

An Approach For Assessment Of Waterborne Bioavailable Organic Contaminants Using Semipermeable Membrane Devices (SPMDs)

*Ksenia Pazdro
Institute of Oceanology,
Polish Academy of Sciences, Sopot, Poland*

1. Introduction

A large amount of anthropogenic, organic pollutants has entered the global aquatic environment during the past decades. Many of them, like polycyclic aromatic hydrocarbons, pesticides, polichlorinated biphenyls and dioxins are considered to be hazardous to the environment. Their mobility through air and water, accumulation and/or transformation processes in the environment and finally their biomagnification, constitute a real risk to human health, wildlife and the environment [1,31]. Most of organic micropollutants are hydrophobic and biochemically resistant that cause the compounds bioconcentrate in the fatty tissues of organisms. Knowledge of the potential bioavailability of a pollutant, present in the environment is essential for ecosystem risk assessment and further effects studies [11,34]. This has induced many countries to promote monitoring programs and stepwise evaluation processes. Limitations in nearly all currently employed techniques and analytical methodology impede comprehensive exposure assessments. These limitations include the use of single point in time sampling methods, analytical methods having insufficient sensitivity to determine trace levels of contaminants in water. Bivalve mollusks have been recommended by many as the most suitable monitoring organisms for bioaccumulation of trace contaminants in fresh, marine and estuarine waters [11]. Programs such as the National Oceanic and Atmospheric Administration's National Status and Trends program [19,33] exemplify the utility of this approach to pollutant monitoring. However, monitoring with mussels often encounters some problems, like

natural anatomical and behavioral variability of indigenous populations and mortality of organisms in many harsh environments [13].

To avoid these problems, interest in the use of in situ passive sampling approach for assessing environmental pollutant exposure has increased worldwide. By far the most commonly used passive sampler is semipermeable membrane device (SPMD), first described by Huckins *et al.*, [14].

The objectives of this study are to present the theoretical background of organic contaminants sampling by SPMDs. A field study, undertaken in Atlantic coastal waters of France exemplifies a practical application of SPMDs. The field experiment aimed to compare the occurrence and individual PAHs distribution in SPMDs and in the co-deployed mussels, *Mytilus galloprovincialis* as well as to estimate the ambient water PAH concentrations from the SPMD results.

1.1. SPMD description

Several configurations of membrane devices have been investigated in laboratory conditions. Finally, the most efficient, now commercially available semipermeable membrane device (SPMD) consists of 1 ml of triolein enclosed in polyethylene tubing (2.5 cm wide, 91.2 cm long) [14]. The ability of SPMDs to concentrate trace concentrations of dissolved lipophilic organic contaminants has been achieved by mimicking specific mechanisms of the aquatic bioconcentration (the uptake of a compound by an organisms from the surrounding medium, excluding the dietary route) [15]. The lipid becomes a surrogate for organisms fat pools, whereas the membrane separates lipid and aqueous phases and mimics some of selective capabilities of biological membranes. The molecular size-exclusion limit of polyethylene membrane is similar to that of biological membranes [22], while triolein constitutes a significant fraction of most aquatic organisms [9].

1.2. Sampling approach

In SPMD devices, the uptake of chemicals is based on the process of passive diffusion of lipophilic organic compounds from water column into a neutral lipid enclosed in polyethylene tubing. To describe the sampling kinetics Huckins *et al.* [14,15,16] developed a theory describing the uptake of chemicals by SPMDs and proposed a mathematical model based on the theory of resistance to mass transfer through the membrane. Depending on the properties of contaminant present at a sampling site, environmental conditions and the duration of exposure, the organic compounds sequestered by an SPMD may be in the linear uptake (integrative sampling), curvilinear, and equilibrium partitioning phases of sampling.

Two approaches are generally used to estimate ambient contaminants levels from the concentrations in SPMDs. If the exposure time is sufficient to reach the steady-state concentration for a particular contaminant in the SPMD, then its concentration in water can be estimated by an equilibrium relationship. If equilibrium is not approached then the linear uptake model should be included and the compound concentration in the SPMD is directly proportional to sampling rate. The term which reflects the SPMD sampling potential is sampling rate (R_s). Sampling rate represents the volume of water extracted per day by an SPMD of a specific configuration. The sampling rates values are measured in laboratory flow-through experiments and then applied to estimate contaminant time-integrated concentrations in water or air environment from the amounts accumulated by SPMDs. The sampling kinetics depend strongly on sampler design, chemical structure of sampled compounds and environmental conditions. The chemical structure influence can be related directly to the K_{ow} - octanol water partition coefficients values - universal parameters of thermodynamic partitioning of compound between water and lipophilic phase. There is a number of factors that contribute to modify the laboratory measured values. Several environmental factors must be considered, with temperature effects and membrane biofouling. Biofouling can diminish to a large extent the membrane permeability and reduce SPMD capacity to concentrate the compounds in question. To correct the sampling rates values use of permeability reference compounds (PRC) was suggested [6, 16]. PRC are non-interfering compound with moderate SPMD fugacity added to SPMD lipid prior to exposure.

