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**MONITORING PRIORITY POLLUTANTS IN THE YANGHE RIVER BY
DICHLOROMETHANE EXTRACTION AND SEMIPERMEABLE
MEMBRANE DEVICE (SPMD)**

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Abstract

Traditional dichloromethane extraction and semipermeable membrane devices containing triolein (triolein-SPMD) were used to monitor the presence and concentrations of priority organic pollutants in the Yanghe River. Qualitatively, both approaches give similar information on the types of priority pollutants in this river. After concentrated by SPMD for 28 days, analysis of priority pollutants is more feasible, time-integrative, and the data reflect the bioavailability. Assuming their concentrations in water were relatively stable during sampling period, it is possible to estimate concentrations for most of chemicals with $\log K_{ow}$ larger than 3 by the measured concentrations in triolein. But it is difficult to estimate concentrations for chemicals with $\log K_{ow}$ less than 3. Also, we reported for the first time the field mean R_s s and their variances for individual PCB congener and the concentration distribution of priority pollutants in the river. ©1999 Elsevier Science Ltd. All rights reserved

Keywords: SPMDs, priority pollutants, PCB congeners, The Yanghe River

Introduction

Semipermeable membrane devices (SPMDs), consist of a thin film of a neutral lipid, such as triolein, enclosed in thin-walled layflat tubing made of low density polyethylene (LDPE) or other nonporous polymers [1]. They were proved to be effective in their capacity to accumulate lipophilic substances. Indeed, some chemicals can be concentrated in SPMDs to levels comparable to, or even higher, than the values of their octanol/water partition coefficients (K_{ow}) or bioconcentration factors (BCF) in aquatic organism [1]. The characteristic free volume of polymeric films allows dissolution of organic molecules having cross-sectional diameters less than 1 nm into the membrane and diffusion jump transport through the nonporous polymer [2]. This process mimics the transfer of organic contaminants through respiratory lamellae of fish, which may have similar limitations on the diameters of diffusing molecule [3]. As one of the applications, SPMD provides mean of chemically and time-integrative monitoring priority organic pollutants in aquatic environment, especially for those mostly lipophilic substances.

Since the beginning of 1990s, SPMDs have been applied in the monitoring of hydrophobic pollutants in water [4-6] and air [7,8], especially for trace organic contaminants such as PCBs, PAHs, organochlorines, etc. Water concentrations of priority organic pollutants could be estimated from their concentrations in the SPMD lipid by the developed model [1]. The research work shows also that temperature, water/lipid partition coefficients, device parameters and biofouling affect the sampling rates and therefore cause uncertainties in estimation of water concentrations through lipid concentrations [6,7]. Besides, sampling rates for quite number of priority pollutants were not available even for standard SPMD configuration. More fieldwork is needed to elucidate the uncertainties of sampling by SPMDs in the field studies and under different circumstances.

In this work, triolein-SPMD was deployed for assessing the contamination of priority organic pollution in The Yanghe River, upstream of the Guanting Reservoir in Beijing, China.

Experimental Section

Sampling sites

The Yanghe River flows through a valley and truncates in the Guanting Reservoir that used to be an important water source for Beijing city. Severe pollution incidents have been reported in this area in the past years (unpublished report, 1996). Recently, high concentrations of herbicides, mainly atrazine and acetochlor, were found in the sewage used for irrigation and caused serious damages of agricultural crops (unpublished report, 1996). The presence and concentrations of priority organic contaminants in this river basin attracts special attention of local governments.

In the study seven sampling sites along the river were selected, as shown in Figure 1. In brief, site 1 (upstream Piandi) receives the sewage from Zhangjiakou city (population: 500,000), site 2 receives the industrial sewage and site 3 receives city sewage from the Xuanhua administrative district (population: 100,000), respectively. Site 4 locates at The Yanghe Reservoir designed mostly for storage of water for agricultural irrigation. Downstream from site 5 to 7, the river receives mainly surface run-off from agricultural lands. Because the sampling was carried out in dry season, the flow rate was below 0.2 m/s and relatively constant among sampling sites. Water temperatures ranged from 8.5 to 10.5°C.

The sampling distance is approximately 100 kilometers and the time for water flowing through was estimated to be 5-6 days. It could be inferred that SPMDs in all sites could record most of discharging events during the 28-days exposure.

