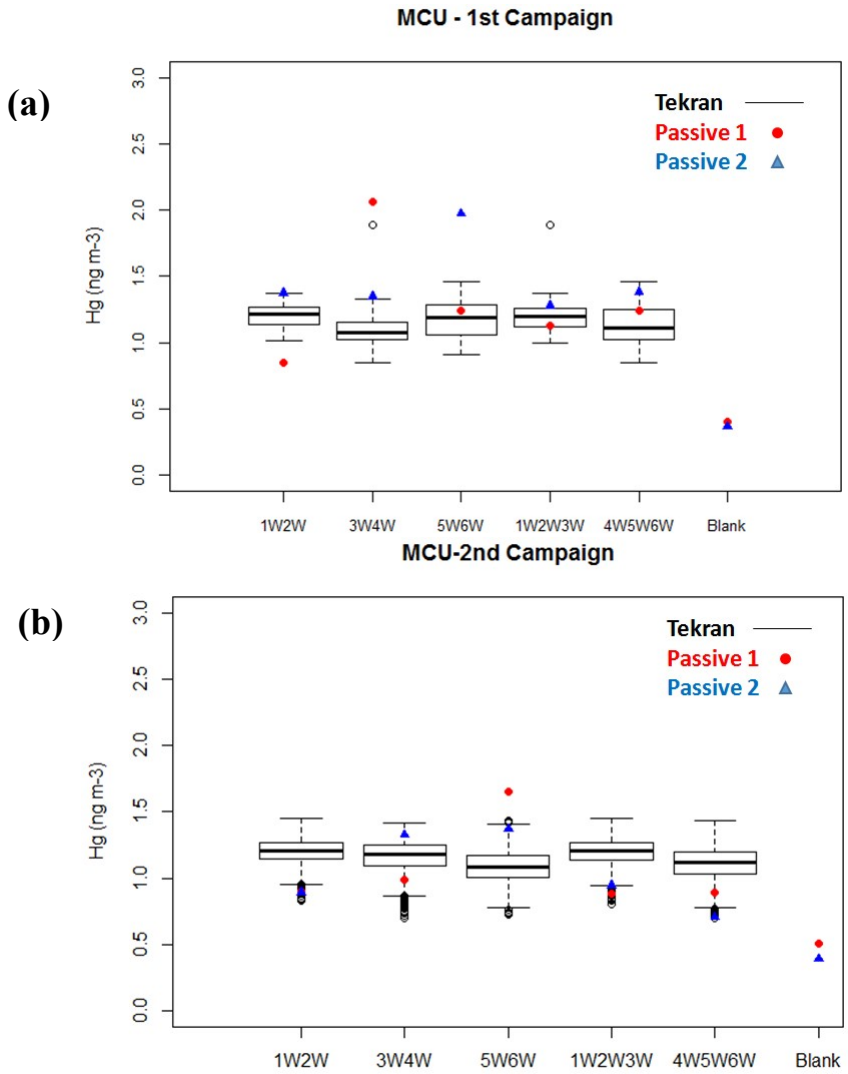


Figure 25. Comparison between the Hg Tekran data distribution, represented by boxplots, and the Hg data concentrations from each single co-exposed passive sample, data points in blue/red, obtained during the 1st (a) and 2nd (b) sampling campaign at Mt. Curcio station.

At BAR station, in general, the results were quite similar to those ones obtained and already discussed for the MCU station. In fact, the response of the passive devices was more precise and accurate with a general underestimation in values during the 2nd campaign in respect to those observed over the 1st one (see Fig. 26). Specifically, only over two bi-weekly periods (1W2W and 5W6W) during the 1st campaign, the divergence from the simultaneous passive systems was about 0.3 and 0.6 ngm^{-3}, respectively. These same sampling devices gave also Hg levels far from the distribution of reference Hg Tekran data (see Fig. 10a). However, with the above mentioned cases as an exception, it is possible to notice good results in terms of precision and accurancy. In fact, the difference of measured values from the co-exposed passive devises was in all other cases null or around 0.1 ngm^{-3}. Furthermore, the Hg concentrations measured by PASs were included or very close to the reference Hg distribution.

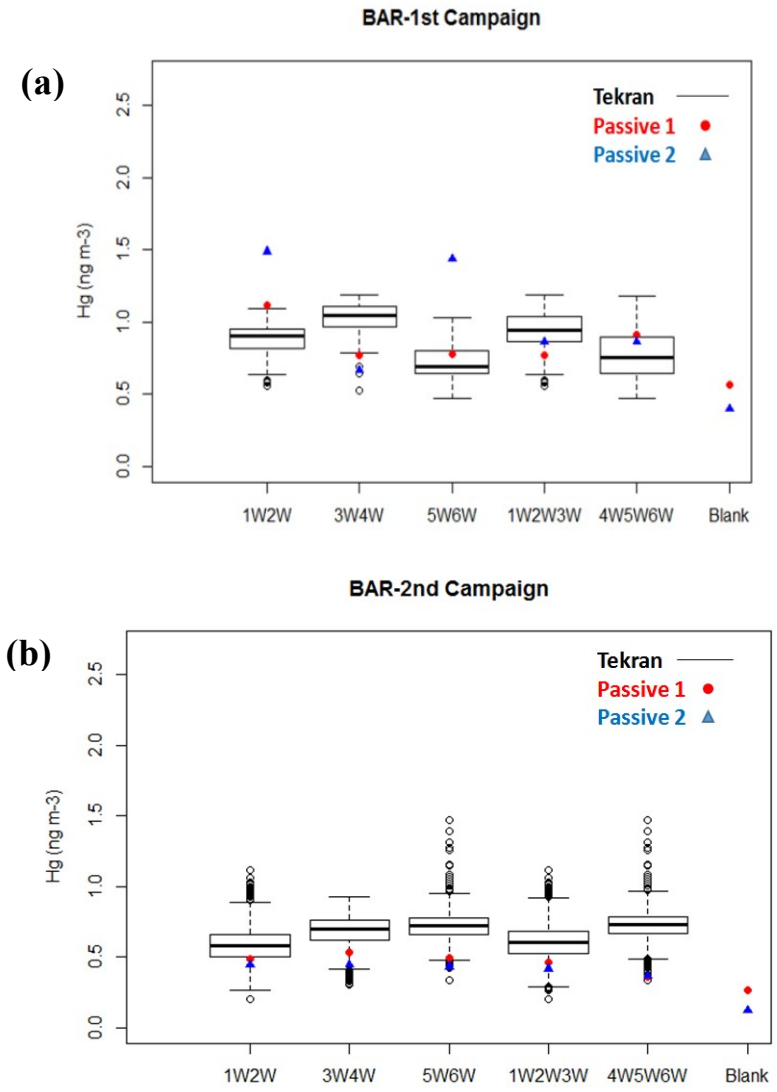


Figure 26. Comparison between the Hg Tekran data distribution, represented by boxplots, and the Hg data concentrations from each single co-exposed passive sample, data points in blue/red, during the 1st (a) and 2nd (b) campaign at the Bariloche station.

At CPO station, the sampling campaigns were negatively influenced by several problems. In fact, the samples of the 1st campaign were affected by extreme meteorological conditions, like very strong winds, which brought dust inside the passive vials. On the other hand, during the 2nd campaign, errors of storage had been done since just one plastic bag had been used, instead of three. These errors probably implied some bias on the results of passives that had measured much higher Hg concentrations than Hg data recorded by Tekran, for both campaigns (Fig.27).