1.3. Practical applications of SPMDs

Since the beginning of the 1990s, SPMDs have become increasingly popular in the monitoring of hydrophobic pollutants in both water and air. Laboratory and field studies in several countries have shown SPMDs to be effective devices at indicating trace organic contaminants like PAHs, PCBs and pesticides in different aquatic systems. The most widespread application of SPMDs was the chemical monitoring of organic contaminants, like polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), organochlorine pesticides and dioxines. SPMDs were used to determine pollutant sources and relative levels at different locations in river water and sediments [29, 10, 17, 4, 25, 26, 18] as well as in marine environment [29,13]. SPMDs were also used as passive air samplers in large scale studies [29,21]. In many cases, SPMDs were deployed side-by-side with aquatic organisms to evaluate the bioavailability and exposure of aquatic organisms to the environmental pollutants [12,27,5,7,26]. In certain cases, SPMDs were deployed in “semi-natural” or man made environments characterized by high level of contamination by anthropogenic

compounds such as irrigation channels [25] and compost [32]. Few studies describe, that SPMD technique may be also integrated with standard bioassays to study toxic effects of bioavailable contaminants [8, 31]. The most completed list of applications is available in [36].

2. Field study

So far comparatively few reports have documented the utility of SPMDs in studying the bioavailable PAHs fraction in marine coastal areas except for the data reported by Axelman *et al.* [2], Peven *et al.*, [27] and Roe-Utvik *et al.*, [35]. A field-based experiment undertaken in Atlantic coastal of France aimed to compare the occurrence and individual PAHs distribution in SPMDs and the accumulation of PAHs in co-deployed mussels.

2.1. Materials and methods

Semipermeable membrane devices (SPMDs) and mussels (*Mytilus galloprovincialis*) were used in a side-by-side field deployment in Atlantic coastal waters ($\varphi = 47^{\circ}25.20\text{ N}$, $\lambda = 02^{\circ}34.37\text{ W}$) in the period from 31st March to 6th June 2000. The SPMDs were placed at approximately 5 m depth, in a perforated stainless steel container to protect the membranes against mechanical damage and to restrict water flow velocity at the membrane surface. Inside the container five standard size (91.4 x 2.5 cm) polyethylene membrane filled with 1 ml (0,91 g) of pure triolein purchased from EST Joseph, MO, were mounted. Mussels (*Mytilus galloprovincialis*) of uniform size (approximately 5 cm) were collected from the potentially uncontaminated site. After gut content purification, the mussels were deployed side by side with SPMDs. A sub-sample of mussels was frozen for analysis of background levels. Field blank SPMDs were exposed to air during the field deployment and retrieval phases to represent airborne contamination during preparation of the sample and processed as deployed samples.

Total exposure time was 67 days. The relatively large volume water samples (100–120 dm³) were collected after 11, 18, 32, 45, and 67 days to establish the levels of contaminants in dissolved and particulate phase. Biofouling of the cages and the SPMDs was notable.

After retrieval, the membrane surfaces were cleaned from periphyton and sediment particles and finally dialysed with n-hexane during 24 hours, including two solvent changes resulting in about 300 ml fractions. Before dialysis two deuterated PAHs were added to establish the recoveries. After collection, mussels were returned to the laboratory and after 24 hours depuration period in clean seawater, were shucked. The shucked soft tissue was homogenized and freeze-dried. 5 g of powdered dry tissue, spiked with internal

standards was then extracted with methylene chloride, applying accelerated solvent extraction technique (ASE).

PAHs were isolated from the lipid mixture using gel permeation column chromatography technique (GPC). The collected fractions, containing the compounds of interest, were passed through activated copper to desulfurize the samples. The clean-up steps were then conducted to enrich the contaminant residues for mass spectrometric analysis.

The final analysis was performed on a GC/MS instrument (Hewlett Packard 6890) equipped with DB-5 column (60 x 0.32 mm i.d., 0.25 μ m thickness) and MS detector running in selected ion monitoring (SIM) mode. The analytical steps are described in details in [23] and [24].

3. Results and discussion

3.1. Comparison of PAH accumulation in mussels and SPMDs

The mussels and SPMDs were analyzed for parent and alkyl homologues and sulphur and oxygen compounds. Different non-substituted and substituted analytes were identified in the samples. 16 of them belong to the priority pollutant PAHs recommended by the U.S. Environmental Protection Agency (U.S. EPA). The SPMDs have been shown to concentrate large variety of polycyclic aromatic compounds from low molecular compound like naphthalenes to high molecular compounds like B (ghi) perylene. The identified compounds are listed in Table 1, together with abbreviations used.

The total priority 16 pollutants PAHs concentrations in lipid tissue of mussels and SPMDs during the exposure are shown in Figure 1. Assuming, that after 32 days both media approached equilibrium phase for most compounds the concentrations have been normalized to the lipid content. The concentrations (on the lipid basis) of PAHs in the SPMDs and in caged mussels were in the same order of magnitude. The concentrations of parent compounds, for the same periods of deployment (32, 45 and 67 days), ranged from 980 to 693 ng/g lipid and from 1198 to 513 ng/g lipid for membranes and caged mussels, respectively. After 67 days of deployment the content of PAHs was slightly higher in the SPMDs than in mussel lipoidal tissues. This might be related to greater capacity of SPMD to accumulate bulk of hydrophobic compounds because of greater lipid content comparing to living organisms [2,27]. In the case of mussels equilibrium state could be reached in shorter time and then the contaminants can be released to surrounding environment. All the samples, including mussels, SPMD and water samples revealed high alkyl-substituted PAH compounds concentrations. This feature is mostly related to the presence of petroleum derived fraction of hydrocarbons (Piccardo *et al.*, 2001).

