

## AIR SAMPLING RATES FOR PCB AND OCP AT MOUNTAIN SITES USING SEMIPERMEABLE MEMBRANE DEVICES

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### Introduction

The industrial production and wide spread use of persistent organic pollutants (POP) led to long lasting human exposure to these compounds. Among them, polychlorinated biphenyls (PCB) and organochlorine pesticides (OCP) were used for many decades and left after-effects that are still present nowadays. Persistent organic pollutants are prone to long-range transport in the atmosphere due to their persistence and volatility, such that they spread to and contaminate areas where they were never used. The transport mechanism favours the accumulation of POP in cold areas such as polar and mountainous regions, where the re-volatilisation decreases<sup>1</sup>. Therefore, mountainous areas are particularly well suited for monitoring contamination of the environment by POP. However, the difficulty to access these remote areas implies the use of novel sampling techniques to achieve an accurate knowledge of the POP deposition and adequate POP monitoring in these regions. Thus, passive air samplers (PAS), uptaking compounds by passive mass transfer, based on the free flow of compounds from the air to an accumulation matrix, are considered as an alternative to the active volume samplers<sup>2</sup>. The potential of semi permeable membrane devices (SPMD) as passive air samplers was demonstrated in the laboratory by Petty and collaborators in 1993<sup>3</sup>. Subsequently, studies to determine the presence of contaminants, their sources and their spatial distributions in air with SPMD emerged and with them some important issues to be addressed<sup>4,5,6</sup>. Among them, the knowledge of the SPMD uptake kinetics at the moment of sampling and the calculation of sampling parameters to determine the performance of the compound uptake. The sampling rate  $R_s$  is defined as the volume of compound incorporated by the passive sampler per unit of time ( $\text{m}^3 \text{day}^{-1}$ ). Assuming ideal conditions of constant temperature, linear compound uptake and that the compounds are totally in gaseous phase we get<sup>7</sup>:

$$R_s = \frac{N_{SPMD}}{C_{air} \times t} \quad \text{Equation 1}$$

where  $N_{SPMD}$  is the amount of compound accumulated in the SPMD (pg),  $C_{air}$  is the air concentration ( $\text{pg m}^{-3}$ ) and  $t$  the period of deployment (days). In this way, in the linear uptake stage, the sampling rate of a compound can be calculated if the SPMD and air concentrations of the compound for a determined exposure time are known and constant.

### Material and Methods

SPMD consisting of LPDE membranes (length 23 cm, width 2.5 cm, thickness  $\approx 67.5 \mu\text{m}$ ) were filled with 0.7 ml triolein 99 % (Sigma-Aldrich, Taufkirchen, Germany) and were heat sealed under inert gas conditions ( $\text{N}_2$ ) in a glove chamber to avoid contaminations. The passive samplers were deployed into Stevenson screen boxes of untreated wood for two consecutive  $\frac{1}{2}$  year exposure periods and a third yearly period including the other two at 3 sites. Low volume and high volume active sampling for OCP and PCB, respectively, were conducted in parallel. Details of the sampling procedures regarding active sampling as well as of the sampling sites are given at <http://www.monarpop.at>. Due to the loss of active sampling data in the first active period, the sampling rates were calculated with the air concentrations determined one year later. It was assumed that under the same

seasonal temperature conditions and far away from input sources, the air concentrations were comparable, and thus used to calculate the sampling rates of the first period.

The SPMD extraction, clean-up and analysis of OCP were done according to standard procedures<sup>8</sup>. For PCB, the same extraction as for the pesticides was followed whereas the spiked standards were <sup>13</sup>C-PCB mixtures (Cambridge Isotope Laboratories, USA). The posterior purification and analysis were described by El-Kady et al.<sup>9</sup>. PCB from high volume active samples were analysed according to Moche und Thanner<sup>10</sup>.

## Results and Discussion

Sampling rates were calculated by use of field data from 3 sampling sites, each located at the top of an altitude profile (Mt. Weißfluhjoch (Switzerland, 2663 m), Mt. Sonnblick (Austria, 3100 m), Mt. Zugspitze (Germany, 2650 m). The OCP compounds chosen were those that exhibited the highest concentrations in all the active air samples and those that were still in the linear uptake. As an example, p,p'-DDT, Dieldrin and  $\alpha$ -Endosulfan are given in Table 1. PCB #28, #52 and #101 according to the IUPAC nomenclature are given in Table 2. This is a semi-quantitative approach because no performance reference compounds (PRC) were used to perform the calculations. Anyway, the study allows us to analyse the sampling rates in different seasons in order to detect possible differences. The sampling rates can be regarded as a theoretic amount of air exchanged in a determined time, where higher values reflect more air exchange capacity of the SPMD. Therefore, higher SPMD accumulation in Period 1 in comparison to Period 2 was determined for OCP due to the higher sampling rate values obtained in the first period (Table 1). This can also be observed by the sampling rate constants calculated for PCB, where higher sampling rates are also observed in Period 1 (May-November 2005) than in Period 2 (November 2005-May 2006), Period 3 (that embraces the other two periods) being an intermediate. Periods 1 and 2 are characterized by being ½ year deployment periods, the main difference between both were the average outdoor temperature during the 6 month deployment. The first period started in late spring until November, covering the warmer season but finishing at low temperatures. The second period covers the winter, but finishes at the end of spring where mild temperatures are predominant.

**Table 1:** Air sampling rates ( $\text{Nm}^3$  air  $\text{day}^{-1}$ ), OCP mean air concentrations determined by low volume air sampling ( $\text{pg}$  OCP  $\text{Nm}^3$  air) and SPMD accumulation ( $\text{pg}$  OCP  $\text{g}^{-1}$  triolein) at 2 sampling sites for Periods 1, 2 and 3.  $\text{Nm}^3$ : 101.3 kPa, 273 K.