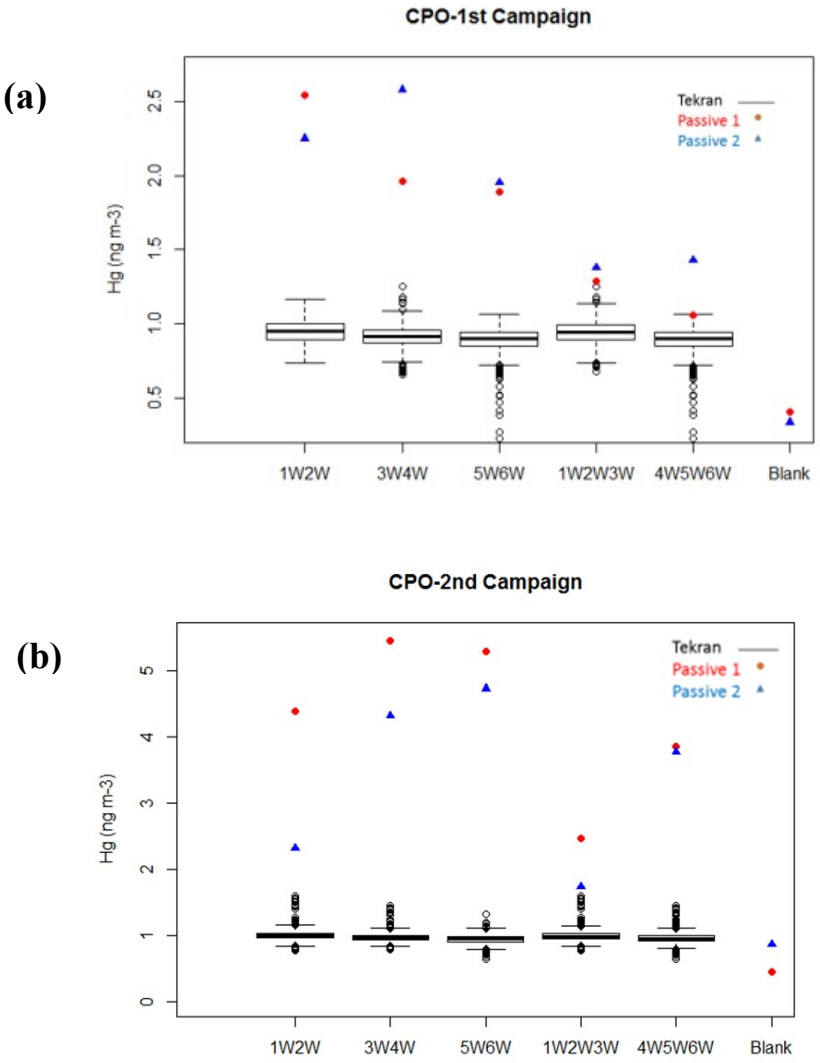


Figure 27. Comparison between the Hg Tekran data distribution, represented by boxplots, and the Hg data concentrations from each single co-exposed passive sample, data points in blue/red, during the 1st (a) and 2nd (b) Campaign at Cape Point station.

Also in terms of precision, not stable results were obtained with a difference of values (Passive 1-Passive 2) ranging from 0.1 to 0.6 ngm^{-3}, in the 1st campaign (see Fig. 27a) and from 0.1 to 2.0 ngm^{-3}, during the 2nd one (see Fig. 27b). As an exception, during the 1st campaign and only for the three-weekly sampling periods (1W2W3W and 4W5W6W) the passive devices registered Hg values closer to the distribution of the reference Hg data. At LIS station, it was possible to carry out only the 1st campaign, which gave back quite good results in terms of reproducibility. There was a general underestimation of passive results in respect to the Hg Lumex data distribution even if, over each observing period, both Hg concentrations measured by the two co-exposed passive devices resulted included within the lower part of the box-plot with reference Hg data. In terms of precision, the results were good

only for the 3W4W observing period, whereas in the other cases a difference of values ranging from 0.2 to 0.4 ngm^{-3}, was recorded (see Fig. 28a).

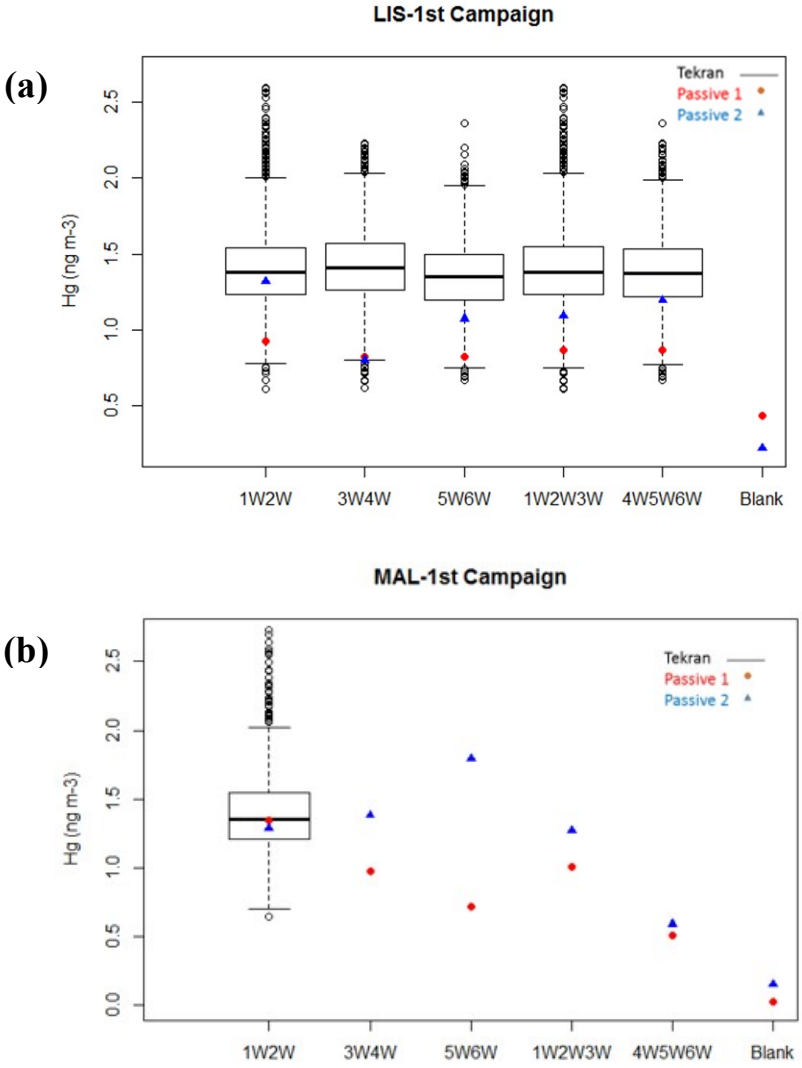


Figure 28. Comparison between the Hg Tekran data distribution, represented by boxplots, and the Hg data concentrations from each single co-exposed passive sample, data points in blue/red, during the 1st Campaign atListvyanka (a) and at Mt. Ailao (b).

At MAL station, there were technical problems of the Tekran instrument, resulting in a data coverage of just two weeks representative only for the 1W2W sampling period. However, for this specific case, the result of the Hg levels measured with passives were in very good accordance with the Hg reference Tekran data, being similar the response of the two simultaneous passive devices and their revealed concentrations very close to the median value recorded, over the same sampling period, by the standard Tekran instrument. For the other cases, for which reference values were not available, it is possible to notice that the precision was quite variable with a difference in values that ranged from 0.1 to 1.0 ngm^{-3}(see Fig. 28b).

Bootstrapping analysis

Due to the small dataset, the bootstrapping analysis was conducted to evaluate if the distribution of the mean Hg concentrations of Tekran and Hg Passive (given by the mean value of the two simultaneous passives) belonged to the same population. The bootstrapping analysis is a random sampling with replacement, based on the inference about a population from sampled data. The population is modelled by a "resampling" of data, then the inference of "resampled" data is conducted.

The bootstrapping analysis has been applied to the dataset of Mt. Curcio (MCU) and Bariloche (BAR), because they showed the more solid and valid dataset, with the largest number of data (10 passives data/Tekran means), and without errors of sampling. The "null hypothesis", which there is no relationship between the populations of Hg mean values of Passives and Tekran data, has been rejected. In fact, like the distribution of the two populations showed, they were not independent (Fig. 29). Furthermore, the analysis highlighted that the distribution of Hg passives data was generally with a broader range than the Tekran distribution.

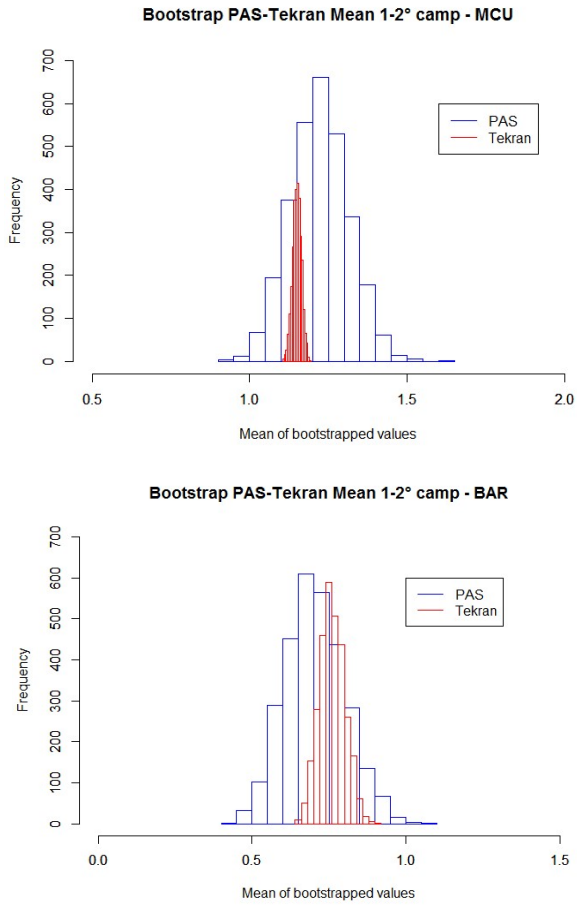


Figure 29. Comparison between Histograms with means of bootstrapped Hg values from Passives (PAS) and Tekran data observed during the campaigns at Mt. Curcio (MCU) (on left) and at Bariloche (BAR) (on right).

Influence of Meteorological parameters on Hg PASs sampling results at MCU Station.

