Monitoring priority pollutants in a sewage treatment process by dichloromethane extraction and triolein-semipermeable membrane device (SPMD)

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Abstract

Semipermeable membrane devices containing a neutral lipid triolein (triolein-SPMD) and conventional dichloromethane extraction were used to monitor the presence and concentrations of priority organic pollutants in a sewage treatment process in Beijing, China. Both samples gave similar information on the presence of target PCB congeners, PAHs, Organochlorine pesticides and substituted benzenes in sewage at all sites. After 20 days' sampling, the concentrations of contaminants in triolein of SPMD were much higher than those in dichloromethane extracts, which resulted in easier analysis, improved the detection limits, and increased the accuracy. Previous field mean sampling rates for SPMD were used to estimate concentrations of PCB congeners in sewage, which compared to their determined concentrations by dichloromethane extraction. The consistency and superiority of SPMD technology were proved for the detection of priority organic contaminants from sewage. Lower removal rates for PCB congeners and PAHs coincided with the persistence of them in environment. More attention should be paid to urban sewage treatment process adopting activated-sludge method, where priority organic pollutants might not be removed, even present higher concentrations after treatment. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Triolein-Semipermeable membrane device (SPMD) consists of a thin film of a neutral lipid triolein, enclosed in thin-walled layflat tubing made of low-density polyethylene or other nonporous polymers. The characteristic free volume of polymeric films allows dissolution of organic molecules having a cross-sectional diameter of less than 1 nm into the membrane and diffusion through

the nonporous membrane (Huckins et al., 1993). SPMDs are passive samplers that provide a means of determining the dissolved portion of lipophilic organic compounds in the aquatic environment. This sampling process is similar to the diffusion of lipophilic organic compounds through biological membranes, such as contaminant transfer through respiratory lamellae of fish (Huckins et al., 1996a).

SPMDs have been used by researchers to monitor trace hydrophobic organic pollutants in many different aquatic environments. Results from these studies demonstrated that SPMDs were effective in concentrated contaminants, such as PCBs, PAHs, etc. (Bennett et al., 1996; Huckins et al., 1996b; Hofelt and Shea, 1997; Huckins et al., 1997; Sabaliunas and Sodergren, 1997;

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In this work, triolein-SPMDs were deployed along a sewage treatment process in Beijing, China, for assessing the contamination of priority organic pollution in sewage, at the same time, for testing SPMD's applicability in sewage. Water samples were also extracted by using conventional dichloromethane for effect comparison.

2.1. Sampling sites

In this study, four sampling sites along the process were selected, as shown in Fig. 1. In brief, site 1 receives the untreated sewage from Beijing city (population: more than 10,000,000), site 2 receives sewage treated by aeration and sedimentation, site 3: sewage after activated-sludge treatment, site 4: treated sewage for discharge after the final sedimentation. There were no major differences in current velocity among the above four sites (below 0.5 m/s) and were relatively constant during the sampling period. Sewage temperature ranged from 12°C to 13.5°C.

2.2. Assembly of SPMDs

2.3. SPMD deployment

After preparation, SPMDs were placed into a low gas permeable and portable cooler, which was solvent-cleaned and cooled with dry ice. During October 1997, Four SPMDs were deployed at each site along the sewage treatment process. SPMDs were suspended 1 m below the surface. After a 20-day exposure, the SPMDs

were retrieved, placed into the portable cooler on dry ice again, and immediately transported to the laboratory for sample processing and residue enrichment. Three controls of SPMDs were used during deployment, retrieve and transportation.

Due to the hardness of water sampling, 2.5 l of sewage samples at each site was collected only once by the end of SPMD exposure, which should have been carried out continuously in order to make a good comparison.

2.4. Sample processing and residue enrichment

Each SPMD was rinsed with tap water, distilled water, 1 N HCl solution for 30 s to remove surface-biofouled residues (Wang et al., 1999). 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. Then it was cleaned up by passing anhydrous sodium sulfate (filled in a column of 4 cm long), silica gel (60–80 mesh, deactivated, 4 cm long) columns. Extra volume of pure cyclohexane was used to elute target compounds remaining on the column. Finally, the extract was treated with copper wool to remove sulfur, filtered through glass filters, reduced in volume (to about 0.5 ml) again, and diluted to 1 ml.

