Global Monitoring Plan on Persistent Organic Pollutants

PROCEDURE FOR AIR MONITORING USING ACTIVE AIR SAMPLERS (HVS)

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Stockholm Convention Regional Centre
URUGUAY

Research Centre
for Toxic Compounds
in the Environment

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1 INTRODUCTION

This procedure has been elaborated to provide support for the Global Monitoring Plan (GMP) on Persistent Organic Pollutants (POPs) under the Stockholm Convention. The programme includes the participating countries in Africa, Asia, Latin America and the Caribbean and Pacific Islands in the projects financed by the Global Environment Facility (GEF) .

The objective of this procedure is to describe the management of active air samplers (HVS) for sampling pollutants, including the main steps for assembling and disassembling, as well as maintenance of the air samplers. This procedure is applicable for the deployment of HVS in urban, suburban, rural and remote areas.

The persistent organic pollutants that are considered to be sampled with HVS are:

Basic POPs (aldrin, dieldrin, endrin, cis-chlordane, trans-chlordane, cis-nonachlor, trans-nonachlor, oxychlordane, heptachlor, cis-heptachlor epoxide, trans-heptachlor epoxide, *p,p'*-DDT, *o,p'*-DDT, *p,p'*-DDE, *o,p'*-DDE, *p,p'*-DDD, *o,p'*-DDD, mirex, hexachlorobenzene, toxaphene Lindane (γ-HCH), α-HCH, β-HCH, chlordecone, pentachlorobenzene, endosulfan).

Polychlorinated dibenzo-p-dioxins (PCDDs), polychorinated dibenzofurans (PCDFs) and polychorinated byphenyls (PCBs).

Polybrominated diphenyl ethers (PBDEs), hexabromobiphenyl (PBB), hexabromo cyclodecane (HBCD).

Perfluorooctane sulfonic acid, its salt and perfluorooctane sulfonyl fluoride.

2 MATERIALS, SAMPLERS ASSEMBLING AND DISASSEMBLING

2.1 MATERIALS

Active sampler, also known as, high or medium air sampling device, is composed by:

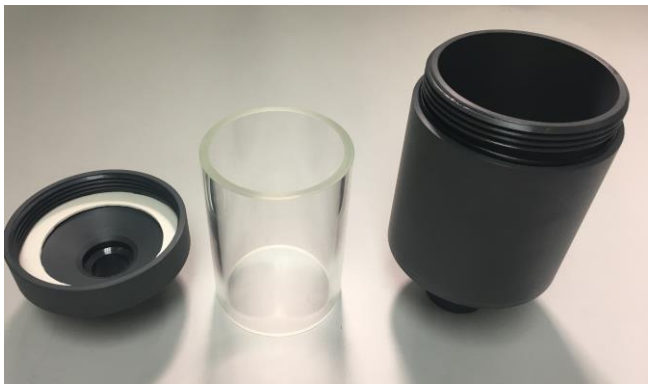
- High/Medium Volume sampler (HVS)
- Adsorbent module
- Filter module

This configuration makes reference to the 'MCV type' sampler, which is the one used by the CSIC, and it is possible to observe slight variations in comparison to other sampling devices, although all of them are based on the same principle, such as those used, for example, in POPs Monitoring Project in East Asian Countries, MONET, GAPS, GAPS-GRULAC, GMP-UNEP and EMEP Program.

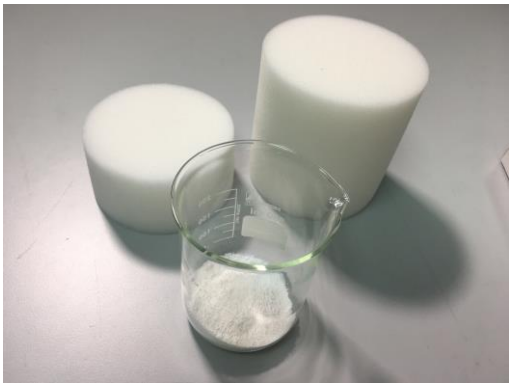
2.2 CONDITIONING THE SAMPLING ADSORBENTS PRIOR SAMPLING CAMPAIGN

2.2.1 Preparing the adsorbent module

The adsorbent module consists of two threaded pieces in which the adsorbents to be used to collect the sample are placed. In addition, there may be some extra devices (i.e.: glass holder) to accommodate the adsorbents. However, this aspect may vary depending on the configuration of the equipment and manufacturers.



