**Appendix 3:**

**Guidance for the Conversion of Data on POPs from mass/PUF to mass/m<sup>3</sup> using Tom Harner´s model and the Stockholm Convention Data Warehouse template**

# <span id="page-1-0"></span>Acknowledgement

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### <span id="page-3-0"></span>1. Introduction

Article 16 of the Stockholm Convention (SC) requested the Conference of the Parties (COP) to evaluate the effectiveness of the Convention every four years after its entering into force. In order to facilitate such evaluation, the Conference of the Parties developed a Global Monitoring Plan (GMP). Ambient air is an important matrix for the effectiveness evaluation of the Convention because it has a very short response time to changes in atmospheric emissions and is a relatively well-mixed environmental medium and includes both chemicals in gaseous form as well as chemicals partitioned onto particles (UNEP, GMP guidance 2019).

The objective of the ambient air sampling networks under the SC Global Monitoring Plan (GMP) is to obtain representative data for assessing baselines, changes over time and space and the regional and global transport of Persistent Organic Pollutants (POPs). Passive sampling provides continuous, cumulative diffusive sampling over integration periods ranging from a few months (generally 3 months) to 1 year.

Passive air sampling (PAS) using a Polyurethane Foam (PUF) disk sampler is the most widely used air sampling method under the GMP and in research studies. It is used to investigate the levels, trends, and long-range transport of POPs and priority chemicals in air like other Semivolatile Organic Compounds. This is also the method used in the two rounds of UNEP/GEF POPs GMP projects. In the chemical analysis of PUF samples collected during PAS, data is expressed in mass concentration by PUF (Cpuf mass/PUF disk).

Data from the chemical analyses of PUF disks is expressed in mass concentration by PUF (C<sub>puf</sub> mass/PUF disk) for comparability the SC Data Warehouse Template uses mass concentration in air (Cair mass/m $3$ ) as a unit of measurement. This guidance supports the conversion of data on POPs from Cpuf mass/PUF disk to Cair mass/m<sup>3</sup> to harmonize it for reporting under the SC Data Warehouse.

### <span id="page-3-1"></span>2. Passive Air Sampling (PAS)

The use of PAS as the main method for the collection of atmospheric POPs has several advantages. For example, they are cost-effective systems, simple to use, can be easily transported and do not require an external power source of electricity. On the other hand, one of the drawbacks is that the data produced is semiquantitative and there are different models for calculating the sample volume collected.

The most widely used method for deriving the effective sampled volume is the model developed by Tom Harner from Environment Canada (Tom Harner's model). It uses a mathematical algorithm that takes into account the physical-chemical properties of the substances and the specific properties of the PUFs. All of these parameters are unique for each of the substances studied, and they are all collected in a formula that can be managed in excel spreadsheets. From this point, it is enough to know some basic parameters of the sampling to convert to mass/m<sup>3</sup>, i.e. the length sampling deployment time in days, the average temperature during the sampling, and the concentration in mass/PUF.

PAS is based on the free flow of analyte molecules (POPs) from the sampled medium (air) to a collecting medium (the PUF disk), due to a difference in chemical potentials of the analyte between the two media (Górecki and Namiesnik 2002).

The uptake of POPs by PUF disks and other materials has been widely studied and described in several studies (e.g. Shoeib and Harner 2002; Pozo *et al.* 2004; Chaemfa *et al*. 2008) and was shown to be air-side controlled and thus a function of the air-side mass transfer coefficient (MTC). During outdoor deployment, a low-wind environment is preserved by housing samplers in protective chambers (Figure 1). Such samplers therefore allow for simultaneous and continuous sampling over long periods. Sampling rates for PUF-disk are typically on the order of ~4 m<sup>3</sup> /day (Pozo *et al*. 2006; Pozo *et al*. 2009; Harner *et al*. 2014) therefore a 3-month deployment provides an equivalent sample air volume of approximately 270-360 m<sup>3</sup>, which is sufficient for the detection of most of the POPs.



**Figure 1.** Schematic representation of the PAS and photos of PAS installed and PUF deployed. Photos: ©UNEP/Victor Estellano.

**Approach to Equilibrium and Equilibrium sampling:** It is imperative to account for approach to equilibrium that may occur for more volatile POPs (e.g., HCB, Pentachlorobenzene, HCBD) (Harner *et al*. 2004; Gouin *et al*. 2005; Pozo *et al*. 2006). Approach to equilibrium results in a gradual reduction in the sampling rate until the net rate goes to zero at equilibrium. This does not vary with windspeed and in some ways, is not a disadvantage. Using PUF disk as equilibrium samplers can result in improved accuracy of derived air concentrations. However, if approach to equilibrium is achieved too quickly e.g., within hours to a few days (e.g. HCBD and Pentachlorobenzene) then the resulting concentration in air will only reflect ambient concentrations during the last few hours or days of deployment. This would not be a concern however, for chemicals with relatively constant ambient air concentrations over period of

weeks to months, which is typical of volatile POPs (e.g. HCB) at background sites (UNEP, GMP guidance 2019).