Sewage sample was filtered through 0.45 µm pre-treated microporous membranes (Beijing Reagent) to remove undissolved matters. Each 500 ml of water was extracted with 40 ml of solvent in three steps and each of 20, 10, 10 ml, respectively. A total of 2 l of the filtered sewage was extracted with 160 ml of dichloromethane. It is known that compounds of interest (PCB, PAH) may sorb to filter membranes more or less. Hence before filtration, those membranes were pretreated in DI water and water-bathed (60°C) for 8 h. After filtration, they were collected for each site, rinsed with enough DI water, then Soxhlet extracted by dichloromethane for 12 h to check the degree of absorption. All extract was cleaned up in the same manner as that of SPMD described earlier, and blown down in volume using high-purity nitrogen, then quantitatively diluted to 1 ml.

2.5. Chemical analysis

Target chemicals included 57 PCB congeners (from di-chlorinated biphenyl to hepta-chlorinated biphenyl), three PAHs (naphthalene, phenanthrene and anthracene), four organochlorine pesticides (allethrin, chlordane, trans-chlordane and endosulfan), two herbicides (atrazine and acetochlor), and 15 substituted benzenes (toluene, xylene, nitrobenzene, chlorophenol, etc.).

Sample analysis was performed on a gas chromatography–mass spectrometry (GC–MS, HP 5890 II/5971A, HP-5 column, 30 m×0.25 mm id×0.25 µm, connected with another HP-5 column, 25 m×0.25 mm id×0.33 µm, carrier gas: He). External standards like Clophen A50 were used in quantitative analysis for PCB congeners and other target pollutants. To avoid interference of polyethylene waxes and lipids, selected ion monitoring mode (SIM) was used (Frame, 1997).

2.6. Quality control

Three field controls of SPMDs accompanied the SPMD sampler arrays during their deployment, retrieve and transportation. They were processed and analyzed exactly as the deployed samples. No PCBs and other pollutants were present in SPMD procedural controls. One SPMD blank (a freshly prepared SPMD) and two reagent blanks (100 ml of cyclohexane and 100 ml of dichloromethane, blow down to 1 ml, respectively) were also taken through the entire clean up and enrichment procedure. No chemicals of concern were found in these blanks either. By standard addition, (five blank waters, 2 l each; five blank triolein-SPMDs, same size as field ones) the recoveries of PCB congeners (level: 1 µg/ml) and other pollutants (level: 20 µg/ml) were between 60% and 93%, with the relative standard deviation less than 20%.

3. Results and discussion

3.1. Variation of routine targets along the sewage treatment process

Table 1 gave the results of routine targets along the sewage treatment process determined during the SPMD

Table 1
Variation of routine targets along four sites determined during SPMD exposure

Sites	Colority	SS (mg/l)	pH	NH ₃ -N (mg/l)	COD (mg/l)
1	222	50	6.9	17.6	101.2
2	168	39	6.9	17.9	85.8
3	39	28	6.9	1.4	23.4
4	9	8	6.9	0.1	14.7
Removal rate (%)	95.9	84	–	99.4	85.5

exposure. It is obvious that all targets declined after treatment except pH value. For example, the removal rates of SS and COD were over 84%, for colority and $\text{NH}_3\text{-N}$, higher than 95.9%. These targets meant treated sewage came up to National Standards of Surface Water (GB3838-88, P.R. China).

3.2. Monitoring effect comparison by using dichloromethane extraction and triolein-SPMD

Tables 2 and 3 gave the presence and concentrations of target pollutants in SPMDs and extracts of filtered sewage. In Table 2, three PAHs could be detected in all samples. For PCB congeners, 23 congeners could be

found in SPMD, while in dichloromethane extracts, eight of these 23 congeners were not detected because of their very low concentrations in sewage (PCB 61, 83, 84, 86, 87, 99, 101, 176) and volume limitation of liquid–liquid extraction. Analysis for PCB and PAH in soxhlet extracts of filter membranes showed very low neglectful levels of target compounds on membranes (less than 5%). So no further calculation was taken. In Table 3, eight substituted benzenes including toluene, xylene, 2,4-dinitrotoluene were detected in SPMDs and sewage extracts, while four OCPs and other target contaminants were not found in both samples.