MCU is a high altitude station (1780 m a.s.l), hence, during the winter season, it is generally characterized by continuous snowfalls, low temperatures, and many storms, whereas during the spring and in summer, the weather is mainly fair and the temperature increases until about 30/35 °C. The first comparison campaign was performed during the winter season, from the 1st of February 2017 until the 15th of March 2017. The temperature for this period was very low, ranging between about -5°C and 10 °C, with a mean value of 1.3± 3.7 °C, while the wind speed recorded was about 4.9 m/s, and ranged from calm wind condition to a maximum value of 24.3 m/s. Moreover, the mean relative humidity was about 67%. Unfortunately, during this period, the meteorological sensors presented some technical problems, resulting in a data coverage for only the last two weeks of the campaign. Due to the scarce dataset of ancillary parameters (only two points), any qualitatively discussion was not possible for this period.

On the other hand, the second campaign, which started on the 31st of May 2017 until the 7th of July 2017, involved two seasons, the spring until the summer solstice, on the 21st of June, and the beginning of summer. During this campaign, the temperature ranged between about 5°C and 30°C, and the mean values calculated over the sampling weeks was increasing gradually. The wind speed ranged between 0 m/s and 20 m/s, while the mean value was of 3.2 ±2.6. Finally, the mean value for the relative humidity of the whole period was about 50%. The spring/summer campaign showed an interesting behaviour of the meteorological parameter and the passives' response. By a qualitative analysis, it seemed that the PASs concentrations were raising with an increase of the temperature and of wind speed (Fig. 30a,b), except for the three-weeks sample 3W4W5W, which did not clearly show this behaviour. The RH ancillary parameter seemed to not cause any influence (Fig. 30c). However, this dataset is still too little to proceed with a quantitative analysis that could confirm with certainty any influence. Hence, further measurements, for longer period could allow to establish or exclude some dependence on the meteorological parameters.

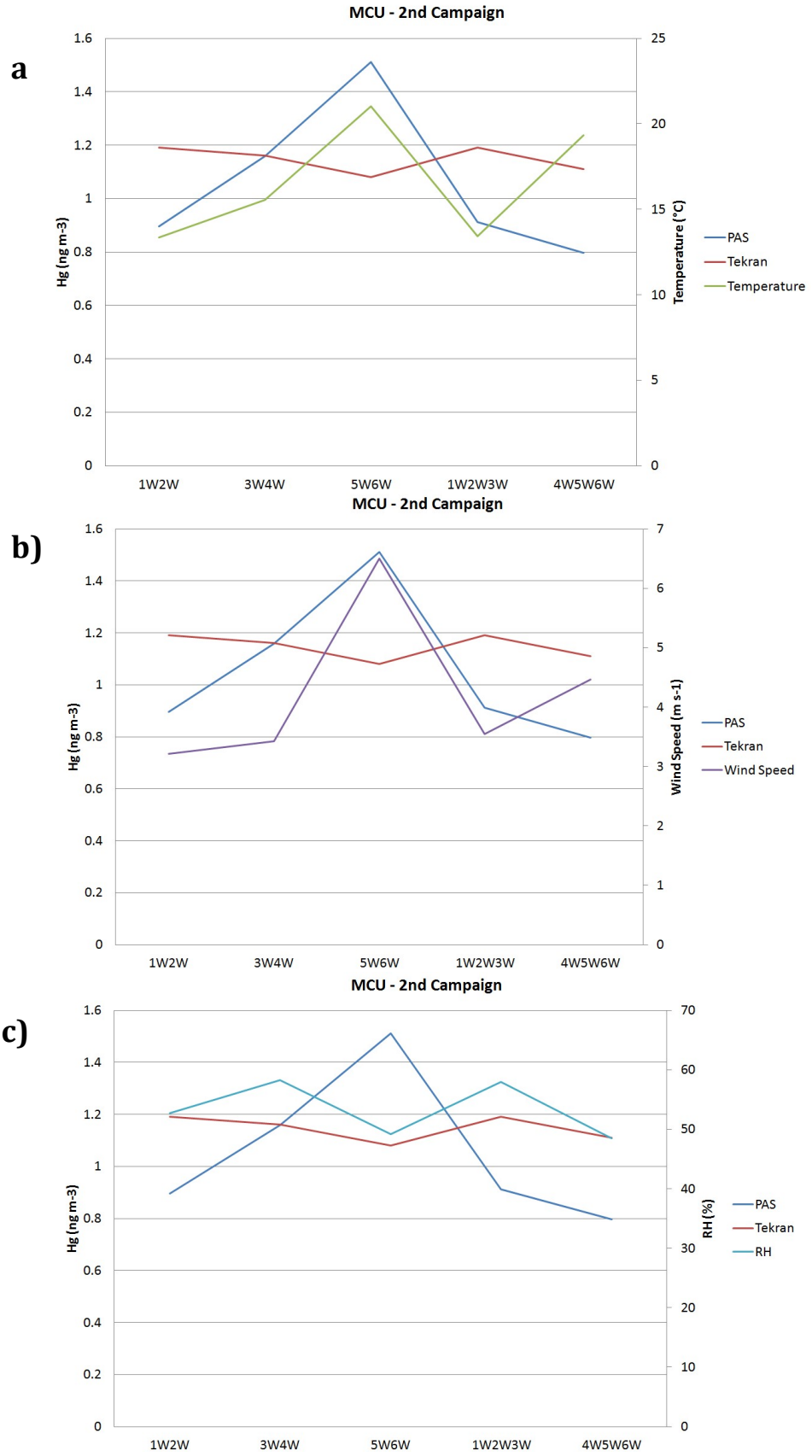
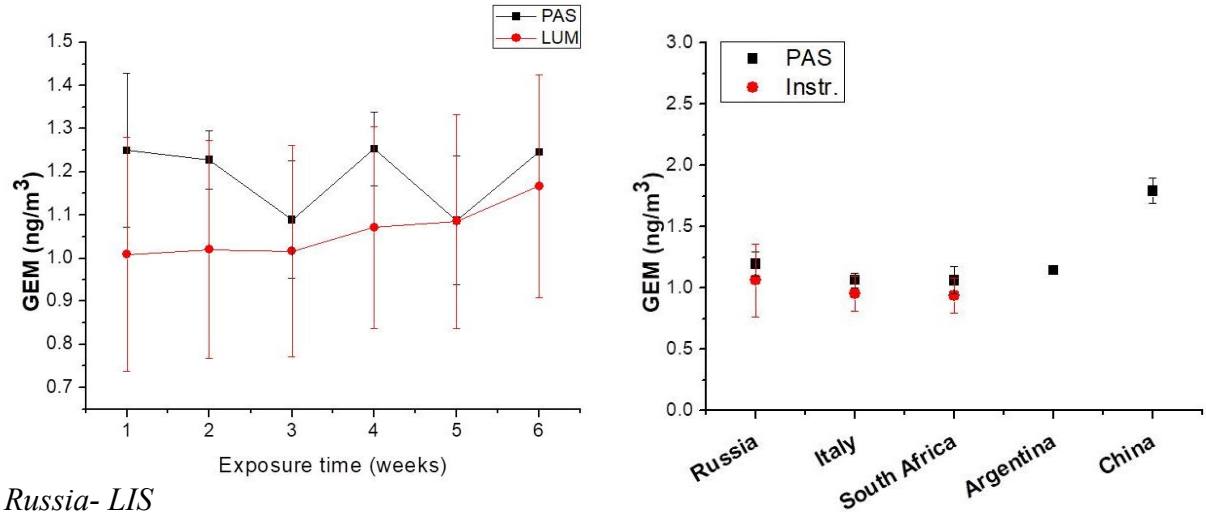


Figure 30. Comparison between Hg pattern from Passives (PAS) and Tekran data observed during the 2nd campaign at Mt. Curcio (MCU) and the meteorological parameters: air temperature (a), wind speed (b), relative humidity RH (c).

3rd Sampling Campaign

Figures 31, shows the results obtained in Russia, Italy, South Africa, Argentina and China sites, respectively where passive sampling devices have been exposed to the atmosphere simultaneously monitored by the analytical equipment. More specifically Figure X depicts the comparison between the GEM mean values of the PASs deployed at Listvyanka for six weeks (February-March 2017) and the mean values calculated on the data reported by LUMEX (on the left) over the same time. All the SDs are overlapping. Similarly, the comparison between the mean values of PASs and Analytical Instrumentation for 6-week sampling reported very similar values for each site (LIS, MCU, CPO), with overlapping SDs. We have got PASs data also from Argentina and China, but some troubles occurred to the electronic equipment during the monitoring campaign, have prevented the comparison of the two sampling methods results (on the right). Mercury concentration from PASs has been calculated using the SR resulting from CNR-Italy outside monitoring campaign, without any treatment due to the influence of temperature, wind-speed and humidity, in order to understand the effectiveness of the sampling devices, regardless of longitude, latitude, proximity to the coasts, at sea level or height.



Russia- LIS

Figure 31. Comparison between different sampling sites during third campaign.