Assembly of SPMDs

The layflat LDPE (pure PE without slip additives, Beijing Plastics Co.) was 2.5 cm in wide and 55 μm in thickness. It was cut into piece of 21 cm in length, soaked in cyclohexane for 24 h to remove trace contaminants, and dried with ultra-pure nitrogen. The ratio of mass of tubing versus volume of solvent was 0.01 g/ml and the total mass of the SPMD was 1.05g. Then, 40 μL (36.4 mg) of triolein (99% pure from Sigma Chemical Co.) was coated onto the inner part of the tubing before the ends were sealed

Figure 1. Sampling sites along the Yanghe River, China.

with a commercial plastic sealer. It is fixed in solvent-cleaned PVC plastic meshed cage (5×3×25 cm).

SPMD Deployment

After preparation, SPMDs were placed into a low gas permeable and portable cooler, which was solvent-cleaned and cooled with dry ice. Four SPMDs were deployed at each site in fall of 1997, at which it was suspended 1 m below the water surface. After a 28-days exposure, the SPMDs were retrieved, placed in portable cooler on dry ice, and immediately transported to the laboratory for sample processing and residue enrichment. Three controls of SPMDs were used during deployment, retrieve and transportation.

At the end of the exposure, 2.5 L of river water was collected at each site.

Sample Processing and Residue Enrichment

After sampling, each SPMD was rinsed with tap water, distilled water and 1N HCl solution for 30 s. Then it was rinsed with distilled water, dried with clean paper, and transferred into a beaker containing 100 ml cyclohexane. It was dialyzed at 13°C for 48 h in the darkness. The solvent was reduced in volume to about 1 ml using a gentle stream of high purity nitrogen, cleaned up with anhydrous sodium sulfate (filled in a column of 4 cm long) and silica gel (60-80 mesh, deactivated, 4 cm long), then treated with copper wool to remove sulfur, filtered through glass-fiber filters, reduced in volume (to about 0.5 ml) again, and diluted to 1 ml using cyclohexane.

The sampled water was filtered through 0.45 µm microporous membrane (Beijing Reagent Co.) to remove undissolved matters. Each 500 ml of water was extracted with 40 ml solvent in three steps and each of 20, 10, 10 ml, respectively. A total of 2 liters of the filtered water was extracted with a total of 160 ml dichloromethane. The extract was cleaned up in the same manner as the clean-up of SPMDs described earlier. The volume was reduced high purity nitrogen and diluted to 1 ml with dichloromethane before analysis.

Chemical analysis

Sample analysis was performed on a gas chromatography - mass spectrometry (Hewlett Packard 5890II/5971A, HP-5 columns , 30 m $\times$ 0.25 mm i.d. $\times$ 0.25 μ m, connected with another HP-5 column, 25 m $\times$ 0.25 mm i.d. $\times$ 0.33 μ m, carrier gas: He). To avoid interference of polyethylene waxes and lipids, selected ion mode (SIM) was used [9]. In this mode, detection limit for PCBs was 0.1 pg. PCBs were characterized according to the references [10,11]. The equipment was set at an initial temperature of 50°C for 1 min. Then the temperature was increased to 250°C with increment of 6°C/min and holding for 30 min.

Quality Control

Three controls of SPMD were processed in accompany with other SPMDs during their deployment, retrieve and transportation. They followed the same clean-up and analytical procedures as samples. Among contaminants measured, PCBs and PAHs were undetectable, while two peaks corresponding to toluene and nitrobenzene were measurable in SPMD controls, but their concentrations were much lower than those in the samples. An SPMD blank (a freshly prepared SPMD) and a reagent blank (100 ml of cyclohexane) were also taken through the entire clean-up and enrichment procedure. No chemicals of concern was found in both blanks. By standard addition, the recoveries of the PCBs and other pollutants both in waters and in SPMDs were found greater than 60% and the relative standard deviation of triplicates was less than 20%.