In sewage extracts, the concentrations of PCB congeners were between 0.1 and 32 pg/ml, while after only

Table 2

Monitoring effect comparison for PAHs and PCB congeners in sewage by using dichloromethane extraction and Triolein-SPMD technology

Contaminants	Site 1		Site 2		Site 3		Site 4	
	<i>W</i> ^a	<i>S</i> ^b	<i>W</i>	<i>S</i>	<i>W</i>	<i>S</i>	<i>W</i>	<i>S</i>
<i>PAHs</i>								
Naphthalene	0.2	34	1.4	29	1	44	1	72
Phenanthrene	0.2	10	0.2	26	0.4	7	0.2	12
Anthracene	0.2	20	0.2	7	0.6	11	0.6	16
<i>PCB congeners</i>								
4, 5, 15, 18, 19, 21	– ^c	–	–	–	–	–	–	–
28, 31, 37, 40, 41, 44	–	–	–	–	–	–	–	–
25	–	46	0.1	78	1	193	–	439
46, 47, 49, 70, 82	–	–	–	–	–	–	–	–
45	–	1	–	36	–	13	–	138
52	3.9	–	2.4	54	–	50	2	21
61	–	–	–	4	–	–	–	5
83	–	46	–	3	–	3	–	2
84	–	4	–	4	–	5	–	78
86	–	2	0.4	2	1.2	3	–	2
87	–	2.5	–	8	4.4	3	–	2
95	1	31	–	13	2.3	387	2	35
99	–	0.6	–	1	0.4	1	–	1
101	–	1.9	–	13	2	3	–	3
105, 129, 134, 136	–	–	–	–	–	–	–	–
110	–	0.6	3	4	2	1	9	1
118	6.6	81	6.6	136	18	298	13	111
120	–	0.6	1.7	12	–	2	5	1
128	0.5	6.3	1	12	1	8	1	5
132	14	93	15.2	26	15	248	19	152
135	2.4	29	2.4	49	7	108	5	40
138, 146, 149, 156	–	–	–	–	–	–	–	–
174, 177, 178, 179	–	–	–	–	–	–	–	–
151	12	40	6.8	15	9	155	9	32
153	7	43	7	12	7	116	9	71
170	17	–	17	–	17	298	18	179
176	–	6.9	–	3	–	4	–	3
180	10	26	20	12	10	169	32	102

^a Sewage, extracted with dichloromethane, 2 l, unit: pg/ml (PAHs), pg/ml (PCB congeners), expressed as concentration in dichloromethane extract.

^b SPMD, 20-day exposure, unit: pg/ml (PAHs), pg/ml (PCB congeners), expressed as concentration in triolein of SPMD.

^c Undetectable.

Table 3

Monitoring effect comparison for substituted benzenes and other target contaminants in sewage by using dichloromethane extraction and Triolein-SPMD technology

Contaminants	Site 1		Site 2		Site 3		Site 4	
	<i>W</i> ^a	<i>S</i> ^b	<i>W</i>	<i>S</i>	<i>W</i>	<i>S</i>	<i>W</i>	<i>S</i>
Toluene	0.2	36.3	136	25	100	73.8	9.2	119
Ethylbenzene	— ^c	—	—	—	—	—	—	—
<i>p</i> -Xylene	0.2	2.5	7.7	1.3	14	1.7	0.2	25
<i>o</i> -Xylene	0.2	3.8	19	2.5	22	3.3	1.6	31
Phenol	—	0.8	44	3.3	2.4	1.1	2.4	8.7
Aniline	1.4	—	4.6	—	0.2	4.8	1.4	2.9
2-Chlorophenol	0.2	—	—	—	—	—	—	—
Nitrobenzene	0.2	—	—	—	—	—	—	—
2,4-Dichlorophenol	—	—	—	—	—	—	—	—
2,3-Dichlorophenol	—	—	—	—	—	—	—	—
2,4,6-Trichlorophenol	—	—	—	—	0.2	—	—	—
2,6-Dinitrotoluene	0.2	—	0.2	340	3.2	6.7	—	1.6
4-Nitrophenol	0.4	1.9	0.6	15.6	1.8	3.3	1.8	2.5
2,4-Dinitrotoluene	0.4	105	1	297.5	0.4	30	0.6	54
Hexachlorobenzene	0.8	—	—	—	—	—	—	—
Atrazine	—	—	—	—	—	—	—	—
Acetochlor	—	—	—	—	—	—	—	—
Decosane	—	—	—	—	—	—	—	—
Allethrin	—	—	—	—	—	—	—	—
Chlordane	—	—	—	—	—	—	—	—
Trans-chlordane	—	—	—	—	—	—	—	—
Endosulfan	—	—	—	—	—	—	—	—

^a Sewage, extracted with dichloromethane, volume: 2 l, unit: µg/ml, expressed as concentration in dichloromethane extract.