Table 1. Abbreviations of individual polycyclic aromatic compounds identified in the SPMDs and mussels samples during the experiment**Tabela 1.** Skróty poszczególnych wielopierścieniowych związków aromatycznych oznaczonych w SPMD i próbkach małż w czasie badań

Compound	Abbreviation
*Naphthalene	N
C1-Naphthalenes	C1-N
C2-Naphthalenes	C2-N
C3-Naphthalenes	C3-N
C4-Naphthalenes	C4-N
*Acenaphthylene	AC
*Acenaphthene	ACE
*Fluorene	F
C1-Fluorenes	C1-F
C2-Fluorenes	C2-F
*Phenathrene	P
*Anthracene	A
C1-Phenathrenes/Anthracenes	C1-P
C2-Phenathrenes/Anthracenes	C2-P
C3-Phenathrenes/Anthracenes	C3-P
*Fluoranthene	Fl
*Pyrene	Py
C1-Pyrenes/Fluoranthenes	C1-Py
C2-Pyrenes/Fluoranthenes	C2-Py
*Benzo(a)anthracene	BaA
*Chrysene/Triphenylene	CHR
C1-Chrysenes	C1-CHR
C2-Chrysenes	C2-CHR
*Benzo(b)fluoranthene	B(b)Fl
*Benzo(k)fluoranthene	B(k)Fl
C1-benzofluoranthenes	C1-BFls
*Benzo(e)pyrene	B(e)Py
*Benzo(a)pyrene	B(a)Py
Perylene	Per
*Indeno[1,2,3-c,d]pyrene	IND
*Dibenz[a,h]anthracene	DBA
*Benzo[g,h,i]perylene	B(ghi)Per
Dibenzothiophene	DBT
C1-Dibenzothiophenes	C1-DBT

C2-Dibenzothiophenes	C2-DBT
C3-Dibenzothiophenes	C3-DBT
Benzonaphthothiophenes	BNTs
C1- Benzonaphthothiophenes	C1-BNTs
Dibenzofuran	DBF
C1-Dibenzofurans	C1-DBF
C1-Dibenzofurans	C2-DBF

*EPA method 8270 PAH compounds

C1, C2, C3, C4 refer to number of alkyl carbon substituents on the parent compound

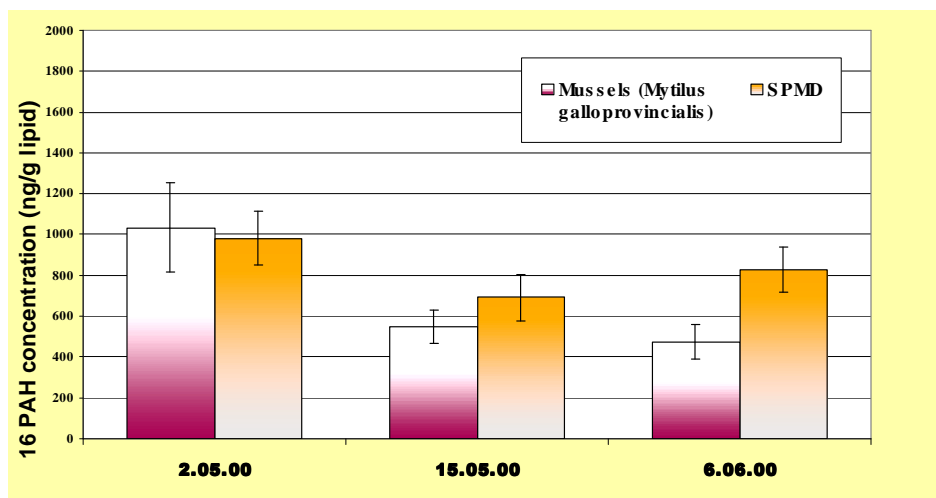


Fig. 1. 16 priority pollutant PAH content in SPMDs and mussels (*Mytilus galloprovincialis*) during the exposure in the year 2000

Rys. 1. Zawartość 16 najważniejszych zanieczyszczeń WWA w SPMD i małżach (*Mytilus galloprovincialis*) podczas ekspozycji w roku 2000

To better understand the different phenomena that govern PAH distribution in mussels, it is necessary to consider each compound individually. The distribution of individual PAH concentrations measured in mussel tissues and SPMDs after the 32 days deployment time are shown in Figures 2 and 3. The significant differences were observed for individual accumulation levels in caged mussels and SPMD. A wider range of compounds was also detected in the SPMDs. These fingerprints show that not only alkyl-substituted compounds, but also the more water soluble, lower molecular weight fraction of PAH is sequestered to higher extent by SPMDs than by mussels. This feature is possibly also caused by their higher volatility than other PAHs [12]. Also

degradation may have promoted the rapid loss from the animals. The release of PAHs from mussels may occur as unmetabolized hydrocarbons by passive diffusion or as a result of active metabolism [30]. The higher molecular weight, less water soluble analytes are sampled by SPMDs at a reduced rate. This phenomenon has been already noted by Huckins *et al.* [14,15]. The reduction may be related to limitations due to molecular size of SPMD pore. On the other hand these larger compounds tend to partition with particulate matter and are ingested by the bivalves and either reside in their gut or are adsorbed. Mussels can directly absorb lower weight PAH through filtered water, while heavier molecular weight hydrocarbons (four or more rings) are mainly ingested in particle form through the digestive system [3,28]. Particulate concentrations in the locality of our experiment and a resulting feeding patterns of the mussels may account for the lack of correspondence with SPMD concentrations observed in the field experiment.

