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Identification of Polychlorinated Biphenyls in Shkodra Lake Water using Bottle Sampling and Passive Sampling Technology

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Application of the comparative methods for monitoring of organic pollutants in the aquatic environment is of increasing interest. The deployment of semi-permeable membrane devices passive samplers was undertaken in Shkodra/Skadar Lake, which is the largest lake in the Balkans region. Its surface is 368 km^2, from which 149 km^2 are included in Albanian territory and the other part belongs to Montenegro. The aim of present study is a preliminary assessment of readily bio-available hydrophobic organic pollutants (HOP) as polychlorinated biphenyl in the lake, using semi-permeable membrane devices (SPMDs) and bottle sampling. The analytical results showed the presence of polychlorinated biphenyl in semi-permeable membrane device sampler. In the bottle samples the most of measurements were below the detection limit (LODs). The identification and monitoring of hydrophobic organic pollutants in Shkodra/Skadar Lake remains an important issue for the future environmental investigations, which are necessary for this important economic and touristic area.

Key Words: Polychlorinated biphenyl, Semi-permeable membrane devices, Bottle samples.

INTRODUCTION

Many non-polar organic substances such as polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyl (PCBs) may cause effects in aquatic environments[1]. The concentrations of hydrophobic contaminants in surface waters fall generally in ng L^{-1}-pg L^{-1} range. The regulatory monitoring and risk assessment of hydrophobic contaminants in surface waters is generally hampered by the inability to measure reliably these low (and sometimes fluctuating) concentrations[2].

The reporting bottle sampling values below limit of detection (LOD) is unlikely to support current water legislation. Solutions for this situation are methods of passive sampling and/or extraction of analytes, which involve measure-ment of the concentration of an analyte as a weighted average over the sampling and/or extraction time. Passive sampling is simple to perform, as well as the following isolation and/or enrichment step. No further sample preparation treatment is usually required.

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This important feature is not, however, valid for the passive sampler called the semipermeable membrane device (SPMD). This sampler is described further because it is the indicator of the bioavailability of organic and organometallic pollutants, most often found in all possible compartments of aquatic food chain[3]. Contaminant accumulation into passive sampling devices is a diffusive process resulting from the difference in chemical activity of contaminant dissolved in water and that in the sampler. These integrative samplers are generally composed of a receiving phase for contaminant accumulation and a membrane to limit mass transfer[4]. The deployment of semi-permeable membrane devices passive sampler was undertaken in Shkodra/Skadar Lake which is the largest lake in the Balkans region. Its surface is 368 km^2, from which 149 km^2 are included in Albanian territory and the other part belongs to Montenegro. The growth of industry and the intensification of agriculture in the lake's catchment area have resulted in increasing anthropogenic influence on the lake, including the input of various organic pollutants. Shkodra/Skadar Lake is surrounded of a number of villages, towns and factories, whose waste waters enter the lake through its tributaries, sublacustrine springs or by fall out and rain out of materials from air[5]. Shkodra Lake is one of the most important multi-dimensional resources of this region as a fishing, hunting, tourism, recreation and aquatic sports resource. The Montenegro part of the Lake has the status of the National Park. A number of organo chlorinated pesticides and polychlorinated biphenyl have already been detected in the waters and tributaries of Shkodra/Skadar Lake using conventional sampling and extraction methodologies[6].

EXPERIMENTAL

Preparation of semi-permeable membrane devices: A semi-permeable membrane device (SPMD) is described for passive *in situ* monitoring of organic contaminants in water[7]. Semi-permeable membrane devices construction and deployment is done as described by Rastall *et al.*[8]. LD-PE membrane was cleaned by pre-extracting 85 cm section of 50 μm thick LD-PE "layflat" tubing in analysis grade *n*-hexane for three 48 h periods with solvent changes after each period. The lipid sequestering phase was prepared according to the method described by Lebo *et al.*[9]. Briefly, 800 μL volumes of 95 % pure 1,2,3-tri[*cis*-9-octadecanoyl]glycerol (triolein, Sigma-Aldrich, Steinheim, Germany) were transferred in a test tube with 10 mL of methanol (Labosi) and shaked for 20 min. Following partitioning, the test tubes were centrifuged at 2000 rpm for 10 min before being stored at -27 °C until the triolein freezes in the bottom of each tube. The process was repeated two times.