The adsorbents may vary depending on the analytes suitable to be collected: polyurethane foams (PUF), polymeric resins (such as amberlites) or activated carbon. In this process the combination of 2 PUF (with different size) and polymer resin XAD-2 is used.



First step consists in placing the smaller PUF inside the glass holder, followed by 10 g of the polymer resin (XAD-2) and finally the larger PUF to cover and sealing the system.

The final stage consists of the placement of the glass holder containing the adsorbents within the adsorbent module. Make sure that the top of the PUF is always the biggest. Finally, screw the top cover, hook an identification tag and it is ready for use.

2.2.2 Preparing the filter module

To place the filter inside the filter module, take the module and, preferably, place it on a flat and firm surface. Afterwards, open the compartment where the filter is located. A filter is taken and properly placed and the module is closed in the same way as it has been opened.

NOTE: In order to avoid contamination episodes, analyst must wear protection gloves during the placement of the filter. It is important to avoid dusty and/or dirty working areas.

2.3 DEPLOYMENT OF THE HIGH VOLUME SAMPLING SYSTEM

Sample identification must be performed before starting the sampling collection episode:

a) Sampling location
b) Sampler identification code (Ver 2.5)
c) Sampling start date and time
d) Expected date and time of sampling completion
e) Target compounds

Sampling collection will be carried out in accordance with the following stages:

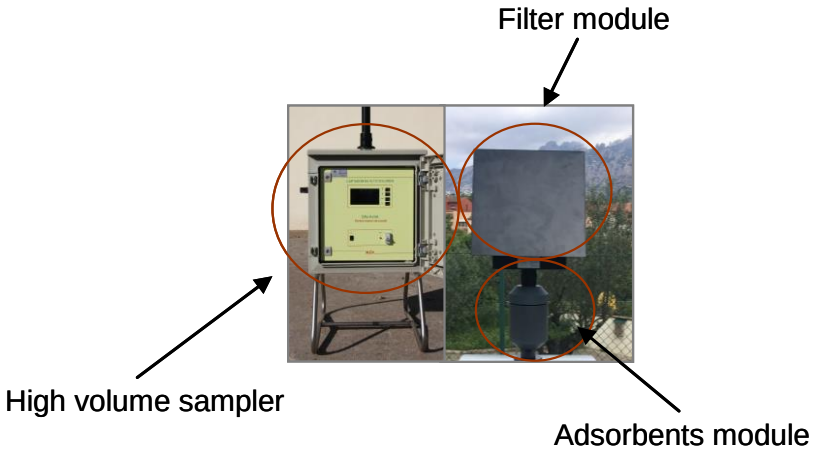
1. Place the air sampling device at the selected site in order to collect the ambient air sample.
2. Put the adsorbent module onto the top of the air sampling device.
3. Put the filter module to the top of the adsorbent module.
4. Once the installation is finished, proceed setting the sampling program. Two important parameters should be defined before the sampling is started:
    a. The flow
    b. Sampling period

Afterwards, sampling can be initiated.

Finally, data related sampling process should be enter in the spreadsheet (attached MsExcel file, See 6), as well as any incidence that could have occurred.

NOTE: The module connections are often made of plastic. It is recommended that the connection be tight, but without overexertion, since the connections often break down with relative ease.

NOTE: During the assembly and removal of the sensors, the technicians must be equipped with latex or equivalent gloves.



2.4 MATERIALS

In addition to the parts that compose the air sampling device, other material to be used is:

- Polyurethane foam adsorbents conveniently conditioned (see 2.6)
- Absorbent (XAD-2, active carbon or equivalent)
- Aluminium foil
- Tweezers: Two
- Cutter or scissors
- Latex or equivalent gloves
- Acetone and/or ethanol to clean the sampler parts
- Garbage bag
- Permanent marker pen
- Notepad to record data and incidents during sampling

2.5 CONDITIONING THE POLYURETHANE FOAMS (PUFs)

Conditioning of the sampling adsorbents aims to eliminate any interferences or unwanted substances which may be contained, and which may have occurred during the manufacture thereof, or incorporated during storage.