Therefore, a preliminary analysis showed that the comparison between the mean concentrations obtained by both PASs and Tekran/Lumex analyzers produced acceptable results also during the 3rd sampling campaign. At the GMOS site located in Argentina, due to several technical problems related to the Tekran analyser, the GMOS QA/QC system recorded as "invalid" most of data, resulting in a final Hg data recorded only by the PAS as reported in Figure 32. The GMOS sites located in the Southern Hemisphere, CPO (South Africa) and BAR (Argentina), recorded mean concentrations of 0.93 ± 0.14 (Tekran Analyser) and 1.06 ± 0.11 ngm^{-3} (PAS) at CPO, and 1.14 ± 0.03 ngm^{-3} (PAS) at BAR, highlighting values normally observed in the Southern Hemisphere which are lower than those observed in the Northern Hemisphere (Sprovieri et al., 2016). In addition, Hg

concentrations obtained by both the systems are in good agreement with those observed during the previous sampling campaigns.

Argentina

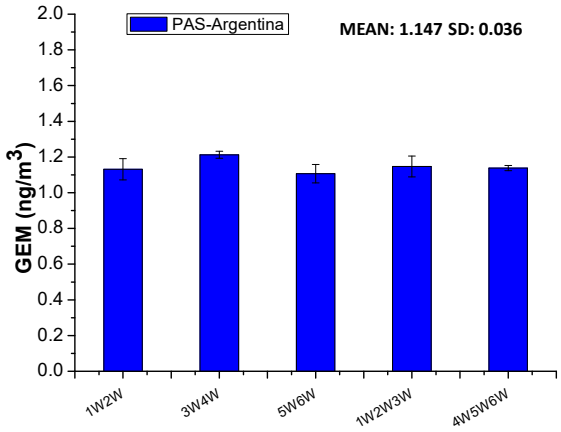


Figure 32. Results at GMOS site located in Argentinaduring third campaign.

Also at the other two sites in the Northern Hemisphere, MCU (Italy) and Listvyanka (Russia) the Hg concentrations recorded are in good agreement with previous data observed, and in particular, at MCU have been obtained Hg values of 0.95 ± 0.14 (Tekran Analyser) and 1.06 ± 0.06 ngm^{-3} (PAS) whereas at LIS of 1.06 ± 0.3 ngm^{-3} (Lumex Analyser) and 1.19 ± 0.1 ngm^{-3} (PAS). Figures 33 shows the results obtained only by PAS in India, Mongolia, Ghana and China, respectively. Mercury concentrations observed at all these sites were higher than those obtained at the other sites involved in the atmospheric monitoring plan, highlighting possible anthropogenic influences on Hg patterns, and characterizing these sites.

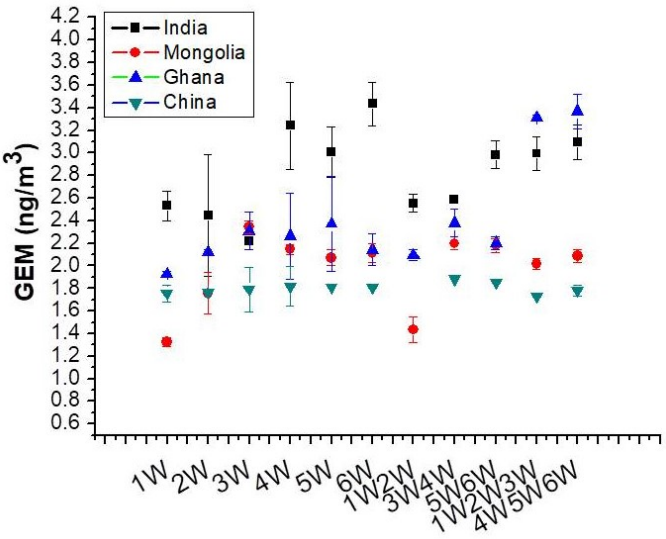
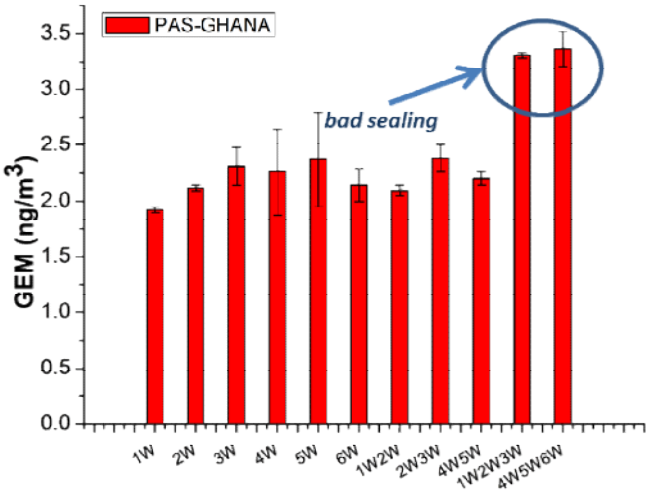


Figure 33. Results in India, Mongolia, Ghana and Chinaduring third campaign

The mean Hg values recorded were of 2.8 ± 0.17 , 1.9 ± 0.07 ngm^{-3}, 2.4 ± 0.14 ngm^{-3} and 1.87 ± 0.11 $ngm^{-3}$for India, Mongolia, Ghana and China, respectively.
Additionally, in the case of India and Mongolia, significant fluctuations in the data reported in different weeks of measurement have been depicted. Sometimes it has been possible to prove that they were related to the bad sealing of the PASs after the exposure (see Fig. 34) . In other cases it has been uncertain whether this issue could be attributed to the extreme measurement conditions (e.g. the strong wind of CPO site that moves the protection grid making sand and aerosols to enter) or to PAS bad handling, storage and shipping.



COSTA RICA data were unusable since measurements were only partially carried out and at the end of the third monitoring campaign, by the PASs designed and developed for the first campaign, then subjected to a bad storage.

5.3 Conclusion

Existing PASs for gaseous mercury have struggled to achieve the accuracy and precision necessary for background monitoring. In fact, the different passive samplers currently developed for Hg monitoring, capable of discriminating such small concentration variability and requiring high accuracy and precision, to date are characterized by high uncertainties due to inadequate detection limits or highly variable sampling Rate, (SRs) that should be addressed (in particular, SRs which need to be well characterized and repeatable). In this final report we discussed the study performed on the development of new Hg passive samplers and the results of two seasonal sampling campaigns at selected GMOS ground-based monitoring sites in order to test them in the field and compare the new Hg PASs samplers with active sampling system commonly used worldwide. The sampling campaigns were carried out at five GMOS sites, two in the Southern Hemisphere [(Cape Point, South Africa (CPO) and Bariloche, Argentina (BAR)] and three in the Northern Hemisphere [(Monte Curcio, Italy (MCU), Mount Ailao, China (MAL) and Listvyanka, Russia (LIS)]. The developed PAS for gaseous Hg have been designed to give information about the average Hg pollution levels over time periods of few weeks to months which seem to provide, as a preliminary analysis,

acceptable performance compared to active samplers in terms of sensitivity. On the other hand, they also presented in some cases, such as at CPO, South Africa, the higher and variable PASs results probably due to uncorrected management and closure of the samplers exposed as well as incorrect storage and shipping of them as scheduled within the method (i.e., triple Ziplock bags). The mean concentrations obtained by PASs at this site were not typical Hg concentrations observed in South Africa and extraordinary higher than those of the Tekran during both campaigns and above all during the second sampling period. In addition, it is important taken into account that these results could be also influenced by the local conditions (i.e., dust, high wind speed, etc.) along with other parameters and factors occurred at the sampling site. Several samplers returned from the South Africa, in fact, showed the presence of dust inside the passive vials. In these cases, it could be also possible that atmospheric components, i.e., atmospheric particulate matter and oxidants, sorb to or react with the diffusive barrier during deployment. Thus, in addition to meteorological (wind speed, relative humidity and temperature), we also should explore in the next future the effect of other factors which could impact the PAS's Sampling Rate. Another important factor we have to take into account, among the others influencing the response of the PASs, also the protective shield generally are not likely to completely eliminate the influence of wind on the thickness of the air-stagnant layer of the PAS like diffusive barriers. Therefore, the preliminary intercomparison results between PASs and the conventional active systems showed some variability and disparities in the data that could be due to some limitations of the samplers. In addition, while it is believed that the sampler takes up predominantly GEM, we cannot rule out the possibility for gaseous oxidized Hg to also pass through the diffusive barrier. Additional field performance tests are needed to characterize TGM/GEM passive samplers, and further development is needed before we can completely confirm the robustness of the method. For example, the CNR-IIA passive samplers need to be further tested at a monitoring site for a larger deployment period, employing in parallel a larger number of passive samplers for established time period in order to obtain a bigger amount of data for a detailed statistical analysis to assess the robustness of the method and of the sampling devices. The ease of deposition (electrospinning) and preparation (UV-irradiation in aqueous solution) as well as the high Hg sensitivity, suggests the chance to investigate the devices features by further comparison of the systems. We measured uptake curves in PASs deployed at a number of sites with ongoing active sampling across a wide range of climatic conditions. Although opinions on exactly how to test the various factors that influence PAS measurements may differ, among the many recommendations put forward for future works, one of the most crucial is the establishing of a factors list that require testing. This would likely facilitate sampler comparisons and in turn enhance future research in the field. In conclusion, further work into the testing of the developed Hg passives is essential to argue their validity in every condition, and after that, to strengthen the GMOS global network, providing an alternately sampling method that will be inexpensive and user-friendly.