Sampling sites: Three sampling sites were selected in the Albanian side of the lake on the basis of anthropogenic influence (Fig. 1). Semi-permeable membrane devices were deployed at each site for 21 days from June to September 2004. All three sampling points from Albanian part (A1, A2, A3) are near villages where

Fig. 1. Map of SPMD sampling and bottle sampling points (A1-Peshkimi, A2- Zogaj, A3-Sterbeq)

anthropogenic pollution is higher than in the other sectors. The bottle samples were collected in 1 L glass bottles in the same sampling points during the deployment time.

Post deployment process: The post deployed semipermeable membrane device and field controls were processed in Hygiene Institute Heidelberg Germany as described by Rastall *et al.*[8]. Membranes were first cleaned up and then dialyzed in 100 mL *n*-hexane (Merck) at 18 °C for 48 h. Interferences including co-dialyzed triolein, methyl oleate and LD-PE oligomers were removed from the semi-permeable membrane devices dialysates using a low pressure size exclusion chromatographic (SEC) system. This consisted of 30.0 cm × 1.2 cm glass column and compatible injection port (Latek GmbH, Eppelheim, Germany) filled with SX-3 Bio-Beads (Biorad Laboratories, Munich, Germany) and eluted with a mixture dichloromethane /*n*-hexane (50:50 vol/vol) HPLC grade at a flow rate of 2.0 mL/min. Compound elution was monitored using a UV-Vis Linear 203 dual channel UV detector (Latek) at 254 nm. The solvent were evaporated to 100 µL for each deployed sample and control.

Chromatographic analysis: The semipermeable membrane device sampler were injected in GC-ECD Agilent 6890 with micro ECD detector with auto sampler COMBI-PAL. Injection was done in splitless mode in 210 °C with flow rate (30 mL/min) and injection volume was 1 μL. The column was capillary SPB-octyl 60 m × 0.25 mm × 0.25 μm. The GC temperature program was 100-220 °C for 6 min with 20 °C/min and 220-280 °C for 20 min with 3 °C/min.

Bottle samples extraction: The bottle samples were extracted by using liquid-liquid extraction method. Shortly, 1 L of water was transfered to the separatory funnel and than 10 μL PCB-29 (with a concentration 2.5 ng/μL) were added as internal standard. A volume of 20 mL *n*-hexane were transfered inside the funnel as an extraction solvent followed by an intensive shaking. After separation of organic phase from water phase, *n*-hexane was dried with 10 g anhydrous potassium sulphate. Sample clean-up was done in a glass column packed with deactivated Florisil with 5 % water (100-200 mesh or 0.075-0.150 mm).

Gas chromatographic analyses of bottle samples: Gas chromatographic analyses were performed with an HP 6890 Series II gas chromatograph equipped with a ^{63}Ni electron-capture detector and a split/splitless injector. The column used was a HP-5, 5 % phenyl methyl silicone, 25 m × 0.33 mm × 0.25 μm film. The split/splitless injector and detector temperatures were set at 280 and 320 ºC, respectively. Carrier gas was He at 19.8 mL/min and make-up gas was nitrogen 10.2 mL/min. The initial oven temperature was kept at 60 ºC for 4 min, which was increased, to 200 ºC at 20 ºC/min, held for 7 min and then increased to 280 ºC at 4 ºC/min for 20 min. The temperature was finally increased to 300 ºC, at 10 ºC/min, held for 7 min. Injection mode was splitless, injection volume was 2 μL. Polychlorinated biphenyl quantification was performed by internal standard method.

