Organohalogen Compounds, Volume 60, Pages 90-93 (2003)

PASSIVE SAMPLING METHOD FOR POPs MONITORING IN CZECH RIVERS - THE PILOT STUDY

Tomas Ocelka[1], Roman Grabic[1], Sarka Crhova[1], Tomas Tomsej[1], Mark Rieder[2], Drahomira Leontovycova[2]

[1]Institute of Public Health in Ostrava, National Reference Laboratory for Analysis of POPs Ministry of Health CR, Partyzanske nam. 7, 702 00 Ostrava, Czech Republic
[2] Czech Hydrometeorogical Institute, Prague, Czech Republic

Introduction

The passive sampling methods as SPMD (semipermeable membrane device) are widely used for determination of water-soluble POPs at the lowest concentration levels[1, 2, 3]. The recent development in membrane technology, standardization and unification of deployment and dialysis of SPMD make possible to use SPMD as a standard monitoring method.

The passive sampling methods (SPMD and biota) have been included into the Czech government program of surface water quality monitoring since 2001. The pilot study was performed at 4 sampling profiles in years 2001-2 using SPMD and bivalves (Dreissena Polymorpha). Following parameters were monitored – PAH, PCB, OCP, PCDD/F, PBDE and toxicity tests. The aim of the study was to obtain data describing situation at four main Czech river flows.

Materials and methods

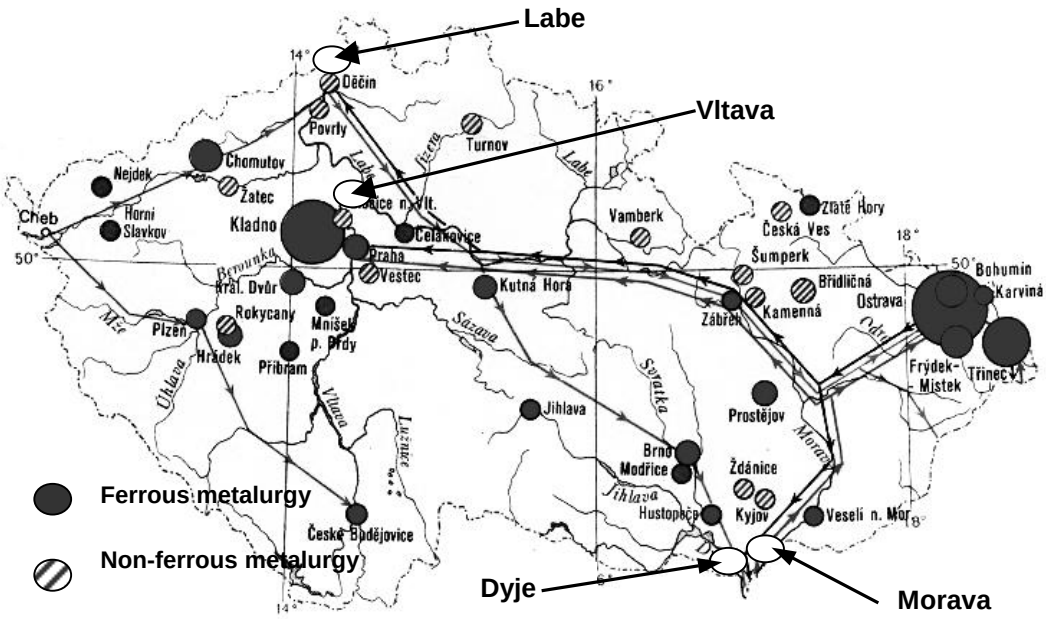
Standard and toxicity test membranes (layflat tube 91 cm length, 2.5 cm width, 1 ml of triolein inside) were used (Environmental Sampling Technology, St Joseph, MO, U.S.). SPMD (semipermeable sampling device) containing 3 standard and 1 toxicity test membrane were deployed at four locations for two sampling periods (aprox. 30 days) in May and June. The membranes were maintained inside protective stainless steel cages pendent on float (about 0,5 m below the surface). Membranes were transported in airtight metal cans. The transport field blanks were exposed during the sampler installation and deinstallation. The membranes were cleaned and dialyzed with hexane in accordance with instructions in tutorial[4]. Combined extracts from two membranes were spiked with isotope labeled internal standards of PCBs, PCDD/Fs and PBDEs, cleaned up and analyzed on GC/MS/MS[5]. The dialysate from the third membrane was splitted to equal aliquots. The one for OCP and PCB analysis was spiked with isotope labeled standards, cleaned up on H_2SO_4 deactivated silicagel column and analyzed on GC/MS/MS (GCQ and PolarisQ, Thermo Finnigan, San Jose, CA, USA) while the second one was used for PAHs determination.