^b SPMD, 20-day exposure, unit: µg/ml, expressed as concentration in triolein of SPMD.

^c Undetectable.

20 days' sampling, their concentrations in triolein of SPMDs came up to as high as 439 pg/ml. For PAHs and other detected substituted benzenes, their concentrations in SPMD were 10–100 times higher than that in dichloromethane extracts. Much higher concentrations of target chemicals in SPMD resulted in easier analysis, improved the detection limits, and increased the accuracy.

Above results inferred the consistency and superiority of SPMD technology compared to conventional dichloromethane extraction technology for the detection of priority organic contaminants from sewage.

3.3. Variation of target priority organic pollutants along the sewage treatment process

Fig. 2 showed that removal rates for PCB congeners and PAHs are less than 10%, while for most substituted benzenes, they are less than 20%, some even presented higher concentrations after treatment (shown in Fig. 3). On the one hand, above results coincided with the persistence of PCBs and PAHs in environment. On the other hand, more attention should be paid to urban sewage treatment process adopting activated-sludge method, where priority organic pollutants might not be

removed entirely, even had higher concentrations after treatment. The use of treated sewage should also be controlled carefully.

3.4. Estimation of aqueous concentrations of target PCB congeners

Dissolved or biologically available concentration of contaminants is the basis for risk assessment in aquatic ecosystem (Chiou, 1985). Many studies indicate that the uptake of organic compounds by SPMDs is in accordance with polymer permeability and equilibrium partition theory. As chemical partitioning coefficient between membrane and water (K_{MW}) and partitioning coefficient between lipid and water (K_{LW}) increase with the lipophilic indicator (K_{OW}), the SPMD sampling rate for this analytes is expected to rise proportionally. For chemicals having K_{OW} higher than 10^3 and lower than 10^5 , it is observed (Sabaliunas and Sodergren, 1997; Wang et al., 1999). However, when K_{OW} increases to above 10^5 , or molecular size of chemicals approaches and exceeds the size of the average available membrane cavities, a switch to diffusion layer control happens, resistance to mass transfer rises, and R_s declines (Huckins et al., 1997).

Fig. 2. Variation in concentrations of PAHs and PCB congeners determined in triolein of SPMD along four sampling sites.

Fig. 3. Variation in concentrations of substituted benzenes determined in triolein of SPMD along four sampling sites.

Huckins et al. (1996b) 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) in Eq. (1)

$$C_L = C_W R_{st} / V_L, \quad (1)$$

where C_L and C_W are the concentrations of a chemical in triolein of SPMDs and water, respectively, R_s the effective daily sampling rate of the SPMD for a particular analyte, in L/d, t the sampling time (d), and V_L is the volume of triolein used in the SPMD. The use of Eq. (1) to estimate chemical C_W requires the SPMD to be still in the linear sampling phase or data on the average R_s during the interval of exposure.

In this study, the uptake of PCBs should not approach equilibrium during the 20 day-exposure because of their large K_{OW} values ($>10^5$), which was shown in Fig. 4. The uptake of PCB congeners remained in the linear sampling phase. Field mean R_s data of same SPMD configuration determined in our previous work of Yanghe river (Wang et al., 1999) for PCB congeners were used in Eq. (1) together with C_L data to give estimated C_W at each site of sewage treatment process. More field mean R_s data for other target compounds are being determined in our future work in order to test estimation effects further.

Estimated concentrations of PCB congeners from SPMD data were much closed to those determined by dichloromethane extraction for all sampling sites

Fig. 4. Comparison of $\log K_{ow}$ values with the upper and lower limit of $\log C_t/C_w$ for PCB congeners (C_t and C_w are concentrations of pollutants in triolein and in sewage, respectively). The upper and lower limits were selected from four sampling sites.

Fig. 5. Plot of logarithm concentrations determined by liquid-liquid extraction versus those estimated by SPMD sampling for PCB congeners.

($R^2 = 0.9559$), as shown in Fig. 5. It should also be noticed that the estimated concentrations of priority pollutants by SPMD sampling reflected biological available forms, while their concentrations in filtered sewage, as extracted by dichloromethane, reflected both dissolved and organic-associated forms. Further attempts are required to optimize this promising methodology, and to increase the accuracy of water concentration estimates for more target contaminants.

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