

SEMIPERMEABLE MEMBRANE DEVICES (SPMD) AS PASSIVE SAMPLERS: DATA INTERPRETATION REGARDING EXPOSURE TIME

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Abstract

Organochlorine compounds were sampled employing Semi Permeable Membrane Devices (SPMD) in remote areas of the Alpine region (Monitoring Network in the Alpine Region for Persistent and other Organic Pollutants: MONARPOP). At each area, SPMD were deployed at different sampling sites characterised by different altitudes. The deployment of the devices was carried out in order to obtain two consecutive ½ year exposure periods and a third annual exposure period embracing the other two. Results obtained by HRGC-HRMS for the different compounds were analysed taking into consideration exposure time, altitude profile and characteristics of the analysed chemicals. Accumulation in SPMD gave a clear indication that the more hydrophobic pesticide compounds present a linear uptake during all the exposure periods. In addition, the accumulation of compounds with lower K_{ow} values is no additive after 1 year exposure because the SPMD uptake is in a curvilinear stage or at equilibrium. All compounds showed a tendency to higher concentrations at altitudes higher than 1400 m a.s.l.

Introduction

The amount and diversity of anthropogenic compounds released to the atmosphere increases from year to year and with them the need to accomplish a correct monitoring and environmental control of these chemicals. Persistent organic chemicals are of public concern due to their spreading around the world and potential damage to ecosystems and living organisms. In search of appropriate methods to monitor and determine this kind of compounds different types of passive samplers were developed. Semipermeable Membrane Devices (SPMD) were initially designed as passive samplers to operate in aquatic environments but lately their use was extended as passive air samplers.¹ This device consists of a membrane, in this case composed of a low density polyethylene (LDPE) that encloses a lipophilic solvent: triolein (MW 885.4). The membrane has transient polymeric cavities of about 10 Å diameter and this size exclusion avoids triolein losses but simultaneously limits the uptake of organic molecules (MW>600 Da) through it.² Consequently, contaminants associated with particulate material are mainly not absorbed unless desorption from the particle followed by diffusion through the membrane occurs. Triolein is a natural triglyceride presented in most organisms. It solidifies at temperatures below 0 °C and is able to dissolve solid fats and simultaneously do not react with absorbed pollutants. Thus, these properties make this lipid suitable to mimic the uptake in living organisms. SPMDs are integrative samplers, accumulating compounds during the exposure time until reaching equilibrium. The air-device exchange of compounds follows first order kinetics and can be divided into three stages a) linear uptake where the uptake is proportional to the concentration of the compound in the device surroundings b) curvilinear stage where the elimination of the absorbed compound achieves importance and c) equilibrium stage where the uptake and release of the analyte in the device are equiparable.^{3,4} When the device is operating in the linear uptake stage, the sampler is called kinetic sampler. In the current work, SPMD were deployed at remote mountain areas over different exposure periods. Organochlorine pesticides characterised by their different properties were

quantitatively analysed by means of HRGC-HRMS. A comparison between results at different exposure times was achieved considering compound properties, altitude profile and the different stages of the uptake of the membrane devices.

Materials and Methods

Preparation, deployment and sampling of SPMD LPDE membrane lay-flat tubes (length 23cm, width 2.5cm, thickness $\approx 65 \pm 2\mu\text{m}$) were filled with 0.7 ml triolein 99 % (Sigma-Aldrich, Taufkirchen, Germany) and heat sealed under inert gas conditions (N_2) in a glove chamber. Then, the SPMD were placed into clean glass vials under nitrogen atmosphere to avoid contaminations and stored at -20°C . These hermetic vials were used to transport the SPMD from and to the place of deployment where were placed in deployment devices. SPMD weights were controlled before and after the exposure. The sampling was conducted in two mountain areas located in the Alpine region. At each area a sampling profile was carried out at the altitude profiles indicated in Table 1. Two sampling campaigns were carried out consecutively: May - November 2005 (Period 1) and December 2005 - May 2006 (Period 2). A third campaign embracing the Period 1 and 2, thus from May 2005 to May 2006 (Period 3) was also performed.