# <span id="page-5-0"></span>3. Calculation of concentration of POPs using Tom Harner's model

A regularly updated template excel file has been developed containing the concentration calculations required for using this model (Harner 2020).

Before using the template, it is important to harmonize the data to be ready to include in the template.

- (a) It is important to pay attention to the mass/disk unit of measurement provided with the data from the lab. The mass can be given in nanograms (ng/disk), picograms  $(pg/disk)$  or even femtograms  $(fg/disk)^{1}$ .
- (b) To filter and to put together the results provided by the lab on the same groups of POPs e.g. Polychlorinated biphenyl (PCB Congeners); Polybrominated diphenyl ethers (PBDE Congeners); Organochlorine Pesticides (OCP Compound); Polyfluorinated Compounds (PFCs); Dioxins and Furans (PCCD\_F Congener)<sup>2</sup>.

### a. How to use Tom Harner's template

<span id="page-5-1"></span>There are different spreadsheets in the template excel file. The spreadsheet titled "Air Volume (m3) & Concentration" is the main one used for the calculations. The other spreadsheets are references and notes containing general information regarding the sources of literature used in preparing the template and the model for the groups of compounds included.

The "Air Volume (m $3$ ) & Concentration" spreadsheet is divided in two main parts: INPUT and OUTPUT (Figure 2).

### INPUT:

Before using the template, carefully read the instructions on "*How to apply this tab"* (Figure 2).

For the calculations the required, parameters that need to be included for the two parts are highlighted in green (Figure 2). These are:

#### **Sampling period:**

- 1. Deployment time in days during the whole period of sampling.
- 2. Average temperature during the sampling period.
- 3. Sampling Rate R, this is set to a default value of 4  $m^3$ /day.

#### **Characteristics of Passive sampling Media (PSM):**

Here the default values of the type of PSM are used.

- 4. Type of sampler used.
- 5. Type of absorbent used.

<sup>&</sup>lt;sup>1</sup> Note: ng= 10<sup>-9</sup>; pg= 10<sup>-12</sup>; and fg= 10<sup>-15</sup>.

<sup>2</sup> **Note:** Dioxin-like PCBs are normally analysed together with the Dioxins and Furans, but the calculation in the excel sheet is done in the same group as marker PCBs.

6. Mass value of the substance/PUF disk

The sampling rate becomes a constant value depending on the type of disk. In the case of the GAPS network and CSIC PUF, the value is '4  $\text{m}^3/\text{day}$ ' (Point 3). Other parameters are provided by the sampling team, and the mass/disk is provided by the lab (Points 4, 5 and 6).



**Figure 2**. Image of the template, with the first section of the spreadsheet with the general information.

### OUTPUT:

This section is divided also in two main parts (Figure 3). To the Left of the Arrow includes all the values from scientific literature used by the model to calculate the concentration. For the calculation no further manipulation is required in this section.

*Note: If needed a compound that was not included in the original file can be added to the left of the arrow. However, to do this is important to have a good understanding of how the model in excel works and what values are needed. It would be best to do such edits in consultation with a specialist (e.g., Tom Harner).* 



**Figure 3**. Division of the OUTPUT section in two parts, to the left and right side of the arrow.

To the right of the arrow (Figure 3 and 4) is the section where the values in mass/PUF (e.g. ng/disk) are included to calculate the concentration in air.

Throughout the spreadsheet, the same logic is applied for all groups of compounds included in the template i.e., PCB, PBDE, OCPs, Dioxins and Furans, PFC, etc.

**Note:** The template includes multiple groups, each group with more compounds or congeners than those monitored under the UNEP/GEF GMP projects. For example, the PBDEs template includes 13 Congeners classified using a "number" (BDE-17, -28, etc), the number of the congeners are included in the first column PBDEs (PUF) (Figure 4), however only 8 are regularly monitored and included in the SC Data Warehouse (DWH). To avoid confusion, the **entire row** of the PBDEs that are not necessary for reporting under the GMP and the SC DWH (e.g. BDE congeners numbers -66, -77, -85, -126, and -156) can be deleted. It is crucial that the **entire row** is deleted (from left and right of the arrow).



**Figure 4**. Section of the spreadsheet on the right of the arrow used for calculating the concentration in air of the specific's groups of POPs.

In this section information needed for the calculation of the POPs concentration can be included (Figure 5).

Following the example of PBDEs in the Figure 5 below in Period 1 the following information has been included:

- (a) Site code DR Congo
- (b) Sample ID COD-9 (2017-III)
- (c) Deployment time of the passive sampler in days 92
- (d) Average temperature of the sampling period in °C 25.5

### (e) Sampling rate in  $m^3$ /day - 4 (default value)



**Figure 5**. Example of spreadsheet including the values for the calculation of the 8 PBDEs + BDE-209.

**Note:** Figure 5 the entire rows of all the PBDEs (BDE-66, -77, -85, -126, and -156) that are not included in the SC DWH were deleted (see Figure 4 for comparison), and BDE-209 was added at the bottom of the sheet. The case of BDE-209 is a special because it is entirely particleassociated, so it will never equilibrate in PUF. The model used for calculating the V $_{\sf air}$  (m $^3$ ) uses the value of R (m $3/$ day), in this case 4, multiplied by the days deployed, in this case 92. In the example given, the BDE 209 V<sub>air</sub> (m<sup>3</sup>) = 368 m<sup>3</sup>. This congener is not included in the original template but can be added.