Results and Discussion

Presence and concentrations of priority pollutants along The Yanghe River

The presence and concentrations of priority pollutants sampled by water were shown in Table 1. The concentrations of these pollutants in water varied from 0.1 μ g/L to 40 μ g/L. Accordingly, it could be noticed from the table that the concentrations of priority pollutants increased when the river received the city and industrial sewage. Higher concentrations observed in The Yanghe Reservoir were attributed, at least partially, to the release of pollutants previously stored in the sediment. Concentrations

Table 1 Concentrations of priority pollutants in waters along The Yanghe River (μ

Contaminants	g/L)						
	S1	S2	S3	S4	S5	S6	S7
Toluene	0.1	4.6	4.6	113.7	0.1	4.6	4.6
ethylbenzene	nd	nd	nd	nd	nd	nd	nd
p-xylene	2.4	0.1	0.1	7.6	0.1	0.8	1.6
o-xylene	2.6	0.8	0.1	2	0.8	1.4	0.8
phenol	0.1	0.1	1.2	0.1	0.1	0.1	0.1
aniline	0.7	0.1	0.1	0.7	0.7	0.7	0.7
2-chlorophenol	0.1	0.5	nd	nd	nd	0.1	0.1
2,4-dichlorophenol	nd	nd	nd	nd	nd	nd	nd
2,3-dichlorophenol	nd	nd	nd	nd	nd	nd	nd
2,4,6-trichlorophenol	nd	nd	nd	nd	nd	nd	nd
nitrobenzene	0.1	0.7	nd	nd	nd	0.1	0.1
2,4-dinitrotoluene	3.5	0.1	nd	1.2	0.3	0.5	nd
2,6-dinitrotoluene	0.6	26.9	39.9	nd	nd	3.9	1.1
hexachlorobenzene	nd	nd	nd	nd	nd	nd	nd
4-nitrophenol	0.3	1.6	0.1	0.3	0.3	nd	5.2
naphthalene	0.4	0.5	0.4	1.1	0.1	nd	0.2
phenanthrene	0.1	0.2	0.2	0.2	0.1	0.1	0.1
anthracene	0.2	0.5	0.6	0.4	0.1	0.2	0.2
acetochlor	nd	0.1	nd	0.1	0.1	nd	0.1
atrazine	nd	nd	nd	0.2	0.1	0.1	nd
allethrin	nd	nd	nd	nd	nd	nd	nd
chlordane	nd	nd	nd	nd	nd	nd	nd
transchlordane	nd	nd	nd	nd	nd	nd	nd

* Concentrations of priority pollutants in waters were estimated from concentrations in dichloromethane.

of most pollutants in river waters decreased very quickly at S5 (2 kilometers from S4), indicating the deposition of pollutants in the reservoir.

The major priority pollutants in the river are toluene, xylene and dinitrotoluene. Polycyclic aromatic hydrocarbons such as naphthalene, anthracene and phenanthrene could be detected. Though high concentrations of herbicides, mainly atrazine and acetochlor, were reported in previous surveys (unpublished document), their concentrations in waters were quite low in this study. Atrazine and acetochlor have been produced in a factory nearby S2 and mainly in the spring. The data in table 1 either indicates a reduced discharge during the sampling period or reflects the successful control of discharge through the efforts of local authority.

More detailed patterns of pollution could be obtained through sampling by SPMD (Table 2), excepting the unexpected lost of SPMDs at site 1 and site 7. Qualitatively, the information on the presence of priority pollutants sampled by SPMD was more complete than that sampled by dichloromethane extraction of waters. The concentrations of these pollutants in SPMD lipid range from 1 to 300 $\mu\text{g/ml}$. Obviously, preconcentrating by SPMD facilitates the chemical analysis when monitoring priority pollutants in waters. In SIM mode of GC/MS, quantitation of target organic pollutants in the lipid becomes much more easier because the majority of polar compounds had not been concentrated and interferes the GC spectra.

The partitioning coefficients of the priority pollutants between water and triolein (K_{tw}) can be obtained from published literature [15], or estimated according to their octanol/water coefficients (K_{ow}) using following equation [15]:

$$\log K_{\text{tw}} = \log K_{\text{ow}} + 0.105 \quad (1)$$

Most of the $\log K_{\text{tw}}$ s for chemicals in Table 1 and 2 are less than 4 (in solid circle) or even lower than 3. According to previous works, the equilibrium between water and triolein should be reached in a shorter sampling period. For examples, our previous research found that the steady states in SPMD lipid for hydrophobic chlorophenols are reached within 3 days [13] and those for nitroaromatics are reached within 6 days [14]. As shown in Figure 2, $\log K_{\text{tw}}$ s for PAHs, toluene, p-xylene, and o-

Table 2 Concentrations of priority pollutants in SPMD lipid along the River ($\mu\text{g/ml}$)