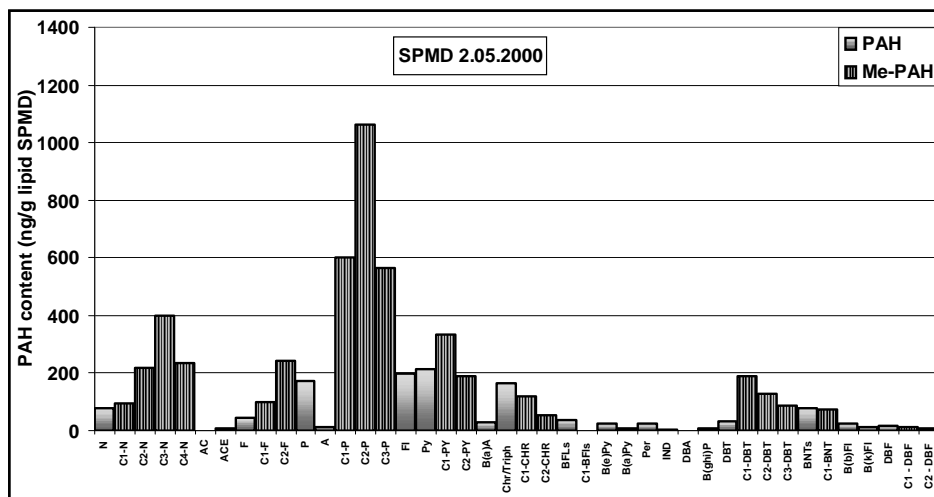


Fig. 2. The distribution of PAH concentrations in SPMD after 32 days of deployment. Abbreviations of PAHs according to Table 1

Rys. 2. Rozkład stężeń WWA w SPMD po 32 dniach przebywania w toni wodnej. Skróty nazw WWA zgodnie z tabelą 1

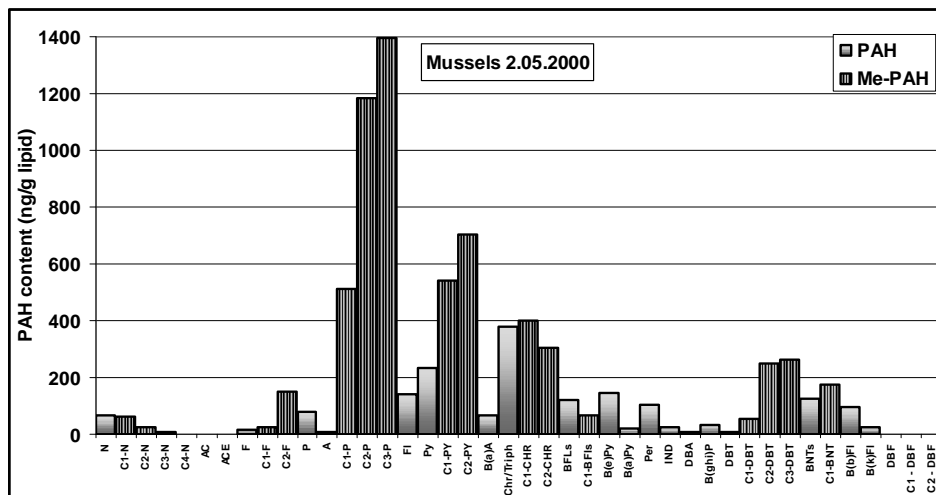


Fig. 3. The distribution of PAH concentrations in mussel soft tissue after 32 days of deployment. Abbreviations of PAHs according to Table 1

Rys. 3. Rozkład stężeń WWA w tkance miękkiej małż po 32 dniach przebywania w toni wodnej. Skrótów nazw WWA zgodnie z tabelą 1

As PAH vary widely in physicochemical properties with log K_{ow} ranging from 3.4 for naphthalene to 6.7 for dibenz(a,h) anthracene, the PAHs were divided into three groups, those low hydrophobic ($\log K_{ow} < 4$), moderately hydrophobic ($4 < \log K_{ow} < 6$) and finally the most hydrophobic ($\log K_{ow} > 6$). The correlation between individual PAHs concentrations in mussels and SPMDs during the experiment was further tested by undertaking a linear regression. When regarding moderate and high hydrophobic compounds, a relatively good correlation was observed between PAH concentrations in SPMD and mussels (Figure 4). Correlation is fairly good for the most hydrophobic PAHs with log K_{ow} values higher than 4. The generated calculations show that, despite of individual differences, PAH concentrations in mussels could be related to SPMD concentrations using linear regression equations with a good accuracy.

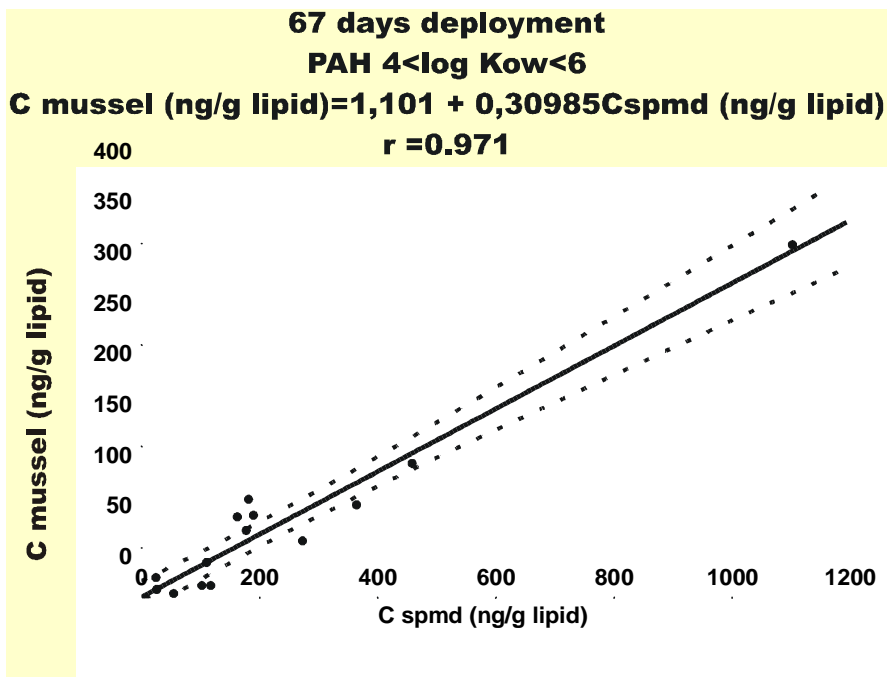


Fig. 4. Correlation between PAH concentrations (ng g^{-1} lipid) in mussels and SPMDs after 67 days of deployment