Conditioning the PUFs:

1. Put the PUFs into a 2000 ml beaker and add ultra pure water till the PUFs are covered. Tighten the PUF to make sure it is completely wet. Add more ultra pure water in case the PUFs are not totally submerged. This process may include the simultaneous cleaning of several PUFs.

2. Put the glass in an ultrasonic bath and sonicate for 15 minutes.
3. Decant this first wash with ultra pure water, remove the water from the PUF and re-wash by repeating steps 1 and 2.
4. Once the two washes have been carried out, any remaining water that may have been trapped in the polyurethane foam is removed. In a Soxhlet body of the appropriate diameter (the foam must not be very compressed), the PUF is introduced and an extraction with quality acetone for residue analysis is carried out for 24 hours.
5. Finally, the excess acetone is removed from the polyurethane foam and a second extraction is carried out with fresh solvent in the same conditions as for the first acetone extraction. The solvent used in the second extraction depends on the type of compounds to be subsequently sampled and analyzed:
    a. Dichloromethane, for basic POPs (Basic-POPs) or the 6 indicator PCBs
    b. Toluene, for dioxin-like POPs, as well as for brominated compounds (PBDEs, HBCDs and HxBBs)
    c. Methanol, in case of fluorinated compounds (PFOS and other related compounds)
6. Afterwards, the excess solvent is removed from the polyurethane foam. Next, the PUFs are placed in a desiccator under vacuum conditions in order to completely remove the solvent residue till the foam is completely dry.
7. Once dry, the polyurethane foams are protected from light by wrapping then in aluminium foil.
8. The PUFs are labelled with the date of cleaning and shelf life and stored in a dark and dry place until use.

NOTE: The conditioning process will be carried out by Reference Laboratory before to the sending of the sampling adsorbents to the participant countries for the ambient air sampling by using high volume samplers.

Conditioning the adsorbent (amberlite XAD-2):

1. Put the amberlite into a Soxhlet body and add methanol (quality for residue analysis) as a solvent. Proceed with the soxhlet extraction for 24 h.
2. After the extraction process, remove the excess methanol and a second extraction with acetonitrile, of equivalent quality, is carried out in the same conditions applied for extraction with methanol.
3. After the second extraction period, the acetonitrile is removed from the resin and a third extraction with toluene is performed in the same conditions as for the 2 previous processes.
4. Afterwards, remove the toluene from the resin. Solvent residues are removed in a desiccators under vacuum conditions, the process being completed when the resin is completely dry.
5. Once dried, the resin is protected from light by wrapping it in an amber or colorless container, but protected with an aluminium foil.
6. The resin is labelled with the date of cleaning and expiration date and stored in a dark and dry place until being use.

Conditioning and filter manipulation:

1. In order to collect particulate matter a filter must be used during sampling. Filters can be made of fibreglass or quartz.

2. In general, for the particular purposes of this project, filters do not require specific conditioning prior to the sampling process, although they must be protected by individually wrapping in aluminium foil in order to avoid contamination episodes.
3. Aluminium foil should be appropriately labelled outside, identifying sampling campaign and data with permanent pen.

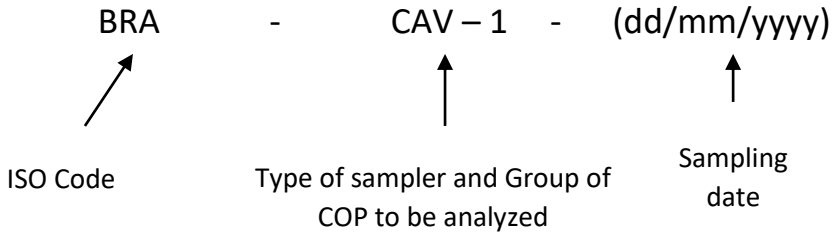
NOTE: PUFs, resins and filters are of SINGLE use. Once used in a sampling can not be reused, recovered or recycled.