Contaminants	S2	S3	S4	S5	S6
toluene ¹	12	150	62.5	1.7	1.2
ethylbenzene	nd	nd	nd	nd	nd
p-xylene	3	15	22.5	1.7	1.2
o-xylene	3	20	30	1.7	1.2
phenol	0.7	23.3	13.3	1.1	0.8
aniline	5.7	14.3	7.1	4.8	1.8
2-chlorophenol	2	nd	nd	nd	1.2
2,4-dichlorophenol	nd	nd	nd	nd	nd
2,3-dichlorophenol	nd	nd	nd	nd	nd
2,4,6-trichlorophenol	nd	nd	nd	nd	nd
nitrobenzene ¹	2	nd	nd	nd	1.2
2,4-dinitrotoluene	112	180	10	10	5
2,6-dinitrotoluene	44	nd	550	6.7	5
hexachlorobenzene	nd	nd	nd	nd	nd
4-nitrophenol	183.5	307.5	133.8	2.5	0.6
naphthalene	42.2	101.5	88.1	0.9	nd
phenanthrene	106.4	224	40	2.7	2
anthracene	239.2	64	86	1.3	0.8
acetochlor	2	nd	5	3.3	1
atrazine	0.6	nd	1.4	1	0.3
allethrin	nd	nd	nd	nd	nd
chlordane	nd	nd	nd	nd	nd
transchlordan	nd	nd	nd	nd	nd

¹ these two compounds were detectable in controls and their concentrations in the table were subtracted from those in controls.

Figure 2. Comparison of $\log K_{ow}$ values with the upper and low limit of $\log C_t/C_w$ for 15 priority pollutants

(C_t and C_w is concentration of pollutant in triolein and in water, respectively.

The upper and low limits were selected from 5 sampling sites)

xylene are within their upper and low limits of logarithm ratios of concentration in triolein to that in water ($\log C_l/C_w$) among 6 sites. But $\log K_{tw}$ s for more hydrophilic pollutants, such as phenol and aniline, are much lower than their upper and low limits of logarithm ratios. Therefore estimation of water concentrations of lipophilic chemical with $\log K_{tw}$ between 3 and 5 can be made through their K_{tw} s or even K_{ow} s according to equation 1. Fluctuation of the logarithm ratios could be due either to the real-time variation of concentrations of pollutants in river waters during 28 days, or to the uncertainties of sampling by SPMD. To verify the causes of errors in estimation of water concentrations through lipid concentrations, continual sampling of water parallel to SPMD sampling is necessary in future work.

Unlike in laboratory simulation where a steady state of concentration in triolein can be observed [13,14], in the field chemicals with lower K_{tw} s are concentrated in triolein-SPMD to much higher levels than their correspondent K_{tw} s (Fig. 2). Obviously, estimation of water concentrations of these chemicals through their lipid concentrations is difficult before the mechanism is elucidated.

Presence and concentrations of PCB congeners along The Yanghe River

There are 57 PCB congeners can be quantitatively measured by valid GC/MS method in the laboratory. Among them, 41 congeners of PCBs could be found both in SPMD lipid and in dichloromethane. 16 other congeners were not detectable in river water. The concentrations of PCBs detected in dichloromethane and in SPMD at the different sites are shown in table 3 and 4, respectively. Qualitatively, both sampling approaches show the consistency for the presence of PCBs at sampling sites, therefore the efficacy of SPMD in monitoring the presence of PCB congeners in water. The presence and concentration distribution of PCB congeners in this river indicate the contamination by industrial sources, mostly the metallurgical industries when comparing with the results reported by other researchers [4,5].

Quantitatively, the PCB concentrations in the dichloromethane range from 0.5 to 100 pg/L (Table 3) while in SPMD lipid they range from 1 to 2000 pg/ml triolein

Table 3 Concentrations of PCB congeners in waters along the Yanghe River (pg/L)*

Congeners	S1	S2	S3	S4	S5	S6	S7
83	0.2	0.2	0.45	0.2	0.2	0.2	0.2
84	0.3	0.6	0.6	0.3	0.3	0.3	0.3
87	0.2	0.2	0.2	0.2	0.2	0.2	0.2
95	2.3	1.6	2.2	0.1	1.1	1.7	1.05
101	0.2	0.2	0.2	0.2	0.3	0.2	0.5
118	6.7	3.2	17.6	5.1	10	11.4	11.1
128	0.5	0.5	0.5	0.5	0.5	0.5	0.5
129(126)	0.5	0.5	0.5	0.5	0.5	0.5	0.5
135(144,123)	2.4	1.2	6.4	1.9	3.6	4.1	4
151	6.9	3.2	3.2	6.6	12.0	12.1	9.4
153	2.6	9.3	8.7	3.4	7.0	9.2	2.5
176	0.6	0.3	0.3	0.3	0.6	0.3	0.3
170	17.9	17.9	17.9	17.9	nd	17.9	17.9
180	10.8	20.3	10.8	10.2	10.15	10.2	26.3

* Concentrations in waters were estimated from concentrations in dichloromethane.