Rys. 4. Korelacja pomiędzy stężeniami WWA (ng g^{-1} tłuszczu) w małżach i SPMD po 67 dniach przebywania w toni wodnej

4. Estimation of ambient water concentration

The ability of the SPMD and the mussels to predict contaminant concentrations in the ambient environment was evaluated through concurrent measurements of PAHs in the dissolved phase in the water column. The freely dissolved concentrations can be estimated from SPMD concentration using the mathematical uptake model developed by Huckins *et al.* (1990,1993). Two approaches are generally used to estimate ambient contaminants levels from the concentrations in SPMDs. For the PAHs for which equilibrium has not been approached the uptake in the SPMDs is expected to be linear and can be described by equation 1

$$C_w = C_{spmd} M_{spmd} / R_s * t, \quad (1)$$

where, C_w is the concentration of analyte PAH in water (ng/dm^3), C_{spmd} the concentration of analyte PAH in SPMD (ng/g SPMD), R_s the SPMD sampling rate (dm^3/day) and t – time of exposure. The compound concentration in the 198 ————— Środkowo-Pomorskie Towarzystwo Naukowe Ochrony Środowiska

SPMD is then directly proportional to sampling rate. If the exposure time is sufficient to reach the steady-state concentration for a individual contaminant in the SPMD, then its concentration in water can be estimated by an equilibrium relationship:

$$C_w = C_{spmd} / K_{spmd} \quad (2)$$

where, K_{spmd} is the equilibrium SPMD-water partition coefficient.

The R_s and K_{spmd} values can be measured in laboratory calibration, flow-through exposures.

The values measured by Huckins *et al.* [16] have been applied in the present study and are given in Table 2.

Table 2. SPMD calibration data for estimating ambient water concentrations (from Huckins *et al.*, 1999)

Tabela 2. Dane kalibracyjne dla SPMD do oceny stężeń w wodzie otaczającej (za Huckins i in., 1999)

	log K_{ow} *	log K_{spmd} **	Sampling Rate*** – R_s (L/day)	
			10°C	18°C
Naphtalene	3,45	2,53	1,9	0,9
Acenaphthylene	4,08	3,16	2,3	1,4
Acenaphthene	4,22	3,59	2,7	2,3
Fluorene	4,38	3,74	3,0	1,7
Phenantrene	4,46	4,13	3,8	3,6
Anthracene	4,54	4,22	2,9	3,6
Fluoranthene	5,2	4,48	3,6	4,5
Pyrene	5,3	4,63	4,5	5,2
Benz(a)Anthracene	5,91	5,16	3,2	3,2
Chrysene	5,61	5,11	3,7	4,8
Benzo(b)Fluoranthene	5,78	5,30	2,8	3
Benzo(k)Fluoranthene	6,2	5,19	2,9	3,9
Benzo(a)Pyrene	6,35	4,99	3,2	3,7
Indeno(1,2,3)Pyrene	6,51	4,69	3,0	3,8
Dibenzo(a,h)Anthracene	6,75	3,68	2,0	3
Benzo(ghi)Perylene	6,9	3,87	1,8	1,9

* K_{ow} - octanol/water equilibrium partitioning coefficient

** K_{spmd} – semipermeable membrane device/water equilibrium partitioning coefficient

*** R_s – sampling rate - volume of water extracted per day by an SPMD

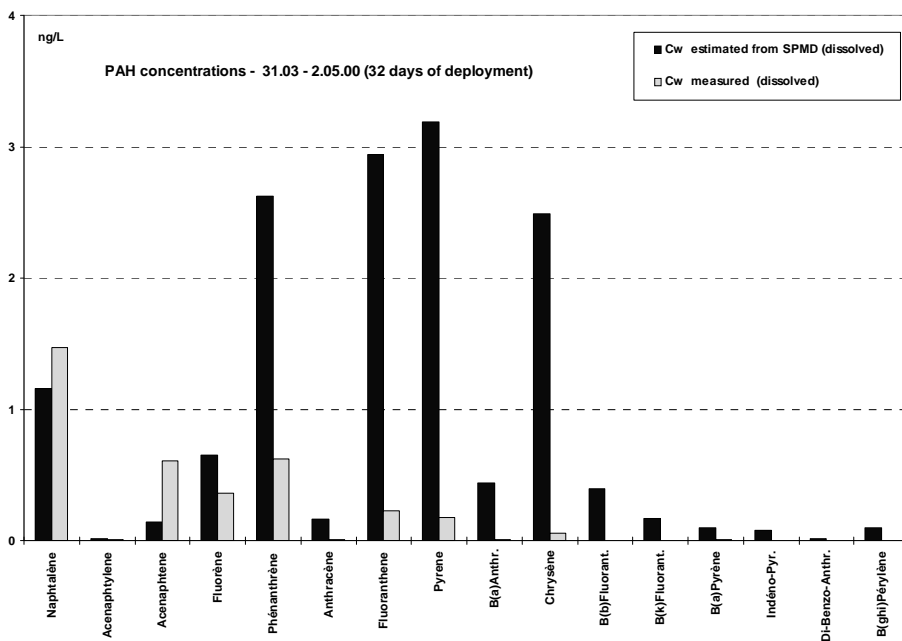


Fig. 5. Comparison of dissolved PAHs concentrations estimated from SPMD and measured using XAD2 preconcentration technique (32 days of deployment)