RESULTS AND DISCUSSION

Eight polychlorinated biphenyl were determined in semipermeable membrane devices dialysates from the three sampling sites. All of polychlorinated biphenyl identified in semipermeable membrane devices dialysates are readily bioavailable for uptake by Shkodra Lake biota and they are distributed in all sampling sites. The total concentration of polychlorinated biphenyl ranged between 13.3-47.4 ng/semi-permeable membrane devices (Table-1). Another compound detected in both sampling points was DDE (Fig. 2). With increasing of the anthropogenic influence in Shkodra Lake, the concentrations of persistent organic pollutants can represent a risk for the biota. Semipermeable membrane devices sampling technology seems to be an efficient method for the monitoring and identification of persistent organic pollutants in Shkodra Lake. Regarding the bottle samples analyses, only a number of volatile polychlorinated biphenyl congeners were identified (PCB-28, PCB-52) and concentrations of the other semi-volatile and non-volatile congeners were not detected (Table-2). The biomimetic passive sampling method was more efficient on

TABLE-1
POLYCHLORINATED BIPHENYLS ABSOLUTE CONCENTRATIONS
(n = 3), IN ng/SPMD FOR THREE SAMPLING SITES

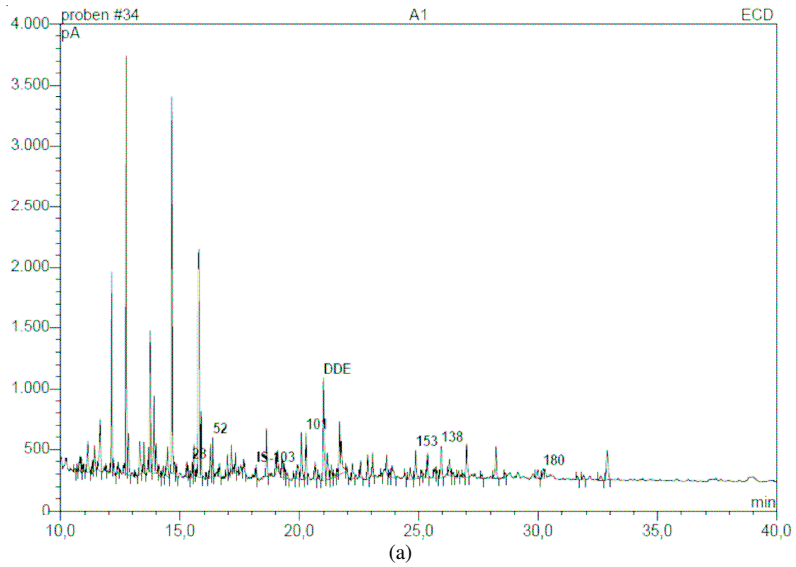
Compound	A1	A2	A3
PCB 28	0.19	0.45	0.21
PCB 52	0.51	1.43	1.06
PCB 103	0.15	0.11	0.12
PCB 101	0.70	2.50	1.02
PCB 153	0.57	1.92	0.47
PCB 138	0.59	2.26	0.52
PCB 193	n.d*	0.32	0.28
PCB 180	0.09	0.91	0.17
Total PCBs	13.30	47.40	17.30

*Not detected.

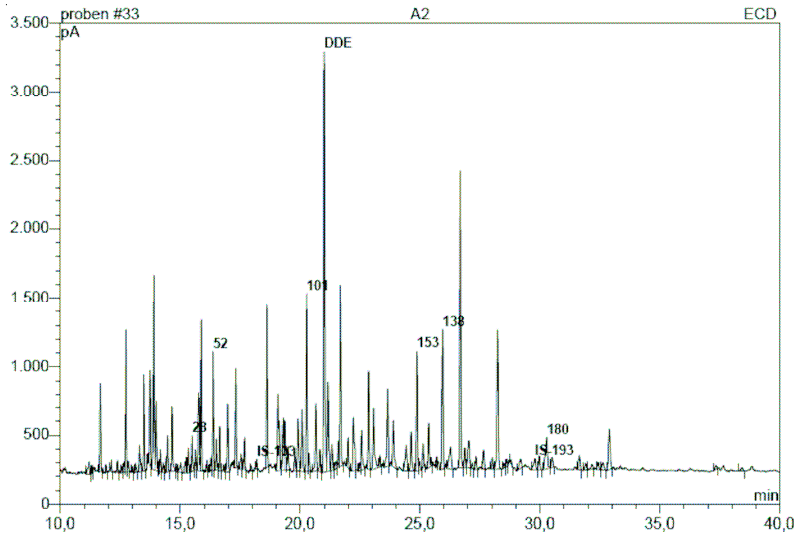
TABLE-2
POLYCHLORINATED BIPHENYLS TOTAL CONCENTRATIONS
(n = 3), IN ng/L for THREE SAMPLING SITES