Table 4 Concentrations of PCB congeners in SPMD lipid along the River (pg/ml)

Congeners	S2	S3	S4	S5	S6
83	2.3	10.0	5.1	3.3	5.7
84	3.2	15.0	7.6	5.1	3.8
87	2.3	10.0	5.1	6.8	2.6
95	8.0	110.3	26.3	27.5	10.0
101	6.5	15.0	16.3	5.1	1.9
118	241.2	522.5	356.3	171.7	40.0
128	5.0	25.0	12.5	8.3	12.5
129(126)	5.0	25.0	12.5	8.3	6.4
135(144,123)	87.1	187.6	128.9	61.7	14.4
151	93.5	160.1	111.4	199.2	57.6
153	51.4	255.5	112.5	75.1	62.5
176	2.5	12.5	6.4	4.2	3.2
170	178.5	1785.0	nd	297.6	223.1
180	209.5	1072.5	775.1	169.2	193.9

(Table 4). It could be inferred that SPMD technology made the monitoring of PCB congeners in ultra-trace levels much more easier and accurate.

In Figure 3, it shows the upper and low limits of logarithm ratios of concentration in triolein to that in water for different PCB congener, and the corresponding $\log K_{tw}$. These $\log K_{tw}$ s are estimated from their $\log K_{ow}$ s [16] following equation 1 [15]. Obviously and unlike other priority pollutants measured, concentrations of PCB congeners could hardly reach equilibrium in triolein in 28 days.

Estimation of aqueous concentrations of priority pollutants and PCB congeners

The dissolved or bioavailable concentration of pollutant is the basis for risk assessment in aquatic ecosystem. SPMD technology complements biota- or sediment-based estimation methods of dichloromethane concentrations. Many studies indicate that the uptake of organic compounds by SPMDs is in accordance with passive-diffusive mass transfer and/or equilibrium partition theory.

The sampling rate (R_s) of a chemical in triolein-SPMD is in fact attributed to the sampling by PE membrane and by triolein. It is generally expected to be proportional to the K_{mw} (partition coefficient between membrane and waters) and K_{tw} of the chemical. Our results (Fig. 2) and the results of other researchers [12,13] show clearly that this principal could be applied to chemicals whose $\log K_{tw}$ s are between 3 and 5. However when molecular size of a chemical approaches or exceeds the size of the averaged available membrane cavities or when $\log K_{tw}$ is more than 5, it will cause a switch from partitioning control to diffusion layer control, resistance to mass transfer should rise and R_s should decline [1,6,7].

Huckins, et al. [6] described the uptake of chemicals by SPMD for which the equilibrium between the SPMD lipid and water is not approached during SPMD exposures (at a constant temperature):

$$C_L = C_w R_s t / V_L \quad (2)$$

where C_L and C_w are the concentration of a chemical in SPMD and in water, respectively. R_s is the effective daily sampling rate of the SPMD for a particular pollutant and expressed in L/d. V_L is the volume of triolein used in the SPMD and t is

Table 5 Estimated SPMD sampling rates for PCBs along the Yanghe River (n=5)