Rys. 5. Porównanie stężeń rozpuszczonych WWA oszacowanych z SPMD i zmierzonych przy zastosowaniu techniki prekoncentracji XAD2 (po 32 dniach przebywania w toni)

Figure 5 presents an exemplary comparison between estimated dissolved PAH concentrations in ambient water after 32 days time of exposure and mean values of measured concentrations. The concentrations estimated by SPMD method represent also time-integrated concentrations in dissolved phase, while values measured using XAD technique represent time-averaged concentrations in dissolved phase during the deployment. The estimated concentrations are on the same order on magnitude for both methods (ng/L). The levels of agreement appear to be similar as shown by Utvik *et al.* [35]. However, the results indicate some less or more systematic differences. The ratio between the dissolved phase determined by SPMD and by XAD extraction method show that only for few low molecular weight compounds like naphthalene the estimation is close or below 1, whereas for medium and high molecular weight compounds are overestimated (up to 100). An overestimation may be related to use of non-corrected sampling rates of contaminants. On the other hand, many of high hydrophobic PAHs, like benzo(ghi)perylene were not

detectable during the study, which makes the comparison more complicated. Simultaneously, because concentration factors of SPMD and mussels are 10^2 to 10^5 , the contaminants that were likely to be below detection limit of XAD extraction technique samples could have been detected. Similar findings were revealed by Axelman *et al.* [2]. However, there still exist very few studies in which SPMD-based concentration of chemicals in water were compared with concentrations measured by alternative methods of analysis. It is clear that the accuracy of SPMD-derived concentration estimates must be further verified. There are a number of factors that contribute to the uncertainty of estimations (temperature effects, biofouling, etc.) [6,15,35]. The use of permeability reference compounds, added to the membranes before deployment is strongly recommended.

5. Conclusions

Basing on the literature studies the advantages of passive, lipid-filled membrane samplers can be summarised :

- they allow continuous time-integrated, spatial monitoring of organic, hydrophobic contaminants like PAHs, PCBs, dioxins;
- compounds undetected applying conventional methods can be measured and estimated into measurable levels;
- the SPMDs can be exposed to harsh environmental conditions for long time and still remain operative;
- the SPMDs organic compounds mixture can be applied in the toxicity tests;
- SPMD samples are easier to analyse than biological samples.

SPMDs provide a time weighted average relative index of pollution severity, sequester a broad spectrum of chemical classes, concentrate pollutants often metabolized by organisms, can be used in surface waters, sediment, and groundwater environments, function well regardless of water quality, provide a means of obtaining an environmentally relevant mixture of waterborne contaminants for toxicological assessments.

The field study confirmed the potential of SPMDs for use in marine waters monitoring, producing results comparable with conventional technique and living organisms.

In comparison with XAD extraction technique the SPMD method seems to be more suitable for an assessment of the background concentrations of PAH because of substantially lower method quantification limits. Moreover, contaminants sequestered by the SPMDs represent an estimation of the dissolved or readily bioavailable concentration of hydrophobic contaminants in water, which is not provided by most analytical approaches. However, to make

this utility more accurate an application of permeability reference compounds should be also improved. Currently existing mathematical model for kinetics should also be improved for the same reasons. Then, finally the SPMDs could become a bridge between analytical chemistry and biomonitoring methods

Acknowledgements: The field study was supported by French regional authorities (Pays de la Loire). Dr Jacek Tronczynski is acknowledged for supervising the study.

References

1. **Alexander M.:** Aging, Bioavailability of Overestimation of Risk from Environmental Pollutants. *Environ.Sci.Technol.*, 34, 20, pp 4259-4265, 2000.
2. **Axelmann J., Naes K, Naf C, Broman D.:** Accumulation of polycyclic aromatic hydrocarbons in semipermeable membrane devices and caged mussels (*Mytilus edulis*). In relation to water phase distribution. *Environ. Toxicol. Chem.* 18, pp 2454-2461, 1999.
3. **Baumard P., H.Budzinski, P.Garrigues:** Polycyclic Aromatic Hydrocarbons in Sediments and Mussels of the Western Mediterranean Sea. *Environ.Toxicol.Chemistry*, 17, 5, 765-776, 1998.
4. **Bennett, E.R., Metcalfe, T.L., and Metcalfe, C.D.:** Semi-permeable Membrane Devices (SPMDs) for Monitoring Organic Contaminants in the Otanabee River, Ontario. *Chemosphere* 33, pp. 363-375, 1996.
5. **Bergqvist, P.-A., Strandberg, B., Ekelund, R., Rappe, C., and Granmo, A.:** Temporal Monitoring of Organochlorine Compounds in Seawater by Semipermeable Membranes Following a Flooding Episode in Western Europe. *Environmental Science & Technology* 32, pp. 3887-3892, 1998.
6. **Booij, K., Sleiderink, H.M., and Smedes, F.:** Calibrating the Uptake Kinetics of Semipermeable Membrane Devices using Exposure Standards. *Environmental Toxicology and Chemistry* 17, pp. 1236-1245, 1998.
7. **Chambers D.:** Semipermeable membrane devices used to estimate bioconcentration of polychlorinated biphenyls. *Journal AM.Water Ressources Association.* 35, 1, pp. 143-153, 1999.
8. **Cleveland L., E.Little, J.D.Petty, B.T.Johnson, J.A.Lebo, C.E.Orazio, J.Dionne, A.Crockett:** Toxicological and chemical screening of Antarctica Sediments: use of whole sediment toxicity tests, Microtox, Mutatox and semipermeable membrane devices (SPMDs). *Mar.Pollut.Bull.* 34 (3), pp. 194 – 202, 1997.
9. **Chiou C.T.:** Partitioning coefficients of organic compounds in lipid-water systems and correlations with fish bioconcentration factors. *Environ.Sci. Technol.*, 19, pp. 57-62, 1985.
10. **Ellis, G.S., Huckins, J.N., Rostad, C.E., Schmitt, C.J., Petty J.D., and MacCarthy, P.:** Evaluation of Lipid-Containing Semipermeable Membrane Devices (SPMDs) for Monitoring Organochlorine Contaminants in the Upper Mississippi River. *Environmental Toxicology and Chemistry* 14, pp. 1875-1884, 1995.