6. Elements & Recommendations for Global Monitoring Plan

As stated in the studies on Stockholm GMP,

The Global Monitoring Plan should:

- Outline a strategic and cost-effective approach and build on, but not be limited to, existing and scientifically sound human health and environmental monitoring programmes to the extent possible, with the aim of providing appropriate and sufficient comparable data for the effectiveness evaluation of the Convention;
- Be practical, feasible and sustainable;
- Be inclusive, achieve global coverage and contain at least core representative data from all regions;
- Be designed to go beyond the first monitoring report and address long-term needs for attaining appropriate representative data in all regions;
- Provide for supplementing data, where necessary, taking into account the differences between regions and their capabilities to implement monitoring activities. Such progressive enhancement should be planned at the outset;
- Enable phased enhancement of the ability of parties to participate in regional arrangements for producing comparable data.

Furthermore with reference to Hg Air Monitoring activities, the CNR-IIA team agreed on the following:

- currently comparable air mercury monitoring data are provided by several networks including the GMOS for the global coverage, and a number of regional and national monitoring networks such as NADP, AMNet, APPMMN, AMAP, EMEP, etc. as extensively presented in the previous sections above,
- the map of existing networks and their spatial distribution, however, show geographical coverage gaps of large areas (i.e., Africa, Latin America and Caribbean, Russia) that are key for Long-Range transport analysis and identification of source-receptor regions relationship,
- a relevant potential contribution can come from the GEO (Group on Earth Observations) Flagship GOS^{4}M (www.gos4m.org) *"Global Observation System on Mercury"* in building the GMP for the Minamata Convention (MC). GEO is an intergovernmental program on Earth Observation signed by over 100 countries which include most, if not all, of the countries that signed and eventually already ratified the MC. UN Environment should explore the possibility of establishing a formal agreement between the GEO Secretariat and the MC Secretariat (UN Environment) that may ensure an open and efficient cooperation among the Parties involved that may help to leverage the future effort of Countries to build national expertise on mercury air monitoring, QA/QC protocols and data sharing,
- significant progress have been made in recent years in developing PASs (passive air sampler) based on different adsorbent types and diffusive sampler devices. The team

recognized the need to promote an inter-comparison among these different PASs in order to assure data comparability and reproducibility.
current gaps in geographical coverage of air monitoring networks may be filled by using PASs at existing monitoring sites used for the POPs as part of the GMP of the Stockholm convention.

7. References

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Annex A- Characteristics of the mercury vapour source

A small amount of liquid elemental mercury is kept in a closed thermostatted container, according to Figure A. The mercury concentration in the source is determined by the mercury vapour pressure (P_{Hg}) over the liquid mercury phase. Since P_{Hg} is strongly dependent on temperature, it is necessary to know exactly the temperature in the calibration vessel (i.e. the temperature of the liquid mercury phase). The temperature should be measured by the accuracy equal to or better than ± 0.1 °C. A thermometer that is certified traceable to an international standard shall be used. The pressure in the source shall be maintained equal to the ambient by help of a narrow capillary tube. The principles of using the saturated mercury source for calibration are described below.

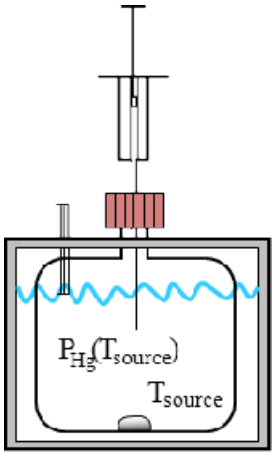


Figure A.1. A saturated mercury vapour source consisting of pure liquid mercury housed in a thermostatted water bath.

Figure A.1 shows how a sample of gaseous mercury is collected from a saturated mercury vapour source. A syringe is inserted via a septum on top of the flask containing liquid elemental mercury in equilibrium with its vapour. The syringe is conditioned by slowly moving the plunger up and down one or two times. A certain volume is then collected and used as a standard amount of mercury. The mercury concentration in the source C_{Hg}, can be calculated by help of the Ideal Gas Law according to,

$$C_{Hg} = \frac{P_{Hg}(T_{source})}{R\,T_{source}} A_{Hg} \qquad \text{ng } \mu l^{-1} \qquad \text{Equation A.1}$$

Where A_{Hg}, R and T_{source} are the standard atomic weight of Hg (200.59 u), Ris the ideal gas constant (8.314 J K^{-1} mol^{-1}) and T_{source} is the temperature in K [1].
It should be noted that the mercury concentration in the syringe will only be equal C_{Hg} when the temperature of the syringe is equal to T_{source}. Hence, if the temperature of the syringe happens to be lower than T_{source}, some of the gaseous mercury may condense on the surfaces inside the syringe. On the other hand, if the mercury source temperature is lower than the ambient the concentration in the syringe will be lower than in the source. An accurate and

precise correction for the temperature difference between the syringe and that of the source can be made [1] and the result is,

$$C_{Hg}(\text{syringe}) = \frac{P_{Hg}(T_{source})}{R\,T_{syringe}} A_{Hg} \qquad \text{ng } \mu l^{-1} \qquad \text{Equation A.2}$$

To use equation A.2, $P_{Hg}(T_{source})$ must be substituted by a mathematical function that describes the saturation pressure of mercury. If using the expression proposed by Ebdon at al., 1989 [2], the following equation is obtained.

$$C_{Hg}(\text{syringe}) = \frac{D}{T_{syringe}} 10^{-(A + \frac{B}{T_{source}})} \qquad \text{ng } \mu l^{-1} \qquad (T_{syringe} \geq T_{source}) \qquad \text{Equation A.3}$$

$T_{syringe}$ is the temperature of the syringe in Kelvin;
T_{source} is the temperature of the mercury source in Kelvin;
A is a constant with numerical value -8.134 46;
B is a constant equal to 3 240.87;
D is a constant equal to 3 216.523;

Equation A.3 shall be used to calculate the mass concentration of mercury vapour samples collected from a mercury vapour source using a syringe.

Equation A.3 is identical to that recommended in the recent European Standard NEN-EN 15852 [1] and resembles the equations recommended in many mercury instrument manuals and standards.
Remarks:

- Equation A.3 takes account of two different temperatures – the temperature of the mercury source and that of the syringe.
- Equation A.3 is only valid for situations where $T_{syringe}$ is equal to or higher than the temperature of the mercury source (T_{source}).
- It is recommended to keep the temperature of the mercury source at least some degrees Celsius below room temperature.

High accuracy is required for the determination of T_{source} as mentioned above. This is because the vapour pressure of mercury is exponentially dependent on temperature. Therefore, T_{source} appears in the exponential term of Equation A.3. The temperature of the syringe can normally be considered as equal to the room temperature and it is enough to measure this temperature with an accuracy of ± 1 ^{o}C.

References

[1] NEN-EN 15853 (en).Ambient air quality - Standard method for the determination of mercury deposition.ICS 13.040.20, June 2010.

[2] Ebdon L.; Corns W. T.; Stockwell P. B.; Stockwell P. M.; Application of a computer-controlled adsorber/desorber system to monitor mercury in air or gas samples: Part 1. Calibration and system description; Journal of Automatic Chemistry (1989), Vol. 11, No 6, p. 247-253

Characteristics of the Tekran 2505 mercury vapor source

It is recommended that the Tekran Model 2505 Mercury Vapor Primary Calibration Unit be used to perform manual injections and standard additions on the 2537. With this instrument a small amount of liquid elemental mercury is kept in a closed thermoelectric temperature controlled container, and no water bath is needed. The mercury concentration in the source is determined by the mercury vapour pressure (P_{Hg}) over the liquid mercury phase. Since P_{Hg} is strongly dependent on temperature, it is necessary to know exactly the temperature in the calibration vessel (i.e. the temperature of the liquid mercury phase). The temperature of the source is determined automatically by the 2505 and reported digitally. The 2505 is powered by 110 V line power. The temperature resolution of 0.001 °C and an accuracy of ±0.05 °C. A Hamilton digital syringe is used to draw predetermined amounts of mercury vapour from the device. The concentration of mercury obtained by the syringe can be determined by the temperature of the mercury chamber. Manual injections and standard additions should be performed by a trained technician following the instructions in the Tekran 2505 User Manual.

Figure A.2.The Tekran 2505 Mercury Vapor Primary Calibration Unit

Annex B- Cleaning of gold traps

A pair of gold cartridges (gold traps), i.e. glass tubes containing a large gold surface, is used in the Tekran 2537 mercury analyser to trap gaseous mercury from ambient air. The two cartridges continuously undergo adsorption/desorption cycles during the measurements. After prolonged use, deactivation may occur. One option is to remove the gold traps and install a new matched pair (this is typically performed annually or as needed). In certain situations cleaning of the cartridges may be an alternatively suitable solution. A possible monthly standard cleaning procedure is presented here.