PCB congeners	Field mean Rs (L/d)	SD	Rs Normalized to 1g Triolein Configuration
15, 16, 18, 19, 26	0.065	0.047	1.791
25	0.084	0.055	2.305
31, 28, 21, 45	0.065	0.047	1.791
37	0.065	0.047	1.791
40	0.079	0.059	2.169
41	0.071	0.043	1.949
44	0.046	0.020	1.257
47	0.065	0.047	1.791
49	0.062	0.013	1.709
52	0.087	0.052	2.383
61	0.051	0.021	1.414
83	0.058	0.020	1.598
84	0.048	0.024	1.325
86	0.098	0.058	2.692
87	0.075	0.047	2.059
88	0.065	0.047	1.791
95	0.061	0.060	1.688
99	0.060	0.022	1.650
101	0.042	0.008	1.152
110	0.137	0.061	3.758
118	0.137	0.083	3.772
120	0.055	0.022	1.513
128	0.072	0.043	1.989
129(126)	0.065	0.046	1.795
132	0.049	0.038	1.355
135(144,123)	0.137	0.083	3.770
138	0.066	0.046	1.802
141	0.065	0.046	1.798
151	0.081	0.045	2.215
153	0.049	0.038	1.352
156	0.069	0.043	1.907
158	0.065	0.047	1.791
170	0.037	0.010	1.026
176	0.060	0.050	1.654
179	0.078	0.037	2.153
180	0.087	0.088	2.405

the sampling time. The use of equation 2 to estimate C_w requires the SPMD to be still in the linear sampling phase or the average sampling rate during the interval of exposure to be known. When equilibrium is approached during the exposure, equation 3 can be used to estimate C_w directly from C_L , providing K_{tw} is known:

$$C_L = C_w K_{tw} \quad (3)$$

As shown in Fig. 2, water concentrations of pollutants with log K_{tw} values between 3 and 5 could be estimated from lipid concentrations based on equation 3.

Equilibrium of PCBs should not be approached during the 28-days exposure because of their large log K_{tw} values (i.e., >5), thus it was assumed that uptake remained in the linear sampling phase. We calculated each R_s for all quantified PCB congeners at each site using directly measured C_w values, and then the field mean R_s for each PCB congener was estimated (Table 5). The field mean R_s s are associated with variances generated from the variation among the 5 sampling sites. As shown in Fig. 3, the variations of C_L/C_w s are mostly within one order of magnitude, therefore estimation of the relative constant field mean R_s s should be possible.

For example, the field mean R_s for dichlorinated biphenyl was 0.06 L/d, associated with variance of 33%; for trichlorinated biphenyl, 0.07 L/d with variance of 42%; for tetrachlorinated biphenyl, 0.09 L/d with variance of 45%; for pentachlorinated biphenyl, 0.12 L/d with variance of 55%; for hexachlorinated biphenyl, 0.08 L/d with variance of 21%; for heptachlorinated biphenyl, 0.06 L/d with variance of 37%. These variances reflect the influences of the environmental variables (site to site) and analytical precision. In table 5, these R_s s are normalized to 1g triolein configuration by multiplying a factor of 27.5 regarding to the difference in lipid volume. After normalization, the field observed R_s of SPMDs for PCBs (1 L/d -3 L/d) were higher than those chemicals whose log K_{ow} are less than 5 [5,7,8,12,13]. Since some of the accumulated residues would be in the membrane, an estimated membrane/lipid partition coefficient (K_{ML}) of 0.1 for PCBs was used to derive C_L [9].

The calculated R_s for each PCB congener was used in equation 2 to estimate C_w at each sampling site. For the chemicals with log K_{tw} values less than 5, C_w was directly

Figure 3. Comparison of $\log K_{tw}$ values with the upper and low limit of $\log C_l/C_w$ for PCB congeners

(Legend is the same as that in Fig. 2)

Figure 4. Plot of logarithm concentrations determined by dichloromethane extraction versus those estimated by SPMD sampling mostly for priority pollutants with $\log K_{ow}$ larger than 3. (Concentrations of PCB congeners were estimated by equation 2 and others by equation 3.)

estimated from C_L (derived from K_{ML}) and respective K_{tw} , according to equation 3. In Fig. 4, it gives the estimated concentrations of PCBs and priority pollutants from their concentrations in SPMD lipid.

From Fig. 4, it shows that the estimated concentrations for most of chemicals, such as PCBs, PAHs, toluene, and xylenes, are very close to those measured through dichloromethane extraction for all sampling sites. Concentrations of priority pollutants with their $\log K_{tw}$ between 3 and 5 could be estimated with relative large variations. Concentrations of hydrophilic pollutants, such as 2,6-dinitrotoluene, 2,4-dinitrotoluene, 4-nitrophenol, phenol and aniline could be hardly estimated. It should also be noticed that the estimated concentrations of priority pollutants by SPMD sampling reflect the bioavailable forms while their concentration in the water, as extracted by dichloromethane, reflect both dissolved and organic carbon-associated forms.

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