Global Monitoring Plan on Persistent Organic Pollutants

PROCEDURE FOR AIR MONITORING USING ACTIVE AIR SAMPLERS (HVS)

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Stockholm Convention Regional Centre
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Research Centre
for Toxic Compounds
in the Environment

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1 INTRODUCTION

This procedure has been elaborated to provide support for the implementation of 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 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 persistent organic 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, endosulfan sulfate).

Polychlorinated dibenzo-p-dioxins (PCDD), polychorinated dibenzofurans (PCDF) and polychorinated byphenyls (PCB).

Polybrominated diphenyl ethers (PBDE), hexabromobiphenyl (PBB), hexabromo cyclododecane (HBCD).

Perfluorooctane sulfonic acid (PFOS), 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 PREPARING THE SAMPLING ADSORBENTS AND FILTER 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. Adsorbents placed into the adsorbent module will capture the gas fraction of the air sample. In the process described in this procedure, the combination of 2 PUF (with different size) and polymeric resin XAD-2, accommodated in a glass holder, is used.

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

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

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

2.2.2 Preparing the filter module

The filter located into the filter module will capture the solid fraction (particles) of the air sample. 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 has to be 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. A couple of clean tweezers can also be used to help to properly place the filter on the support surface. It is important to avoid dusty and/or dirty working areas.

2.3 OTHER MATERIALS AND TOOLS

In addition to the parts that compose the air sampling device, other materials to be used are:

- Polyurethane foam (PUF) and adsorbent (XAD-2, active carbon or equivalent) conveniently conditioned (See 2.5)
- Aluminium foil
- Tweezers: Two
- Cutter or scissors
- Latex gloves or equivalent
- Acetone and/or ethanol to clean the sampler parts and tweezers
- Garbage bag
- Permanent marker pen
- Sticker labels
- Notepad to record data and incidences during sampling

2.4 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 (See 2.6)
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:

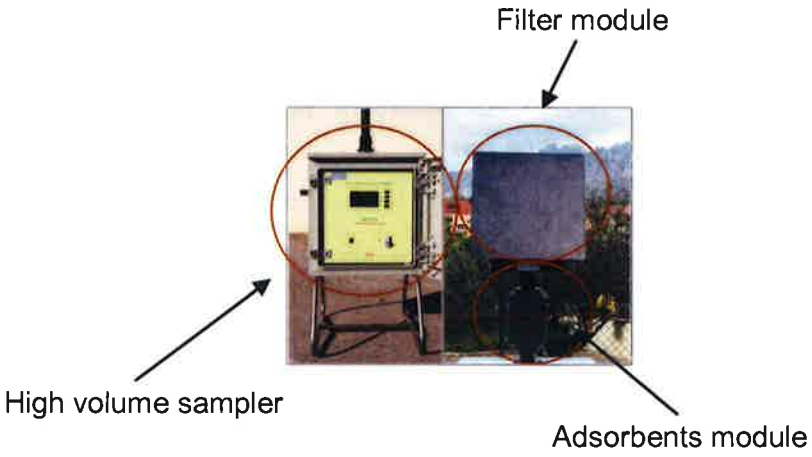
1. Place the air sampling device at the selected site in order to collect the ambient air sample.
2. Put the adsorbent module onto the top of the air sampling device.
3. Put the filter module to the top of the adsorbent module.
4. Once the installation is finished, proceed setting the sampling program. Two important parameters should be defined before the sampling is started:
   a. Flow. After setting a certain flow, the instrument always performs automatically an internal autocalibration before sampling starts, no further manual calibration steps are required.
   b. Sampling period. The sampling period will be consistent with the set up flow and the volume of sample expected to be collected.

Afterwards, sampling can be initiated.

Take pictures of each sampling campaign.

Finally, data related to the sampling process should be enter in the spreadsheet (attached MsExcel file, See 6), as well as any incidences 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.



2.5 CONDITIONING OF THE SAMPLING ADSORBENTS AND FILTER

Conditioning of the sampling adsorbents and filter 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.

NOTE: The conditioning processes will be carried out by the Reference Laboratory before to the shipment of the adsorbents and filter to the laboratories that will perform the sampling, therefore they will be ready to use upon arrival.

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 soaked. 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 beaker 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 must be removed. In a Soxhlet body of the appropriate diameter (the foam must not be very compressed), the PUF is introduced and an extraction with acetone (quality for residue analysis) is carried out for 24 hours.
5. Finally, the excess of 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 analysed:
    a. Dichloromethane (quality for residue analysis), for basic POPs (pesticides) or the 6 Indicator PCB
    b. Toluene (quality for residue analysis), for dioxin-like POPs, as well as for brominated compounds (PBDE, HBCD and PBB)
    c. Methanol (quality for residue analysis), in case of fluorinated compounds (PFOS and other related compounds)
6. Afterwards, the excess of 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 dried, the polyurethane foams are protected from light by wrapping them in aluminium foil.
8. The PUFs are labelled at the aluminium foil with the date of cleaning and expiration date and stored in a dark and dry place until use or shipment.