2.6 IDENTIFICATION OF SAMPLERS AND PUFs

In order to properly identify the samplers and PUFs, a UN Environment code has been defined consisting of a set of letters and numbers that will unequivocally identify: the country where samplers are installed, the sampling year, as well as the number of campaign within that year, and the compounds to be determined. The samplers will be identified with the corresponding code.

In this sense, a UN Environment code is always composed of: a first set of three letters that make reference to the country, followed by a hyphen and the letters CAV (related to high volume sampler) and a number of sampler that corresponds to the compounds to be determined, and followed, in parentheses, of the sampling date.

An example of identification code would be:



- The first set of three letters corresponds to the country's abbreviation according to ISO code used by UN. (See Table 1 and http://unstats.un.org/unsd/methods/m49/m49alpha.htm).
- The number after the hyphen, CAV to define the nature of the sample (active air sampling) and a number corresponding to the group of substances to be analyzed (See Table 1).
- Finally, the sampling date.

Table 1: The first number: sampler code. It shows, at the same time, analysis type and laboratory in charge of the analysis

SAMPLER Nº	CORRESPONDS TO:
1	Analysis of Basic-POPs pesticides, and PCB indicators in the Reference Laboratory
2	For dioxin-like POPs in the Reference Laboratory (PCDD, PCDF and dioxin-like PCB)
3	Analysis of brominated POPs (PBDE, HBCD y PBB) in the Reference Laboratory
4	Analysis of PFOS in the Reference Laboratory

2.7 SAMPLER DISASSEMBLY

Once the sampling is accomplished, all elements composing the sample should be collected, taking care to avoid any undesirable episode of contamination that could question the validity of the sample. A sample consists of the filter and the adsorbents. The adsorbents may vary depending on the configuration of the sampling system. The steps to stop the sampling are:

1. Stop pumping if no automatically stopped.
2. Unscrew the filter holder module.
3. Remove the filter and wrap it in Aluminium foil
4. Label the outside of the aluminium foil wrapping the filter.
5. Remove the adsorbent module and cover with aluminium foil the access ports to the adsorbents.

The adsorbent module and the filter should be shipped to the laboratory and stored in the freezer at approximately -18 ° C until being analyzed or sent to the corresponding Reference Laboratory.

Once a year it will be necessary to make sampling blanks, which consists of adsorbents and filters that are not exposed in the air samplers. To do this, adsorbents and filters conditioned and wrapped in aluminium foil are to be used, the same as those to be changed but labeled "0". They are manage at the same time as the filters and absorbents that are going to be changed in the samplers and are maintained thus while the process of assembly of the fresh filter and adsorbents. Once this process is finished, they are wrapped again, labeled and transported and stored together with the corresponding sample. It will be used filters and absorbents as substances or groups of substances to be collected in the conventional sampling.

Take pictures of each sample campaign.

NOTE: In order to avoid contamination episodes, analyst must wear protection gloves during the placement of the filter. It is important to avoid dusty and/or dirty working areas.

2.8 MAINTENANCE

The high and medium air samplers require preventive maintenance depending on the use that must be made by the manufacturer or trained personnel.

3 AIR SAMPLING

3.1 GENERAL CONSIDERATIONS ABOUT SAMPLING SITES

Ambient air sample collection by high or medium air samplers is commonly carried out in a 'forced' or 'active' way. In other words, air sample is collected with a pump, through a filter followed by one or more adsorbents. Therefore, some minimum requirements, such as the availability of electrical power supply, should be considered before active sampling is proposed as a sampling strategy for ambient air collection, for instances, in remote areas. More, it is a critical point that in some occasions enables or disables potential sampling locations. Alternatively, this source of electricity can be achieved through electricity generators that are based on combustion engines. In these cases, it is extremely important to ensure that the gases derived from the combustion are not collected by the sampler.

In addition, other requirements to be met include the availability of meteorological observations, so that auxiliary measurements such as atmospheric composition, wind speed, temperature and humidity could be registered.

3.2 SAMPLING PROCEDURE

Air samplers are placed in the selected area for sampling. Once the adsorbent module and filter have been placed, the sampling is programmed. Typically, sampling is set as to collect of approximately 1000 m^3. This volume allows collecting a sample quantity above the limits of detection and determination of the current instrumental techniques.