Analysis Membrane devices were cut into slices and spiked with ^{13}C -Chloropesticides standards (Cambridge Isotope Laboratories, USA). Then they were extracted for 24 hours with 100 ml cyclohexane each by use of a rotating shaking machine. The extracts were placed at the top of a mixed columns filled with 10 g silica gel, 5 g Al_2O_3 and 2 g Na_2SO_4 from the bottom to the top and eluted with a mixture *n*-hexane/dichloromethane 1:1. After that, the extracts were eluted through a C18 modified silica column with acetonitrile followed by the concentration of the eluate to 0.2 ml under nitrogen stream at 45°C . Then the extracts were transferred into vials and spiked with pentachlorotoluene as recovery standard. Finally the eluates were concentrated to 20 μl and the vials were stored at -20°C until instrumental analysis. The compounds were determined by high resolution gas chromatography (HRGC) on a Rtx-Dioxin2 column (Restek, Germany). The GC is coupled with a high resolution mass spectrometer MAT95 (Thermo GmbH, Germany) operated in single ion monitoring mode. The standard recoveries for OC were between 50 and 110 %. SPMD blanks and clean-up blanks were also conducted as an internal quality control. The organochloropesticides (OC) quantified were α and γ hexachlorocyclohexane (HCH) pentachlorobenzene (PeCB), hexachlorobenzene (HCB), chlordane (cis-CHL), dieldrin, 4-4'-DDT, 2-4'-DDT, 4-4'-DDE, 2-4'-DDE and α - and β -endosulfan.

Results and Discussion

All analysed compounds present higher accumulation in the Period 1 than in the Period 2 (Table 1). Both periods correspond to $\frac{1}{2}$ year exposure but different seasons at the end of the sampling. The mass transfer air-device at low temperatures tends to be under membrane control leading to an increased accumulation of compounds.⁵ SPMD exposure in Period 1 finishes in winter, thus the higher compound concentrations can be influenced by temperature. Analyzing the results obtained at the different altitudes for both profiles, a very similar pattern is observed at the altitude profile in the periods 1 and 2 for the compounds 2,4'-DDT, 4,4'-DDT, cyclodiene pesticides cis-chlordane, dieldrin and α -endosulfan and β -endosulfan. The Period 3 presents also the same pattern at the different heights as the periods 1 and 2 for these specified compounds. It is also remarkable that the sum of compounds accumulated in Period 1 and Period 2 assembles the amount of these chemicals accumulated in the whole year (Period 3). We can infer for these compounds that the membrane devices are still working as kinetic samplers due to the additivity of the Period 1 and 2 when comparing to the Period 3. By use of these passive devices, the total accumulation for these chemicals through the year can be measured in order to obtain an annual average value for these compounds. The molecular structure of this group of compounds occupies more volume in their spatial distribution and this generates more steric impediment to go through the membrane. On the other hand, they have high K_{ow} values that determine high affinity for the triolein. The accumulation of these compounds is also characterized by a tendency to higher values at heights above 1400 m.a.s.l in the altitude profile. As an example for this group, the altitude profiles for the DDT isomers are plotted in Figure 1.

In the case of 4,4'-DDE the Period 3 assembles the pattern of Period 2 where the accumulation of compounds in the Period 3 is even lower than the accumulation in Period 1. 2,4'-DDE shows an intermediate behaviour between the DDT isomers and 4,4'-DDE; the profile patterns are similar for periods 1, 2 and 3 but the amount of 2,4'-DDE accumulated in the annual period is lower than the sum of both $\frac{1}{2}$ year exposure periods. It may be

that DDE compounds are more easily exchanged through the membrane device than i.e. DDT compounds and the elimination rate acquires importance. As the passive sampler devices of the Period 3 are sampled together with the Period 2, the similarity in the pattern of the height profile for periods 2 and 3 can be related to the stage of the uptake (curvilinear uptake or proximity to the equilibrium) for DDE compounds in these passive samplers.

Consequently, the results achieved after one year exposure for 4,4'-DDE tend to be similar to the last ½ year exposure (Period 2) in the whole height profile. Therefore, we can not consider the obtained accumulation (Period 3) as the annual accumulation for these compounds. Proceeding that way it would overlook the real concentrations reached at these sampling sites for the DDE isomers.