Conditioning the polymeric resin (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, the excess of methanol is removed and a second extraction with acetonitrile, of equivalent quality, is carried out in the same conditions applied for the extraction with methanol.
3. After the second extraction period, the acetonitrile is also removed and a third extraction with toluene, of equivalent quality, is performed in the same conditions as for the 2 previous processes.
4. Afterwards, remove the toluene from the resin. The last solvent residues are removed in a desiccator under vacuum conditions; the process is completed when the resin is completely dry.
5. Once dried, the resin is protected from light by placing it in an amber or colorless container, but protected from light by wrapping it with an aluminium foil.
6. The resin is labelled at the aluminium foil with the date of cleaning and expiration date and stored in a dark and dry place until use or shipment.

Conditioning and filter manipulation:

1. In order to collect particulate matter a filter must be used during sampling. Filters can be made of fiberglass 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 with a permanent pen.

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

2.6 IDENTIFICATION OF SAMPLERS

In order to properly identify the samplers and the materials used during sampling, 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 compounds to be determined and the sampling date. 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:

BRA - CAV – 1 - (dd/mm/yyyy)

ISO Code

Type of sampler and Group of POPs to be analysed

Sampling date

- The first set of three letters corresponds to the country's abbreviation according to ISO code used by UN. (See 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 analysed (See Table 1).
- Finally, the sampling date.

Table 1: The first number: sampler code. It shows analysis type.

SAMPLER Nº	CORRESPONDS TO:
1	Analysis of basic POPs (pesticides), and Indicator PCB
2	Analysis of dioxin-like POPs (PCDD, PCDF and dioxin-like PCB)
3	Analysis of brominated POPs (PBDE, HBCD y PBB)
4	Analysis of fluorinated compounds (PFOS and other related compounds)

2.7 SAMPLER DISASSEMBLING

Once the sampling is accomplished, all elements composing the sample must 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, since the two fractions (gas and particles) have to be analysed together to report the result for a certain sample. 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 to ship it to the laboratory.
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 to ship it to the laboratory. Once in the laboratory, transfer the components of the adsorbent module (i.e.: PUFs and/or XAD-2 or active carbon) to a glass or plastic flask with a screw cap (avoid Teflon) properly labelled.

The adsorbents and the filter should be stored in the freezer at approximately -18 ° C until being analysed or sent to the corresponding Reference Laboratory.

Take pictures of each sampling campaign.

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

NOTE: In order to avoid contamination episodes, analyst must wear protection gloves when transferring the adsorbents and removing the filter. A couple of clean tweezers can also be used to help to properly remove the filter from the support surface. It is important to avoid dusty and/or dirty working areas.

2.8 MAINTENANCE

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

3 GENERAL CONSIDERATIONS ABOUT AIR SAMPLING

3.1 SAMPLING SITES

Ambient air sample collection by high or medium volume 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 instance, in remote areas. 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 module 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 about 24 h at a flow of 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 1000 m^3 is a longer aspiration period.

4 PRACTICAL DETAILS ABOUT AIR SAMPLING

For the purposes of this project, each sampling episode will be carried out during 3 days (aprox. 72 h) at about 30 m^3/h (500 l/min), though flow could be lower if the air sampler cannot reach this setting. In this case, sampling period could be somewhat longer till a minimum amount of 2000 m^3 air is collected.

5 STORAGE, PACKAGING AND SHIPMENT

The Reference Laboratory will send to each country the filters and adsorbents, including the cleaned/conditioned PUFs and polymeric resin, following the procedure described in this document (See 2.5).

Once received, all these materials must be stored in a dark and dry place until use.

After sampling, the adsorbents and filters should be stored in the freezer at approximately -18 ° C until being analysed or sent to the corresponding Reference Laboratory.

For the Latin American and the Caribbean Region:

The sample, composed by the 2 PUFs, the XAD-2 and the filter, will be sent to the CSIC for the analysis of all POPs with the exception of fluorinated compounds (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 XAD-2 and the filter, will be sent to the University of Orebro for the analysis of fluorinated compounds (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 XAD-2 and the filter, will be sent to the IVM for the analysis of all POPs with the exception of fluorinated compounds (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 XAD-2 and the filter, will be sent to the University of Orebro for the analysis of fluorinated compounds (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 Reference Laboratory.

6 DOCUMENTATION

An MsExcel file is provided to document each sampling event. The MsExcel file contains a summary of all information related to the location where the sampling takes place and other details about the sampling:

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
Sample volume (units):	Final volume
Meteorological cond.:	Temperature (average, range,...) during sampling and/or other meteorological data available

7 ABBREVIATIONS

GEF Global Environment Facility

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

ISO International Organization for Standardization

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