Dreissena polymorpha used in this study were taken from flooded gravel pit (very clean place). The organisms were exposed for 60 days in same time range as SPMD in cages pendent on same float. Exposed Dreissena were frozen and delivered to laboratory for analysis. The samples were dried at room temperature, mixed with pre-cleaned sand and natrium sulphate and extracted after addition of isotope labeled standard. The extract was cleaned up as mentioned above. Dry weight and fat content were determined.

Results and Discussion

The four Czech rivers were sampled in pilot study: Vltava, Labe, Dyje and Morava. The sampling sites are described in figure 1. Vltava River is tributary of Labe, Dyje and Morava Rivers are tributary of Danube River.

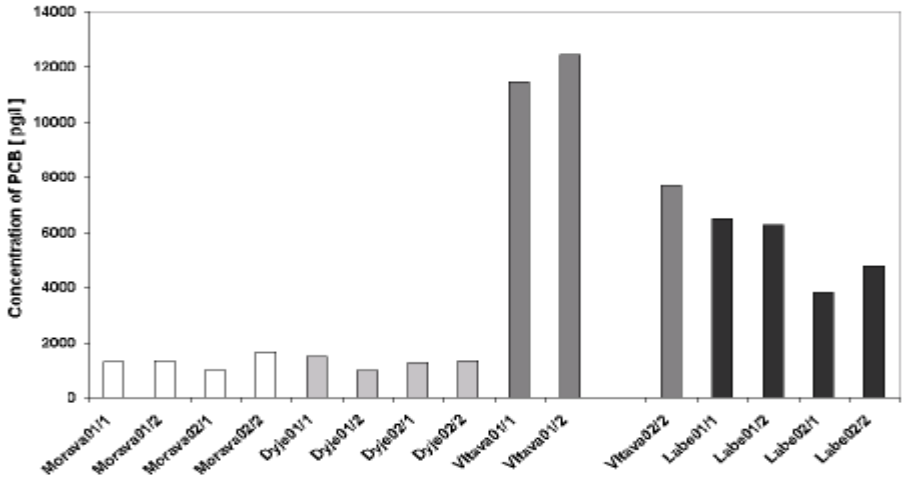
Fig. 1 The map of sampling sites



The primary results were obtained as ng(pg)/SPMD and ng(pg)/g of fat. The SPMD results were recalculated to ng(pg)/g of triolein by factor 0.9. The SPMD data from 1st and 2nd sampling period were summarized to get sampling time comparable with Dreissena Polymorpha. The SPMD data were recalculated using published formulas and uptakes ratios to obtain concentration of water dissolved PCBs[6].

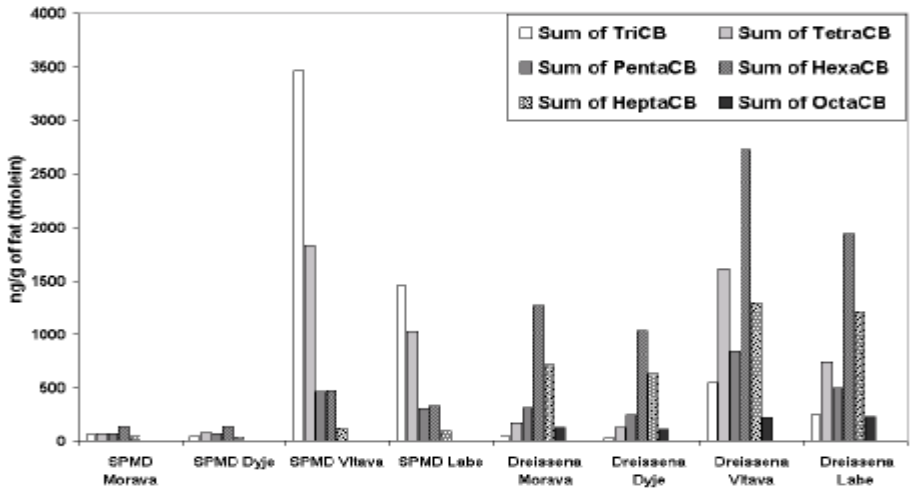
The comparison of data from 2001 and 2002 is shown in fig 2. The sampling was performed in same year period at stabilized water level. The figure shows only slight variation of PCB concentration at sampling profile. Surprisingly, Vltava River is more polluted by PCBs than Labe at border with Germany. 1st period Vltava River data from year 2002 are missing cause float with sampling equipment was stolen. The significant difference (order of magnitude) was observed between concentrations measured in rivers passing rural areas (Dyje and Morava) and those flow through industrialized big cities (Vltava, Labe).