OCP	Sampling rates ( $\text{Nm}^3$ air $\text{day}^{-1}$ )			Air concentrations ( $\text{pg}$ OCP $\text{Nm}^3$ air)		
	Period 1	Period 2	Period 3	Period 1	Period 2	Period 3
<i>CH-01-8 (2663 m a.s.l.)</i>						
p,p'-DDT	9.4	4.3	6.5	2.5	1.5	1.9
Dieldrin	4.1	1.8	3.3	3.1	2.0	2.5
$\alpha$ -endosulfan	7.3	3.4	5.8	46.9	48.9	48.3
<i>AT-47-6 (3100 m a.s.l.)</i>						
p,p'-DDT	9.1	1.6	6.5	0.45	0.38	0.41
Dieldrin	5.0	1.9	3.9	1.8	1.4	1.6
$\alpha$ -endosulfan	8.6	4.4	6.7	46.5	35.8	41.1
<i>SPMD (pg OCP <math>\text{g}^{-1}</math> triolein)</i>	<i>CH-01-8 (2663 m a.s.l.)</i>			<i>AT-47-6 (3100 m a.s.l.)</i>		
OCP	Period 1	Period 2	Period 3	Period 1	Period 2	Period 3
p,p'-DDT	4378	1366	4872	776	129	1077
Dieldrin	2423	754	3332	1679	531	2440
$\alpha$ -endosulfan	65368	34981	112879	75596	33410	110796

It is interesting that the sampling rates for each compound remain in a certain range, as to be expected theoretically, independent of the sampling site (Tables 1 and 2). For the same period of deployment, if the sampler design is kept constant and considering a global distribution of the analysed gaseous compounds in these remote sampling sites, the sampling rates would have to be similar under similar sampling conditions. This is the observed effect for the analysed compounds. In addition, differences between the sampling periods are in tendency higher than the differences among the different sampling sites. This fact points out the importance of the temperature in the SPMD uptake and the importance of the predominant temperature at the end of the deployment period. Sampling rates depend on the environmental temperature because of its influence on the compound properties but are independent of the compound air concentrations. This implies that for a determined temperature,  $R_s$  is constant.

It is possible, that in spite of the favoured mass transfer through the membrane at higher temperatures, the lower  $K_{oa}$  values also determined by higher temperatures cause lower sampling rates as a predominant effect such as it is observed in period 2 and 3. It has to be also considered, that Period 2 embraces the coldest period of the year where at these altitude height points the triolein can be frozen (temperatures  $< -4^{\circ}\text{C}$ ). Environmental temperatures below this point can imply a higher resistance of the triolein in the total mass transfer generated for the different triolein state. The triolein mass transfer resistance is usually considered negligible, but this assumption is not valid below the triolein freezing point. Therefore, temperatures  $< -4^{\circ}\text{C}$  do not imply a membrane controlled uptake and consequently a SPMD uptake enhance, hindering the compound uptake and as a consequence, decreasing the average sampling rate of the calculated period.

Sampling rates for PCB were already determined in laboratory and in field experiments<sup>11,12</sup> and are of the same order of magnitude to those obtained here. However, a direct data comparison is not possible due to differences in the SPMD design (surface area  $A=165\text{ m}^2$  instead of  $A=460\text{ cm}^2$  for 1 mL triolein in the classical design). A study performed by Ockenden and co-workers<sup>13</sup> compared sampling rates for PCB compounds in different seasons and the SPMD sampling rates obtained in winter were higher as the here determined for Period 1 which finished in winter at the 3 sampling sites.

The deployment conditions included sheltering of the SPMD in Stevenson screen boxes. However, the sampling sites were close to the top of the altitude profiles and thus, higher wind exposure and turbulences could be expected. Under these conditions, the air boundary layer is small and the total mass transfer is controlled mainly by the membrane. In the case of membrane controlled uptake, the temperature plays a key role because the mass transfer through the membrane is greatly influenced by the environmental temperature. This temperature effect would be not observed if the total mass transfer were air boundary layer controlled because the compound diffusion coefficients in air are not greatly influenced by the temperature<sup>12</sup>.

**Table 2:** Air sampling rates ( $\text{Nm}^3\text{ air day}^{-1}$ ) and PCB mean air concentrations determined by high volume air sampling ( $\text{pg PCB Nm}^3\text{ air}$ ) at 3 sampling sites for Periods 1, 2 and 3.  $\text{Nm}^3$ : 101.3 kPa, 273 K.

<i>PCB</i>	<i>Sampling rates (<math>\text{Nm}^3\text{ air day}^{-1}</math>)</i>			<i>Air concentrations (<math>\text{pg PCB Nm}^3\text{ air}</math>)</i>		
	<i>Period 1</i>	<i>Period 2</i>	<i>Period 3</i>	<i>Period 1</i>	<i>Period 2</i>	<i>Period 3</i>
<i>CH-01-8 (2663 m a.s.l.)</i>						
# 28	1.3	0.27	0.34	5.7	23.5	14.6
# 52	2.7	0.58	0.53	5.3	13.3	9.3
# 101	6.2	1.0	1.7	3.2	8.1	5.7
<i>AT-47-6 (3100 m a.s.l.)</i>						
# 28	2.8	0.38	0.92	7.9	2.8	5.3
# 52	5.0	0.57	1.8	3.4	1.7	2.5
# 101	11.4	1.3	3.6	1.8	0.9	1.3
<i>DE-21-6 (2650 m a.s.l.)</i>						
# 28	1.6	0.30	0.6	5.4	15.4	10.4
# 52	2.8	0.82	1.3	3.2	5.4	4.3
# 101	6.1	1.5	2.3	2.2	4.0	3.1

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