11. **Farrington J.W.:** Biogeochemical Processes Governing Exposure and Uptake of Organic Pollutant Compounds in Aquatic Organisms. *Environmental Health Perspectives*, 90, pp. 75-84, 1991.
12. **Herve, S., Prest, H.F., Heinonen, P., Hyötyläinen, T., Koistinen, J., and Paasivirta, J.:** Lipid-filled Semipermeable Membrane Devices and Mussels as Samplers of Organochlorine Compounds in Lake Water. *Environmental Science & Pollution Research* 2, 24-30, 1995.
13. **Hofelt, C.S. and Shea, D.:** Accumulation of Organochlorine Pesticides and PCBs by Semipermeable Membrane Devices and *Mytilus edulis* in New Bedford Harbor. *Environmental Science & Technology* 31, pp. 154-159, 1997.
14. **Huckins, J.N., Tubergen, M.W., and Manuweera, G.K.:** Semipermeable Membrane Devices Containing Model Lipid: A New Approach to Monitoring the Availability of Lipophilic Contaminants and Estimating their Bioconcentration Potential. *Chemosphere* 20, pp. 533-552, 1990.
15. **Huckins, J.N., Manuweera, G.K., Petty, J.D., Mackay, D., and Lebo, J.A.:** Lipid-Containing Semipermeable Membrane Devices for Monitoring Organic Contaminants in Water. *Environmental Science & Technology* 27, pp. 2489-2496, 1993.
16. **Huckins, J.N., Petty, J.D., Orazio, C.E., Lebo, J.A., Clark, R.C., Gibson, V.L., Gala, W.R., and Echols, K.R.:** Determination of Uptake Kinetics (Sampling Rates) by Lipid-Containing Semipermeable Membrane Devices (SPMDs) for Polycyclic Aromatic Hydrocarbons (PAHs) in Water. *Environmental Science & Technology* 33, pp. 3918-3923, 1999.
17. **Lebo, J.A., Gale, R.W., Petty, J.D., Tillitt, D.E., Huckins, J.N., Meadows, J.C., Orazio, C.E., Echols, K.R., Schroeder, D.J., and Inmon, L.E.:** Use of the Semipermeable Membrane Device (SPMD) as an In Situ Sampler of Waterborne Bioavailable PCDD and PCDF Residues at Sub-Part-Per-Quadrillion Concentrations. *Environmental Science & Technology* 29, pp. 2886-2892, 1995.
18. **MacRae, J.D. and Hall, K.J.:** Comparison of Methods Used to Determine the Availability of Polycyclic Aromatic Hydrocarbons on Marine Sediment. *Environmental Science & Technology* 32, pp. 3809-3815, 1998.
19. **Martin M, Richardson B.J.:** Long-term contaminant biomonitoring: views from Southern and Northern hemisphere perspectives. *Mar.Poll.Bull.*22, 533-537. 1991.
20. **Meadows, J.C., Echols, K.R., Huckins, J.N., Borsuk, F.A., Carline, R.F., and Tillitt, D.E.:** Estimation of Uptake Rate Constants for PCB Congeners Accumulated by Semipermeable Membrane Devices and Brown Trout (*Salmo trutta*). *Environmental Science & Technology* 32, pp. 1847-1852, 1998.
21. **Oeckenden W.A., Steinnes E., Parker C., Jones K.:** Observations on Persistent Organic Pollutants in Plants: implications for their use as passive air samplers and for POP cycling. *Environ. Sci.Technol.* , 32, pp. 2721-2726, 1998.
22. **Oppenhuizen A., Velde E., Gobas F., Liem D., Steen J.:** Relationship between bioconcentration in fish and steric factors of hydrophobic chemicals. *Chemosphere* 14, pp. 1871-1896, 1985.