Subsequently, in the column (ng/disk) (Figure 5) the values obtained by the laboratory during the analyses can be included. The values are normally in ng/sample = ng/disk, however it is important to double check the units because they can sometimes be in a different unit that would need to be transformed.

Finally, the concentration in air  $C_{air}$  (ng/m<sup>3</sup>) can be obtained (Figure 5).

In Figure 5, the values highlighted in blue are the Limits of Quantification (‹LOQ). In cases where the values were below the limits of detection  $(\angle$ LOD)<sup>3</sup>, or quantification  $(\angle$ LOQ)<sup>4</sup>, the values of LOQ are always used to adapt to the format required under the DWH.

In general, the concentrations of dioxin-like POPs are much lower than those of the other POPs (for instance, in fg/m $^3$ instead of pg/m $^3$ ). For this reason, dioxin-like POPs are calculated in a special manner following a different approach. The UNEP/GEF GMP1 and GMP2 projects have included two independent PUF disks in the same sites. These two PUFs were combined to make a single sample extract. In cases where that the concentration was too low and the two PUFs were not enough for the analyses, the extracts from other subsequent periods were combined all together. In many cases the PUF disk sample from the whole year were combined and analysed as a single sample from 8 PUFs (Figure 6).

<sup>&</sup>lt;sup>3</sup> LOD is the lowest quantity of a substance that can be distinguished from the absence of that substance (a *blank value*) with a stated confidence level (generally 99%) and is defined as 3 \* standard deviation of the blank. The LOD can change from instruments and laboratories.

 $4$  LOQ is defined as 10  $*$  standard deviation of the blank, or  $\sim$ 3 times the LOD.

During the calculation, if more than one PUF was used for the analyses, the results are divided by the number of PUFs included. In the example of figure 6, the values of dioxins in column B, are from 2 PUFs (see row Unit pg/2 PUF) over the same period (season code). In column E, there are 4 PUFs (row Unit pg/4 PUF) and 4 periods (season code = I+II+III+IV) whereas in column F there are 4 PUFs but only two periods (season code = I+II). For the calculation of the sampling period (days) and the average temperature (°C), if two or more periods are included, the average deployment time and temperature is used.



**Figure 6**. Example of calculation of dioxin-like POPs.

### <span id="page-9-0"></span>4. Data Warehouse (DWH)

The DWH supports the GMP of the Stockholm Convention on the data collection and handling along with data analysis and visualization and assists the regional organization groups (ROG) and the global coordination group (GCG) in producing the regional and global monitoring reports. It constitutes a publicly available repository of valuable information that can serve as a useful resource for policy makers and researchers worldwide. Almost all data from the GMP first and second phases is stored in the DWH.

The DWH was developed by the Stockholm Convention Regional Centre in the Czech Republic through the Research Centre for Toxic Compounds in the Environment (RECETOX) and the Institute of Biostatistics and Analyses, Masaryk University, Brno, Czech Republic, under the guidance of the GMP Global Coordination Group, and based on Chapter 6 of the Guidance on the Global Monitoring Plan for Persistent Organic Pollutants relevant to data handling [\(UNEP/POPS/COP.6/INF/31\)](https://www.pops-gmp.org/res/file/UNEP-POPS-COP_6-INF-31_English.pdf).

The Reporting spreadsheet of the DWH is an excel file, that include four spreadsheets (Figure 7).

**Introduction** Data sheet Example sheet Code lists.  $\left( \widehat{+}\right)$ 

**Figure 7**. Reporting file of the DWH with the four spreadsheets.

The first spreadsheet is the introduction where it is explained how the file was conceived and how the information should be included in the other spreadsheets.

a) Data sheet is the table into which the reported data should be filled.

- b) Example sheet is an example of a table with filled data indicating which fields are required and which are not mandatory.
- c) Code lists for items with defined inputs. The data should be included into the Data sheet as defined in the code lists.

#### Data sheet

Data sheet is divided in three different classes or section of the DWH template: a) SITE, b) SAMPLING ATTRIBUTES and c) MEASURMENT (Figures 8).



**Figure 8**. Sections of the spreadsheet of the Data Sheet took from the Example sheet, showing how the data should be filled.

*IMPORTANT NOTE 1: No ambient air collected using a passive air sampler can be reported in concentration without the required use of a model. Current models may be useful, but there is no scientific consensus on this approach. One of the most used models is the Tom Harner´s model.*

*IMPORTANT NOTE 2: Many laboratories that work in the field of POPs work according to upperbound criteria, others on the contrary prefer to work according to lower-bound criteria. In other words, this refers to using the LOQ as concentration data for those cases where the substance is below the LOD or is simply not detected or consider 0 as concentration value for the lowerbound approach.*

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