Compound	A1	A2	A3
PCB 28	n.d.*	n.d.	n.d.
PCB 52	0.55	1.69	2,34
PCB 103	0.33	0.49	1.11
PCB 101	n.d.	n.d.	n.d.
PCB 153	1.05	n.d.	n.d.
PCB 138	2.00	n.d.	n.d.
PCB 193	0.49	0.34	n.d.
PCB 180	1.46	n.d.	n.d.
Total PCBs	5.88	3.52	3.45

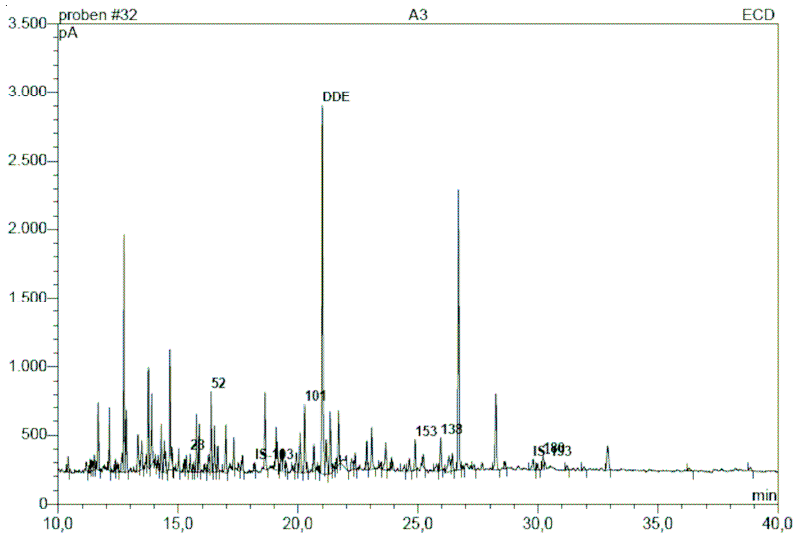
*Not detected.



(a)



(b)



(c)

Fig. 2. GC-ECD chromatograms produced by deployed SPMD dialysates [(a) sampling site A1, (b) sampling site A2, (c) sampling site A3]

identification of the freely dissolved polychlorinated biphenyl in natural water of Shkodra Lake because its exposure time was longer and enabled the accumulation of the organic pollutants. The bottle sampling analytical results represent the total concentration and provides useful information about the presence of the pollutants at the moment of sampling. From previous investigations, a total of 39 compounds were identified in semipermeable membrane devices dialysates from the six sampling

sites. Several compounds remained unidentified. 14 of 15 targeted polycyclic aromatic hydrocarbons (PAHs) were present in dialysates from one or more sampling sites indicating that these compounds are both readily bioavailable and widely distributed in Shkodra/Skadar Lake[8]. Polychlorinated biphenyl in waters of Shkodra Lake were not identified by using other integrative passive sampler Membrane Enclosed Silicone Collector (MESCO)[10].

Conclusion

Semipermeable membrane devices sampling technology combined with chemical analyses resulted an efficient method in the capacity to accumulate the freely dissolved fraction of polychlorinated biphenyl in Shkodra Lake. For the ecological risk assessment, the bioavailable fraction is of substantial interest. semipermeable membrane devices sampling allowed the detection of very low concentration of polychlorinated biphenyl that we could not be identified with conventional sampling methods in Shkodra Lake. The further identification and monitoring of hydrophobic organic pollutantss in Shkodra/Skadar Lake remains an important issue for the future environmental investigations, which are necessary for this important economic and touristic area.

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