23. **Pazdro K., Tronczyński J.:** Developpement de capteurs pour le suivi de la contamination chimique et de la biodisponibilite des contaminants organiques en milieu marin cotier. Report IFREMER No 03/2001, pp 32, 2001.
24. **Pazdro K., Moisan K., Tronczyński J.:** Assessment of Bioavailable Polycycling Aromatic Hydrocarbons in French Coastal Waters: Mussels and Semipermeable Membrane Devices Approach, Chemosphere, in press, 2002.
25. **Petty, J.D., Huckins, J.N., Martin, D.B., and Adornato, T.G.:** Use of Semipermeable Membrane Devices (SPMDs) to Determine Bioavailable Organochlorine Pesticide Residues in Streams Receiving Irrigation Drainwater. Chemosphere, 30, pp. 1891-1903, 1995.
26. **Petty, J.D., Poulton, B.C., Charbonneau, C.S., Huckins, J.N., Jones, S.B., Cameron, J.T., and Prest, H.F.:** Determination of Bioavailable Contaminants in the Lower Missouri River following the Flood of 1993. Environmental Science & Technology 32, pp. 837-842, 1998.
27. **Peven, C.S., Uhler, A.D., and Querzoli, F.J.:** Caged Mussels and Semipermeable Membrane Devices as Indicators of Organic Contaminant Uptake in Dorchester and Duxbury Bays, Massachusetts. Environmental Toxicology and Chemistry 15, 144-149. 1996.
28. **Piccardo M.T., Coragdeghini R., Valerio F.:** Polycyclic aromatic hydrocarbon pollution in native and caged mussels. 2001.
29. **Prest, H.F., Huckins, J.N., Petty, J.D., Herve, S., Paasivirta, J., and Heinonen, P.A.:** Survey of Recent Results in Passive Sampling of Water and Air by Semipermeable Membrane Devices. Marine Pollution Bulletin 31, pp. 306- 312., 1995.
30. **Pruell R.J., J.Lake, W.Davis, J.Quinn:** Uptake and depuration of organic contaminants by blue mussels (*Mytilus edulis*) exposed to environmentally contaminated sediment. Mar.Biology, 91, 497-507, 1986.
31. **Sabaliunas, D. and Sodergren, A.:** Use of Semipermeable Membrane Devices to Monitor Pollutants in Water and Assess Their Effects: A Laboratory Test and Field Verification. Environmental Pollution 2, pp. 195-205, 1997.
32. **Strandberg, B., Wagman, N., Bergqvist, P.-A., Haglund, P., and Rappe, C.:** Semipermeable Membrane Devices as Passive Samplers to Determine Organochlorine Pollutants in Compost. Environmental Science & Technology 31, pp. 2960-2965, 1997.
33. **Serrano R., F.Hernandez, F.Lopez, J.Pena:** Bioconcentration and Depuration of Chlorpyrifos in the marine Mollusc *Mytilus edulis*. Arch.Environ.contam.Toxicol., 33, pp. 47-52. 1997.
34. **Sharpe S., McKay D.:** A framework for Evaluating Bioaccumulation in Food Webs. Environ.Sci.Technol., 34,12, pp. 2373-2379, 2000.
35. **Utvik T.I.R., G.Durell, S.Johnsen.:** Determining produced water originating polycyclic aromatic hydrocarbons in North Sea waters: comparison of sampling techniques. Mar.Poll.Bull. 38, 11, pp. 977 – 989, 1999.
36. <http://www.waux.cerc.usgs.gov/spmd>

Próba wyznaczenia stężeń organicznych, bio-przyswajalnych zanieczyszczeń w wodzie przy zastosowaniu syntetycznych błon półprzepuszczalnych (SPMD)

Streszczenie

Jednym z głównych problemów dotyczących losu organicznych zanieczyszczeń wprowadzanych do środowiska przez człowieka, jest określenie ich potencjalnej przyswajalności przez organizmy żywe. Rzetelne oszacowanie poziomów stężeń w otaczającym środowisku jak również ich specjacji jest konieczne do wyjaśnienia mechanizmów wpływu zanieczyszczeń organicznych na funkcjonowanie ekosystemu jak również do określenia zależności pomiędzy zanieczyszczeniami rozpuszczonymi w kolumnie wody a realną ekspozycją organizmów. W ostatnich latach obserwuje się znaczny wzrost zainteresowania zastosowaniem pasywnych technik pomiarów „in situ”. Jedną z najbardziej obiecujących technik w przypadku zanieczyszczeń organicznych jest zastosowanie SPMD - syntetycznych błon półprzepuszczalnych wypełnionych neutralnym lipidem, opracowanych przez Huckinsa i wsp. W ramach publikacji opisano teoretyczne założenia działania SPMD i oraz zagadnienia dotyczące kinetyki pobierania zanieczyszczeń przez SPMD. Eksperyment przeprowadzony w morskich wodach przybrzeżnych ilustruje praktyczne zastosowanie syntetycznych błon półprzepuszczalnych w badaniach środowiskowych. SPMDs oraz małże z gatunku *Mytilus galloprovincialis* zostały umieszczone równolegle w toni wodnej w celu określenia bioprzyswajalnej frakcji wielopierścieniowych węglowodorów aromatycznych (WWA) rozpuszczonych w wodzie. Jednocześnie pobrano duże objętości wody w celu zmierzenia stężeń WWA w wodzie. Wyniki przeprowadzonego eksperymentu wykazały że zarówno SPMDs jak i małże efektywnie zateęzały związki z grupy WWA o szerokim zakresie polarności i mas cząsteczkowych. Całkowite stężenie WWA w małżach i w SPMD kształtowało się na podobnym poziomie. Pomimo różnic w przypadku pojedynczych związków wykazano, że stężenie WWA w małżach można określić na podstawie stężenia w SPMD stosując równania regresji liniowej. Na bazie stężeń WWA w SPMD oszacowano stężenia w otaczającej wodzie i porównano ze stężeniami zmierzonymi. Szacowanie na podstawie stężeń w SPMD pozwoliło na określenie stężeń WWA, niewykrywalnych klasyczną metodą ekstrakcji na żywicy typu XAD.

Przeprowadzony eksperyment potwierdził możliwość stosowania syntetycznych błon półprzepuszczalnych jako wiarygodnego narzędzia monitorowania poziomów zanieczyszczeń organicznych oraz badania ich bioprzyswajalności w środowisku morskim.