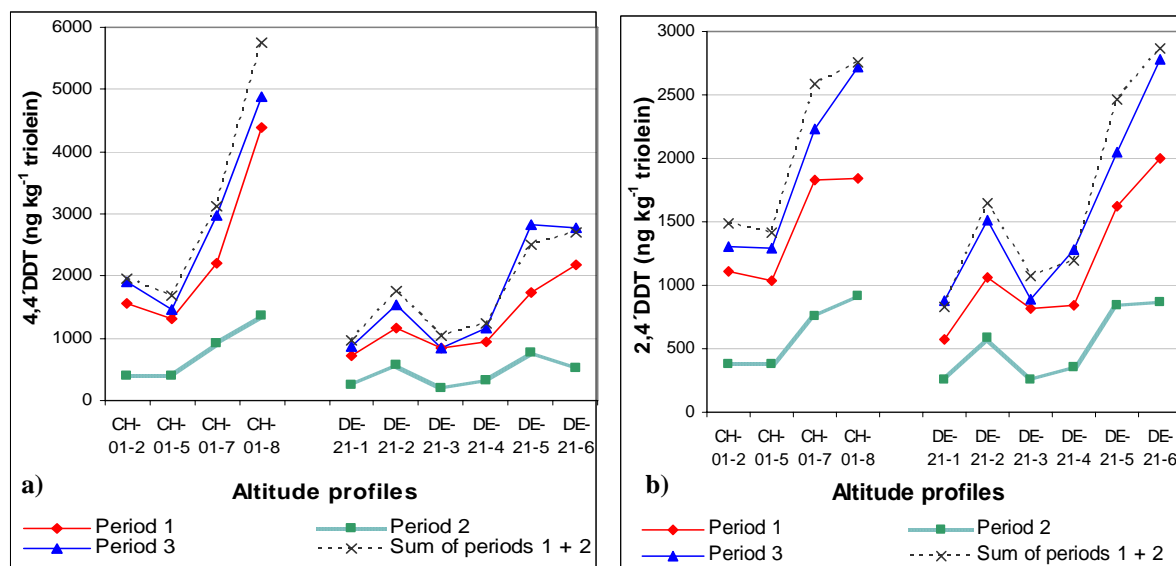


Figure 1: a) 4,4'-DDT and b) 2,4'-DDT concentration at the altitude profiles for the periods 1, 2 and 3. The sum of periods 1 and 2 is also depicted.

Regarding α -HCH and γ -HCH there is no similarity between the patterns of the periods 1, 2 and 3. Period 2 presents a tendency to decrease for both isomers while the annual period (period 3) increases significantly at altitudes above 1400 m.a.s.l. There is an accumulation increase for the period 3 at the height profile and tends to reach the sum of the concentrations in periods 1 and 2. In spite of period 3 not having pattern similarities with the other periods, it describes the same pattern at both profiles for both isomers. This tendency is also visible for the profile obtained in the period 2 for α and γ -HCH. PeCB and HCB have similar profile patterns and concentration values for the periods 2 and 3. Due to the lower K_{ow} values (thus lower K_{oa} values) of these compounds in comparison to DDT and cyclodiene pesticides, a membrane control uptake could be expected. Low K_{oa} values increase the membrane resistance for the mass transfer regarding the overall resistance. This implies that the whole mass transfer process is limited by this step generating a membrane control uptake stage. In summary, the analysed compounds seem to be in different uptake stages regarding the sampling device, being very differently influenced by the period of exposure, inherent properties and height profile. As a general tendency, an increase of concentration above 1400 m a.s.l. is observed in all compounds.

Table 1: Concentration of organochlorine compounds (ng organochlorine kg⁻¹ triolein) at two altitude profiles. The percentage values indicate the difference between the annual period and the sum of the two half year periods. CH-01: Switzerland Klosters, DE-21: Germany Eschenlohe.