To perform continuous mercury measurements two pairs of sample gold traps are required. After cleaning the cleaned gold traps should be tested against a reference pair ofgold traps, i.e. an additional pair that is not used for sampling. *If the tested cartridges show a deviation of more than 5 % a more profound treatment with Aqua regia (three parts of concentrated hydrochloric acid (HCl) and one part of concentrated nitric acid (HNO_3) is needed.*

Cleaning procedure of gold cartridges in an ultrasonic bath

Prior to cleaning the cartridges are rinsed with deionised water (3.5) using a clean syringe and immersed overnight in deionised water (3.5). The actual cleaning takes place the next day in an ultrasonic bath with a solution of deionised water (3.5) and an alkali detergent[1]. The solution consists of 300 ml of deionised water and 12 ml of the detergent.

Use disposable (rubber) gloves during the whole procedure!

The complete cleaning procedure:

I

a. With a 12 ml plastic syringe draw 10 ml of the solution into the cartridge and immediately force it out again; repeat this procedure 10 times;

b. Fill the cartridge again with the solution and place in into the ultrasonic bath for 9 minutes;

Repeat procedure a. and b. 10 times for both cartridges (A and B). Make sure not to mix the cartridges. Finnish by rinsing with deionised water.

II

a. With a new 12 ml plastic syringe draw 10 ml of deionised water into the cartridge and immediately forced it out again. Repeat this procedure at least 10 times using fresh deionised water each time.

b. Finnish the cleaning by flushing pure Argon or Nitrogen (3.1)/(3.2) gas through the cartridges. The Argon/Nitrogen gas should be flushed through each of the cartridges for at least 5 minutes.

Testing of the cleaned cartridge pair

The cartridges are tested in a Tekran 2537A analyser (preferably with an analyser not used for sampling). In this test the adsorption capacity of the cleaned cartridges are compared with a reference gold cartridge pair that not is used for continuous sampling.

Testing procedure

Start background air sampling with the reference cartridge pair. The instrument should be run using the same frequencyand timing that is normally used during sampling (5 min sampling cycles at a sampling rate of 1.0 L per min). Check the performance of the instrument, i.e. that it is yielding expected background TGM values and that the zero air values are sufficiently low (should be close to zero).

a. Measure a sequence of five complete cycles on each cartridge;

b. Install the cleaned cartridge pair. Start the instrument and perform a zero air test. Measure a sequence of five complete cycles on each cartridge.

The average values from the cleaned cartridges should be within ± 5 when compared to each other and should also not differ more than 5 % in comparison to the reference cartridges.

[1]Labosol-U-Ultraschall-Reiniger. This detergent is provided by the German company neoLab (www.neolab.de).

Annex C - Cleaning of equipment used for TGM/GEM measurements

All parts that are in contact with the sample air shall be cleaned extensively before use. Plastic or nitrile non-talc gloves shall be used during all steps of the cleaning procedure.

A suitable cleaning procedure is given below.

1) Wash with an alkaline detergent. Rinse thoroughly with ultrapure water

2) Leach with 2 % HCl (3.7) for at least 48 h. This can be done in a polyethylene tank.

3) Rinse thoroughly with ultrapure water (3.5) and dry in a clean laminar flow hood.

Store the cleaned equipment in double plastic bags.

Annex D - Recalculation of concentrations and air volumes to reference conditions

TGM and GEM concentration values are presented as the mass of Hg^0 per volume. Since actual air volumes vary with temperature and pressure, standardised volumes are used. With instruments using MFC and MFM the air volume is often standardised to a certain reference temperature and pressure. The default setting of, for example the Tekran model 2537A/B instrument, is 273.15 K and 101325 Pa. Concentration values can easily be recalculated to a certain reference condition according to,

$$C_{ref} = \frac{P_{ref}\,T}{T_{ref}\,P} C \quad (ng\ m^{-3}) \qquad \text{Equation D.1}$$

whereT_{ref} and P_{ref} correspond to the desired reference condition and T, P and C relate to the actual temperature, pressure and concentration, respectively [1]. To convert GEM concentrations obtained at varying temperature and pressure each individual value must be recalculated using Equation 7.1. Whereas when recalculating from one reference condition to another the relation between C_{ref} and C is a constant.

Likewise, may a volumetric flow rate value be recalculated to a standardised flow rate, according to,

$$F_{ref} = \frac{T_{ref}\,P}{P_{ref}\,T} F \qquad \text{Equation D.2}$$

whereT_{ref} and P_{ref} correspond to the desired reference condition and T, P and F relate to the actual temperature, pressure and volumetric flow rate, respectively [1].

The GMOS reference temperature and pressure are 273.15 K and 101325 Pa, respectively.

Annex E - Tekran Check and Maintenance List

Site Name:	**Country:**
Operator:	**Date:**

Each Visit Checklist:

2537 Analyzer and Data	**Check (X) if OK**
2537 date time correct	
Peak status = OK, OKF, or NP	
Sample volume 5.0 L	
Baseline voltage 0.100-0.250 V	
Baseline deviations < 0.100 V	
Calibration zero = 0.000	
SPAN RespFctr ≥ 6 x 10^6	
Span difference A vs B ≤ 5%	
Argon tank ≥ 200 psi	
Regulator ≥ 30 psi	
2537 lamp light off	
2537 perm light blinking	
1102 warm to touch	
1102 drierite blue	
Comments:	

Tekran Check and Maintenance List Annex E

Site Name:	Country:
Operator:	Date:

Biweekly Checklist:

2537 Analyzer and Data	Check (X) if OK
Replace soda lime trap	
Replace sample inlet filter	
Instrument meets weekly specifications	
Comments:	

Tekran Check and Maintenance List Annex E

Site Name:	Country:
Operator:	Date:

Quarterly Checklist:

Each Quarter	Check (X) if OK or Insert Value	Second Quarter	Check (X) if OK or Insert Value
Sample line leak check		2537 flow rate, instrument (lpm)	
Cartridge A, mass injected (pg)		2537 flow rate, measured (lpm)	
Cartridge A concentration (pg/m^3)		2537 flow rate, % difference (%)	
Cartridge A, manual injection % difference		2537 scale factor	
Cartridge B, mass injected (pg)		**Fourth Quarter**	**Check (X) if OK or Insert Value**
Cartridge B concentration (pg/m^3)		Change 2537 heater coils	
Cartridge B, manual injection % difference		Change 2537 zero air canister	
Trap heating coils bright orange		Change 2537 DFU filter	
Instrument shelter air ≤ 15 ng/m^3		2537 flow rate, instrument (lpm)	
Change 2537 sample filter		2537 flow rate, measured (lpm)	
Clean Teflon line from 2537 to soda lime		2537 flow rate, % difference (%)	
2537 leak check		2537 scale factor	
		Rinse heated sample line	

Tekran Check and Maintenance List Annex E

Site Name:	Country:
Operator:	Date:

As-Needed Checklist:

2537 Analyzer and Data	Check (X) if OK
Change 2537 lamp	
Install new matched gold cartridges	
Clean 2537 Teflon valves	
Replace 2537 Teflon valves	
Clean 2537 cuvette	
Replace 2537 cuvette	
Service 2537 pump	
Replace septum	
Check perm source temperature	
Check perm vent flow	
Replace filter holders and fittings	
Replace Argon cylinder (< 200 psi)	
Replace 2537 (record serial number)	
Comments:	