Fig. 2 Sum of Tri to Deca CBs sampled by SPMD in 2001-2 (pg/l of water)



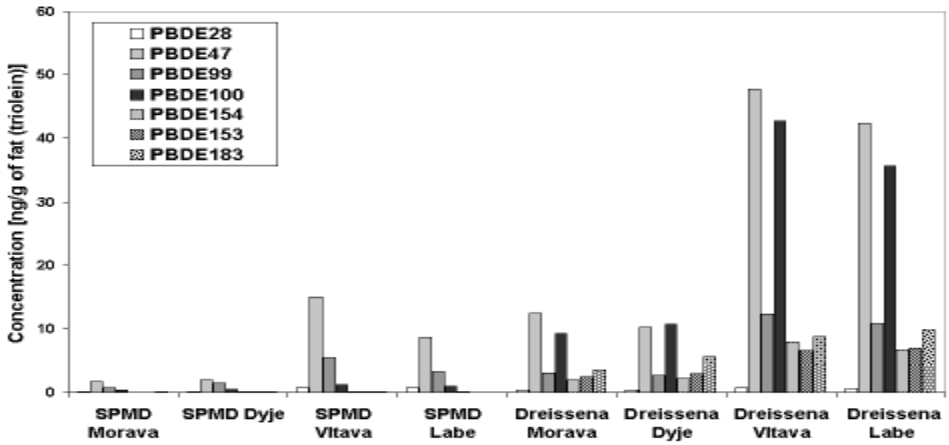
Concentrations of Tri to Deca CBs sampled by SPMD and Dreissena (in 2001) are shown in fig. 3. Significant differences among sampling sites are apparent from this figure. In SPMD samples, Tri and Tetra CB are prevailing in congener profiles of more polluted rivers –Vltava and Labe. In spite of this finding Hexa and Hepta CBs are dominant in Dreissena samples while Tri CBs was found lower by factor 5 compare to SPMD.

Fig. 3 PCB congener profiles in SPMD and Dreissena Polymorpha (data from y. 2001)



Similar changes in total concentration and congener profile were observed also in case of PBDE as it is shown in fig.4.

Fig. 4



It is evident that different sampling mechanisms are participating on uptake POPs. While only bioconcentration process takes part in SPMD case, concentration in Dreissena Polymorpha is resulting from bioconcentration, bioaccumulation and metabolisation going parallel. SPMD method seems to be suitable for monitoring of POP transport, identification of contamination sources. However, Dreissena and other "biota samplers" are essential for evaluation of POP bioaccumulation, biomagnification and possible health risk. Using of standard membranes makes possible to compare the data sampled anywhere in the world, if it is known some sampling data (water temperature, organic carbon content, sampling duration etc.). Important advantage of SPMD is immediate deployment. The results of this pilot study were used as reference values for measurements done after catastrophic flood in summer 2002.

References

1. Huckins, J. N., Manuweera, G. K., Petty, J.D., Mackay, D. and Lebo, J.A. (1993) Environ. Sci. Technol. 27, 2489-2496
2. Gale, W.R., Huckins, J. N., Petty, J.D., Peterman, P.H., Williams, L.L., Morse, D., Schwartz, T.R., Tillitt, D.E. (1997) Environ. Sci. Technol. 31, 178-187
3. Rantalainen, A.L., Ikonomou, M.G., Rogers, I.H. (1998) Chemosphere 37, 6, 1119-1138
4. Huckins, J. N, G. K., Petty, J.D., Lebo, J.A., Orazio, C.E., Clark, R.C., Gibson, V.L. (1998) SPMD technology - A tutorial: Columbia, Missouri (Available from Columbia Environmental Research center, U.S. Geological Survey Biological Resources Division, 4200New Haven Road, Columbia, MO 65201)
5. Grabic, R., Novak, J., Pacakova, V., (2000) J. High Resol. Chromatogr., 23, 10, 595-599
6. McCarthy, K.A., Gale, W.R., (1999) Water -resources investigation report 99-4051 (Available from U.S. Geological Survey Information Services, Box 25286, Federal Center, Denver, CO 80225)