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Site code	05.2005 -11.2005 Period 1		12.2005-05.2006 Period 2		05.2005-05.2006 Period 3		Sum of Period 1+Period 2		(Period 1 + Period 2) / Period 3 (%)		Altitude (m)	Difference in SPMD weight before and after exposure (%)
	α -HCH	γ -HCH	α -HCH	γ -HCH	α -HCH	γ -HCH	α -HCH	γ -HCH	α -HCH	γ -HCH		
												Period 1
CH-01-2	2870	4585	1366	2206	1905	1971	4235	6791	45.0	29.0	1410	-0.2
CH-01-5	2815	4188	1362	2200	1881	1600	4178	6389	45.0	25.0	1600	-1.0
CH-01-7	3313	4081	1383	2005	4011	5889	4697	6086	85.4	96.8	2540	2.6
CH-01-8	2874	3962	1230	1859	4631	6174	4104	5822	112.8	106.1	2663	0.5
DE-21-1	2887	7416	1452	4178	2561	6840	4339	11594	59.0	59.0	830	1.6
DE-21-2	3354	7862	1475	4537	2041	4386	4829	12400	42.3	35.4	1030	-0.7
DE-21-3	3001	7022	1282	2989	1865	3033	4283	10012	43.5	30.3	1230	-0.2
DE-21-4	3272	7290	1244	3103	2168	4333	4516	10394	48.0	41.7	1450	-0.1
DE-21-5	3242	6854	1371	3645	3228	6835	4613	10500	70.0	65.1	1650	0.6
DE-21-6	3700	6188	851	1921	4039	9435	4552	8109	88.7	116.3	2650	54.2
	PeCB	4,4'-DDT	PeCB	4,4'-DDT	PeCB	4,4'-DDT	PeCB	4,4'-DDT	PeCB	4,4'-DDT		Period 2
CH-01-2	885	1108	486	377	581	1309	1370	1485	42.4	88.1	1410	0.7
CH-01-5	862	1038	484	376	637	1295	1346	1414	47.3	91.6	1600	0.4
CH-01-7	1256	1828	937	759	1041	2230	2194	2588	47.5	86.2	2540	5.5
CH-01-8	1494	1847	1204	913	1341	2718	2698	2759	49.7	98.5	2663	2.4
DE-21-1	796	577	857	255	949	876	1653	832	57.4	105.2	830	4.7
DE-21-2	869	1056	1330	584	1010	1508	2199	1641	45.9	91.9	1030	0.9
DE-21-3	687	813	869	262	889	895	1556	1075	57.2	83.3	1230	1.0
DE-21-4	767	842	962	353	1125	1274	1729	1195	65.1	106.6	1450	1.3
DE-21-5	632	1624	1131	837	1066	2050	1763	2460	60.4	83.3	1650	2.4
DE-21-6	2374	2003	1886	860	2865	2783	4260	2864	67.3	97.2	2650	27.6
	dieldrin	β -endo	dieldrin	β -endo	dieldrin	β -endo	dieldrin	β -endo	dieldrin	β -endo		Period 3
CH-01-2	1439	2472	664	1339	2271	3586	2103	3811	108.0	94.1	1410	0.8
CH-01-5	1669	2958	663	1335	2185	4137	2331	4293	93.7	96.4	1600	1.3
CH-01-7	2267	5443	775	2347	3356	7631	3041	7790	110.3	98.0	2540	9.4
CH-01-8	2423	5785	754	2463	3332	7191	3177	8248	104.9	87.2	2663	5.1
DE-21-1	1350	2928	645	1162	2023	4259	1995	4089	101.4	104.1	830	7.6
DE-21-2	2080	4802	1164	2622	2925	7817	3245	7424	90.1	105.3	1030	4.5
DE-21-3	1522	4005	661	1548	2190	5158	2183	5553	100.3	92.9	1230	0.1
DE-21-4	1753	4163	778	1767	2491	5886	2531	5929	98.4	99.3	1450	0.4
DE-21-5	2819	8740	1296	3423	3692	12296	4115	12163	89.7	101.1	1650	4.8
DE-21-6	2276	6425	696	3032	3350	10268	2972	9457	112.7	108.6	2650	22.1

Acknowledgements

MONARPOP is funded by the EU Interreg III B Alpine Space Programme (Alpine Space) and by the participating partners: in particular, by the Austrian Federal Ministry for Agriculture, Forestry, Environment and Water Management (lead partner), by the Bavarian State Ministry of the Environment, Public Health and Consumer Protection, by the Swiss Federal Office for the Environment. In addition, by the Austrian Federal Environment Agency (project management), the German Federal Environment Agency, the GSF-National Research Center for Environment and Health, the Regional Agency for Environmental Prevention and Protection of Veneto, the Regional Agency for Environmental Protection of Lombardia and the Slovenian Forestry Institute. Additionally, we would like to thank the Swiss Federal Office for the Environment (FOEN - BAFU) for financial support.

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