Annex F -Lumex Check and Maintenance List

Site Name:	**Country:**
Operator:	**Date:**

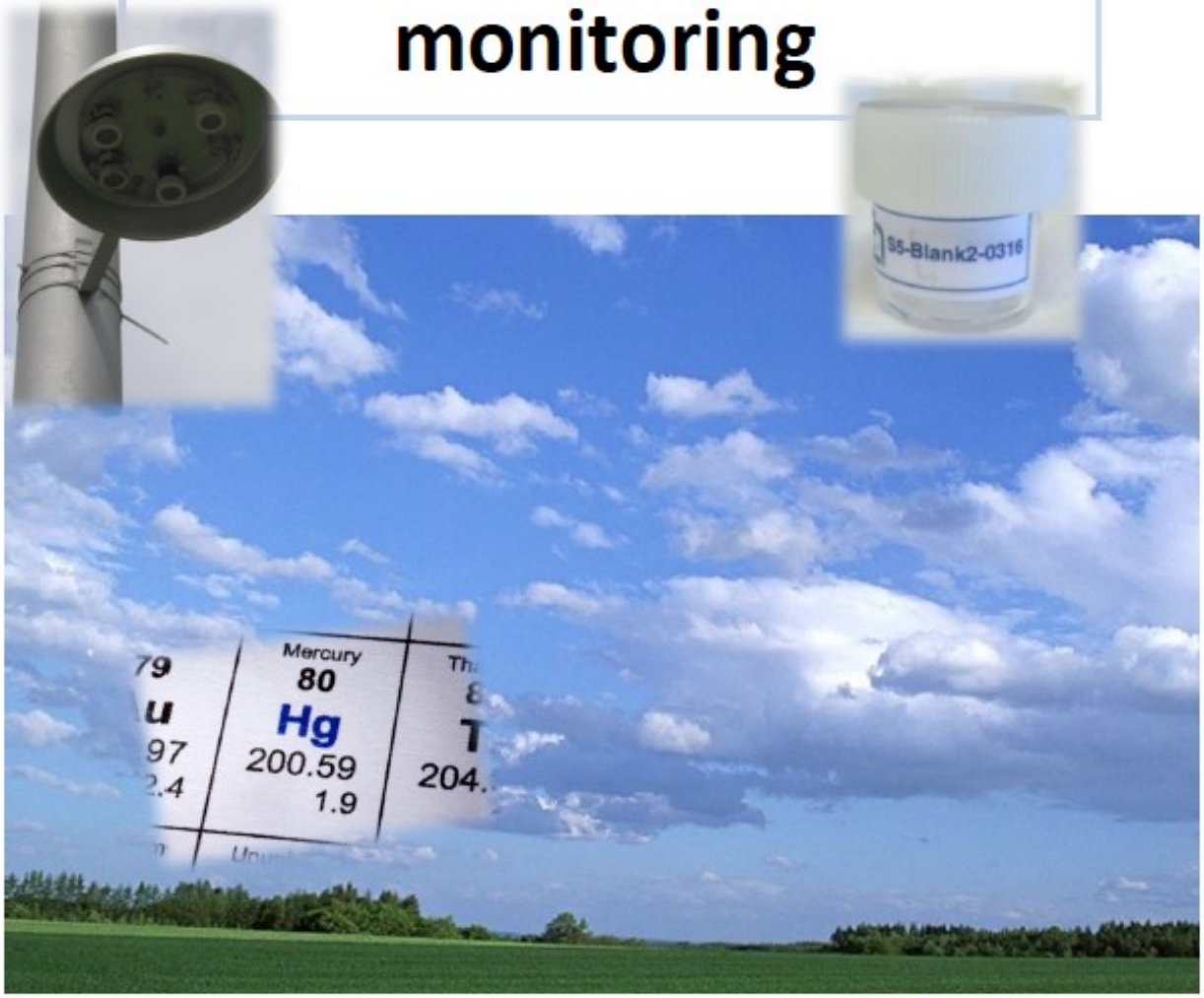
Maintenance Checklist:

Task	**Frequency**	**Comment, Expected value/ required condition**	**Checked, Adjusted, or Replaced**
Check system clock	Monthly	Maximum allowed deviation: ± 10 s	
Sample line leak check	Monthly	In conjunction with filter change	
Sample line verification with zero air	Every 6 months	Should be tested if lower than normal GEM values are obtained	
Replace sample inlet filter	Monthly	Or earlier if required	
Replace zero air filter	As needed	Or earlier if required	
Service by Lumex technician	Every 6 months	Or earlier if required	
Comments:			

ANNEX G – Practical instructions to use PASs

CNR - Consiglio Nazionale delle Ricerche
Istituto sull'Inquinamento Atmosferico

Practical instructions to use IIA-CNR passive air samplers (PASs) for Hg monitoring



http://www.iia.cnr.it/

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- ✓ *STEP 1. Locating sampling sites pag.3*
- ✓ *STEP 2.Opening the vacuum bags & Substituting the caps pag.4*
- ✓ *STEP 3. Exposing the PASs & Filling in the Sampling Data Sheet pag.5*
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INSTRUCTIONS

Passive Sampling Materials

Each box comprises **N. 1 shelter** and **N. 1 complete passive sampling set**.

Each sampling set includes **up to N. 6 bags**, labelled with sequential numbers, holding the samplers required for a 6-week monitoring campaign.

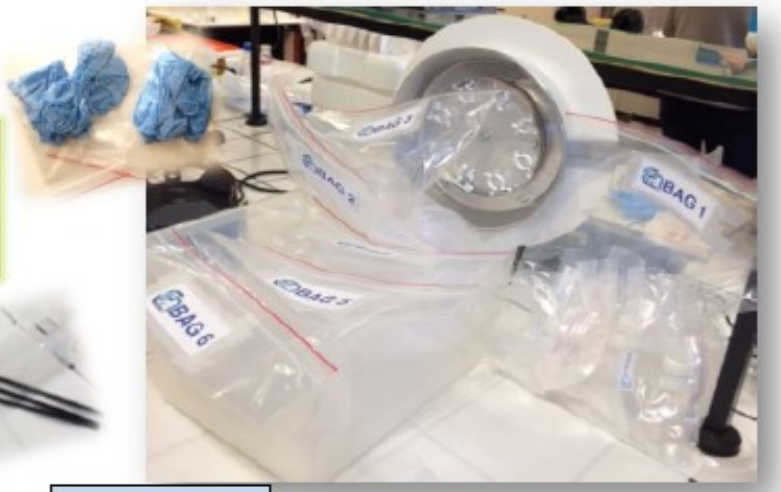
*** Only for GMOS sites: Please note that a weekly sampling will be not carried out, thus the PASs named as A are not included within the bags.*

Both N. 2 and N. 6 bags are not part of the related sampling set.

- Specifically each bag contains a well defined couples of samplers individually kept under vacuum:
  - **Bag 1**: N. 4 couples of under vacuum (u.v.) passive samplers (A1-A2, B1-B2, C1-C2, Blank 1-Blank2)
  - **Bag 2**: N. 1 couple of u.v. passive samplers (A3-A4) **
  - **Bag 3**: N. 2 couple of u.v. passive samplers (A5-A6, B3-B4)
  - **Bag 4**: N. 1 couple of u.v. passive samplers (A7-A8, C3-C4)
  - **Bag 5**: N. 2 couple of u.v. passive samplers (A9-A10, B5-B6)
  - **Bag 6**: N. 1 couple of u.v. passive samplers (A11-A12) **

the box content

- ✓ *N.1 PAS Sampling set*
- ✓ *N.1 Shelter*
- ✓ *Up to N.6 pairs of gloves*
- ✓ *N.3 plastic clamps*



the starting bag (BAG 1)

Bags (from 1 to 6)

An under-vacuum passive sampler

1

Passive Air Samplers (PASs)

Each passive sampler is kept in a vacuum bag and each vacuum bag comprises:

- ***N.4 self-locking clear plastic bags;***
- ***N.1 sealed glass vessel (PASs);***
- ***N.1 open-cap mounting a diffusive barrier***

An alphanumeric code is reported onto each passive sampler for identifying, according to the following scheme:

S2-C2-0316

Specifically, **S2** is a tag related to the sampling site (named as S0, S1, S2, S3, S4, S5, S5, S6, S7, S8, S9 respectively).

C is a tag related to the exposure time:

- all the samples named as **A** will be kept exposed to the air for **1 week**;
- all the samples named as **B** will be exposed for **2 weeks** and finally
- all the samples named as **C** will be exposed for **3 weeks**.
- The samples named as Blank (1 and 2, respectively) will be kept exposed throughout the sampling campaign, but tightly closed.

The final 4 numbers (here reported as 0316) are related to the passive batch fabrication.

The number following the label C (i.e. C**2**) is a serial number related to the sequential sampling within the scheduled sampling procedure.

The monitoring procedure is clarified within the Table 1 following reported.

The vacuum bag

The content of a vacuum bag

The tagged PAS

STEP 1. Locating sampling sites

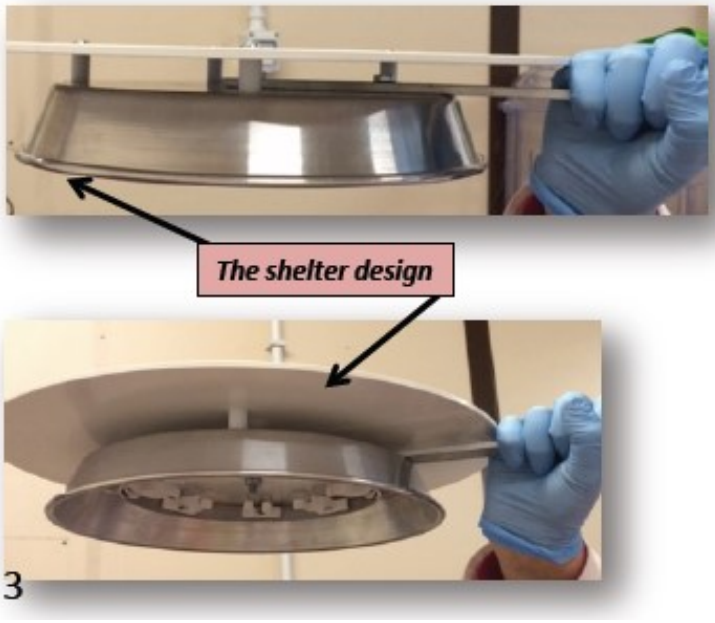
Please, choose the proper place (according to Siting criteria Document – ANNEX 1) where the shelter with passive samplers will be exposed and then locate the shelter.