Sampling period might vary depending on the air sampler employed. In the particular case of high volume samplers, sampling collection could be accomplished in 24 h at a flow of de 45 m^3/h. In case that the apparatus is not capable of acquiring this flow, smaller flows can be

programmed and the sample period is increased. A similar situation would be applicable to medium volume samplers, for which the collection of 1,000 m^3 is a longer aspiration period.

3.3 SAMPLING DATES AND FREQUENCY

Typically, the sampling episode is carried in 3 days at approximately 30 m^3/h (500 l/min), though flow could be lower if the air sampler can not reach this setting. In this case, sampling period could be somewhat longer till a minimum amount of 2000 m^3 air is collected.

All countries are responsible to manage the air samplers on the same dates (at the same time) as set out in the Excel file UNEP-GEF Project / Region -*samples template*-country name.

4 PRACTICAL DETAILS ABOUT THE SAMPLERS

The Reference Laboratory will send to each country the filters and absorbents (PAS) and cleaned/conditioned PUFs following the procedure described in this document (See 2.4).

Once received, PUFs must be stored in a dark and dry place until use.

5 STORAGE, PACKAGING AND SHIPMENT

The PUFs foams are stored at -18° C in the freezer at the laboratories until analysis, or sending to the corresponding reference laboratory.

For the Latin American and the Caribbean Region:

The sample, composed by the 2 PUFs, the resine XAD-2 and the filter, will be sent to the CSIC for the analysis of all POPs with the exception of PFAS:

Dr. Esteban ABAD HOLGADO
Scientific Researcher
Laboratory of Dioxins
IDAEA/CSIC
C/ Jordi Girona 18-26
08034 Barcelona
Spain

The sample, composed by the 2 PUFs, the resine XAD-2 and the filter, will be sent to the University of Orebro for the analysis of PFAS:

Dr. Heidelore FIEDLER
Profesor
Örebro University
MTM Research Center
School of Science and Technology
SE-701 82 Örebro
Sweden

For the others Regions:

The sample, composed by the 2 PUFs, the resine XAD-2 and the filter, will be sent to the IVM for the analysis of all POPs with the exception of PFAS:

Prof.Dr. Jacob de Boer
Vrije Universiteit Amsterdam
Head Dep. Environment and Health
De Boelelaan 1108
1081HZ Amsterdam
The Netherlands

The sample, composed by the 2 PUFs, the resine XAD-2 and the filter, will be sent to the University of Örebro for the analysis of PFAS:

Dr. Heidelore FIEDLER
Profesor
Örebro University
MTM Research Center
School of Science and Technology
SE-701 82 Örebro
Sweden

The shipment modalities shall be agreed in close cooperation between the country and the international expert laboratory.

6 DOCUMENTATION

An MsExcel file is provided to document each sampling event. The MsExcel file – named "GMP2_ passive air sampling" contains the following worksheets and information:

1. Worksheet "Georeferences"

This worksheet provides a summary of all information related to the location and conditions where the sampling takes place:

Country name:	Full name and ISO_3 code
Site/Location:	Short name assigned
Address:	Physical address
Type of site:	Remote, urban, rural
GPS coordinates:	degrees: Latitude and longitude decimals: Latitude and longitude
Narrative:	Brief narrative description of location
Height of the sampler:	in meter (m)
Institution responsible:	Please provide name of institution undertaking the sampling.
Photo:	Please insert a photo of the sampling site

7 ABBREVIATIONS

GEF Global Environment Facility

GMP Global Monitoring Plan (under the Stockholm Convention on POPs)

ID Identification

ISO International Standardization Organization

POPs Persistent organic pollutants

PUF Polyurethane foam

8 REFERENCES

Active Sampling of Ambient Air. Operation Procedure and Methodology. Research Centre for Toxic Compounds in the Environment (RECETOX). November 2016.

Monitoring Manual for Persistent Organic Pollutants in Ambient Air. Expert Working Group POPs Monitoring Project in East Asian Countries. November, 2013.

UNEP/POPS/COP.7/INF/39 Guidance on the global monitoring plan for persistent organic pollutants