When a sampling site will be designed for Hg monitoring in air, **the shelter should be tied to a pole or a tree by plastic clamps about 2 meters high**.

After choosing the proper place for the sampling site, please fill in the Site survey (ANNEX 2).

The shelter comprises N. 8 labelled seats to keep up to 8 PASs (A-A, B-B, C-C, and Blanks1 and 2).

The shelter placement



STEP 2. Opening the vacuum bags & Substituting the cap

The content of each vacuum bag comprises N.4 self-locking clear plastic sachets, N.1 sealed glass vessel containing the passive film and N.1 diffusive-cap.

When you are ready for air sampling:

1) wear a pair of clean gloves picked up by a locked sachet (size L);

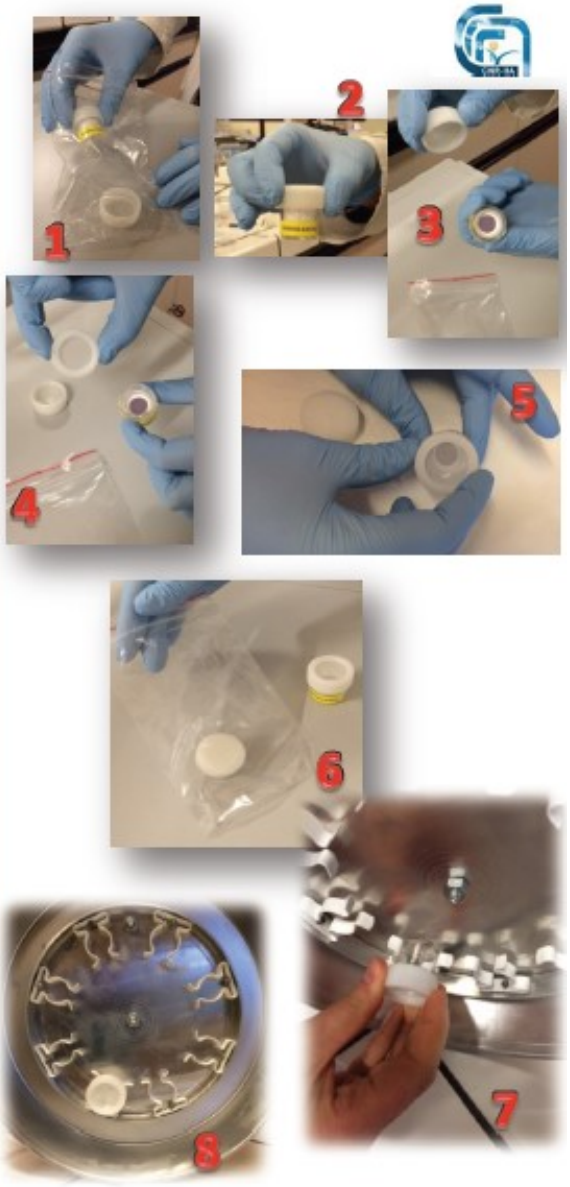
2) cut carefully the bag with scissors making sure not to cut the folded sachets placed inside;

3) remove the content and handle it with gloves (**1**);

4) unscrew the white cap of the glass vessel (**2,3**) and quickly screw the diffusive-cap (**4,5**);

5) <u>immediately use one sachet to storage the unscrewed white cap</u>, another one to keep both the remaining two sachets and the sachet with the cap, then close it (**6**);

6) Please, <u>unscrew the white cap of each PAS when you are ready to start the campaign.</u> Place it into the designated shelter seat, with the diffusive layer facing the air (i.e. the screw cap down) (**7-8**).



4

STEP 3. Exposing the PASs & Filling in the Sampling Data Sheet

7) Expose the PASs for the scheduled exposure time (see Table 1 – Step 4), and fill in the Sampling Data Sheet referred to your network (GMOS or WHO) (see ANNEX 3);

8) *Each sachet may be placed inside the respective coming bag that will be locked and then properly stored (please, choose a cool, dark and dry container).*

Use gloves when handling samples; opening and closure of PAS samplers must be carried out as close as possible to the sampling sites (shelters); store caps immediately to prevent contamination.

SAMPLING DATA SHEET – EXAMPLE OF EXPOSURES OF PASs

Campaign N. 1

Sampling Site Name: Italy Monte Cimone

Code of each passive sampler	Exposure start at: Start date (DD/MM/YYYY (Day/Month/Year))	Exact Local Time (HH:MM)	Exposure stop at: End date (DD/MM/YYYY (Day/Month/Year))	Exact Local Time (HH:MM)
S15-A1-0516	25/04/2016	10:30	30/05/2016	10:30
S15-A2-0516	25/04/2016	10:50	30/05/2016	10:50
S15-B1-0516	25/04/2016	10:50	30/05/2016	10:50
S15-B2-0516	25/04/2016	10:50	30/05/2016	10:50
S15-C1-0516	25/04/2016	10:30	30/05/2016	10:30
S15-C2-0516	25/04/2016	10:50	30/05/2016	10:50
S15-Blank1-0516	25/04/2016	10:50	30/05/2016	10:50
S15-Blank2-0516	25/04/2016	10:30	30/05/2016	10:30
S15-A3-0516	25/04/2016	10:50	30/05/2016	10:50
S15-A4-0516	30/05/2016	10:50	13/06/2016	10:50
S15-A5-0516	30/05/2016	10:30	13/06/2016	10:30
S15-A6-0516	30/05/2016	10:50	13/06/2016	10:50
S15-B3-0516	30/05/2016	10:50	13/06/2016	10:50
S15-B4-0516	13/06/2016	10:30	27/06/2016	10:30
S15-A7-0516	13/06/2016	10:50	27/06/2016	10:50
S15-A8-0516	13/06/2016	10:50	27/06/2016	10:50
S15-C3-0516	13/06/2016	10:50	27/06/2016	10:50
S15-C4-0516	27/06/2016	10:30	11/07/2016	10:30
S15-A9-0516	27/06/2016	10:50	11/07/2016	10:50
S15-A10-0516	27/06/2016	10:50	11/07/2016	10:50
S15-B5-0516	27/06/2016	10:30	11/07/2016	10:30
S15-B6-0516	27/06/2016	10:30	11/07/2016	10:30
S15-A11-0516	27/06/2016	10:30	11/07/2016	10:30
S15-A12-0516	27/06/2016	10:30	11/07/2016	10:30

Yellow: 1-week sampling; Light blue: 2-week sampling; Green: 3-week sampling

Name of Site Manager: E-mail:

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STEP 4. Monitoring planning & Exposure Times

Where a weekly sampling will be not carried out, the PASs named as A are not included within the bags. Thus both N. 2 and N. 6 bags are not part of the related sampling set (** please note that this is referred only to GMOS sites).

In fact all the samples named as A will be subjected to a 1-week exposure, meanwhile B and C ones will be exposed to air for 2 and a 3 weeks, respectively.

Specifically:

-Bag 1 comprises the complete starting sampling set to be housed onto the shelter on **the first day** of monitoring.

-After **1 week** (the eighth day) the couple of samples named A1 and A2 will be removed, sealed and replaced with A3-A4 from Bag (***step not to be followed at GMOS sites*).

-After **2 weeks** (the fifteenth day) both the couples A3-A4 and B1-B2 will be removed, sealed and replaced with A5-A6 and B3-B4 from Bag 3, respectively.

-After **3 weeks** (the twenty-second day) both the couples A5-A6 and C1-C2 will be removed, sealed and replaced with A7-A8 and C3-C4 from Bag 4, respectively.

-After **4 weeks** (the twenty-ninth day) both the couples A7-A8 and B3-B4 will be removed, sealed and replaced with A9-A10 and B5-b6 from Bag 5, respectively.

-After **5 weeks** (the thirty-sixth day) the couples A9-A10 will be removed, sealed and replaced with A11-A12 from Bag 6 (***step not to be followed at GMOS sites*).

-Finally, after **6 weeks** all the exposed passive samplers will be removed and sealed.

-Environmental parameters (like temperature, %RH, main wind direction..) should be daily reported on a suitable notepad and then joint to the samples at the end of monitoring, to be used for data analyses.

Table 1

	1-week	2-week	3-week	4-week	5-week	6-week
BAG1	A1-A2 B1-B2 C1-C2 Blanks1-2					
BAG2**		A3-A4				
BAG3			A5-A6 B3-B4			
BAG4				A7-A8 C3-C4		
BAG5					A9-A10 B5-B6	
BAG6**						A11-A12

6

STEP 5. Removing the PASs & Filling in the Sampling Data Sheet

9) after each exposition, passive samplers will be removed and sealed with the own white cap coming from the stored bag and properly stored (**dry , dark and cool place**);

10) pack the sealed glass vessel in a sachet and lock it; pack it in a second sachet and lock it; pack it in a third sachet and lock it.

11) Put the diffusive-cap within the fourth bag and lock it too.

12) Depending on the planned exposure timing, replace the removed PAS with another one belonging to the same series (i.e. A with A, B with B and C with C) contained in the following sequential bag using the same care as previously described.

Removal, Packaging, Storage and Transportation

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