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NEW APPLICATION OF SAMPLING METHODS IN SHKODRA LAKE

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SYNOPSIS

Sampling is an important aspect in natural water monitoring which may influence all following steps involved in water quality assessment. A range passive sampling devices for monitoring organic pollutants and heavy metals has been developed during the last decade. In this pilot study it was tested a novel, simple and inexpensive passive samplers of organic compounds and heavy methals. The passive samplers of hydophobic organic compounds consist of an 8 cm polydimethylsiloxane rod used as a collector phase which was deployed for two weeks in lake water and then thermally desorbed and analysed by GC-MS. There were identified a number of PAHs collected in ng/silicon rods. A Chemcatcher variant sampler for heavy metals was deployed in Shkodra Lake. AAS method using graphite furnace as atomizer was used for heavy metals analysis. There were identified a number of bio available forms of heavy metals concentrated in the collecting chelating disk.

INTRODUCTION

Monitoring of inorganic and organic environmental pollutants is an ongoing challenge for the analytical chemist. The determination of persistent organic pollutants (POPs) is of ecotoxicological relevance due to their high toxic potencial, their persistence and their tendency to bioaccumulate. A number of OCPs and PCBs have already been detected in the waters and tributaries of Lake Shkodra/Skadar using conventional sampling and extraction methodologies (MISUROVIC, 2002). The combination of SPMD-based sampling with appropriate bioassays and chemical analysis provided an environmentally relevant tool for the identification of waterborne pollutants in Lake Shkodra/Skadar (RASTALL, 2004). The concentrations of heavy metals in both the water and the sediments of lake Shkodra, in general, is still within the permissible limits of the EU standards (NEZIRI.A, 2006).

In recent years, a number of alternative methods of monitoring water quality has been developed to complement and/or replace spot sampling methods that provide only an instantaneous estimate of the concentration of pollutants at the time and point of sampling (GREENWOOD,

2007). Silicone rubber sheeting can be used as a passive sampling device for hydrophobic organic contaminants in the environment to determine the available concentrations in water and sediments (YATES, 2007). The PDMS rods are a novel, simple and inexpensive approach to absorptive extraction of organic compounds from environmental samples (MONTERO, 2004).

A Chemcatcher variant based on diffusion through a porous CA membrane to a receiving phase, where the analyte is removed by chelation in a chelating EmporeTM disk has been developed for monitoring metals (PERSSON, 2001). In this pilot study it was testet a novel, simple and inexpensive passive samplers of organic compounds and heavy methals. The passive samplers of hydophobic organic compounds consist of a 8 cm polydimethylsiloxane rod used as a collector phase which was deployed for two weeks in lake water and then thermally desorbed and analysed by GC-MS. A Chemcatcher variant sampler for heavy metals was deployed in lake Shkodra. AAS method using graphite furnace as atomizer was used analysing heavy metals.

The aim of this study was the monitoring of persistent organic pollutants and heavy metal levels in water system of Shkodra Lake using passive samplers.

MATERIALS AND METHODS

Sampling sites

Shkodra Lake is located on the border between Montenegro and Albania at 40º 10' North latitude, 19 º 15’ East longitudes. The lake water level also varies seasonally from 4.7 to 9.8 m above sea level. The largest inflow is the Moraca River (Montenegro), which provides more then 62% of the lake water and the outflow is Buna River.

During the last decades the anthropogenic pollution is going to be significant in this area. The Moraca River, the main tributary of the lake, brings most pollutants into the lake from Aluminum Company (KAP), agricultural plantations complex Podgorica landfill, the city drainage collector etc (MISUROVIC, 2002). After the years 90 the industrial activity in Albania is decreased, but the residues (in the form of dumps of ex-mining or chemical industry) of them in environment posed a risk for the human health(MIHO, A. 2005). The sampling stations of 8 cm silicon rod sampler are represented in the Table 1 and Figure 1. The sampling stations of Chemcatcher (Inorganic version) are Zogaj, Peshkimi, Zues.

Figure1. Map of sampling stations

Sample name	Date of deployment	Flow rate (m/s)	Water temperature °C
S1 (Shiroka) Lake	9.05. 2006	0.003	19.2
S2 (Zogaj) Lake	9.05.2006	0.004	19.7
S3 (Peshkimi) River	9.05.2006	0.018	19.2
S4 (Zues) River	9.05.2006	0.128	18.2

Table1. Sampling stations of 8 cm SR

The bare 8 cm silicon rod

The SR were precleaned and condicioned as is described at (MONTERO, 2004). The 8 cm long SR Figure 2, were deployed for two weeks in lake water (9.05.2006 – 23.05.2006). It was measured the temperature of water and flow rate in the deployment time. The samplers were exposed in a metallic holder. After field trial the bare SR 8 cm long were washed under tap water, dried with a tissue paper and stored in the freezer until further processing. From the bare 8 cm silicon rod were taken 1,5 cm SR and used for chemical analysis by thermodesorption–GC-MS with the method as is described at (MONTERO, 2004).

Figure 2. The bare 8 cm silicon rod

Chemcatcher (inorganic version)

The sampler configuration (chelating disk, cellulose acetate diffusion limiting membrane). Chemcatcher® 2nd generation was made of polycarbonate Figure 3. The chelating disks were precleaned with 30 mL 2N HNO_3 and deployed for 2 weeks in October 2007. The post deployment disks were extracted with 30 mL 2N HNO_3 and the extracts were analysed by using AAS/ETA.

Figure 3. Chemcatcher (inorganic version)

RESULTS AND DISCUSSON

The bare 8 cm silicon rod

The results of chemical analyses of 1,5 cm SR taken from bare silicon rod 8 cm long are reported in the Table 2 in ng/1,5 cm SR. There are identified some PAHs (naphthalene, fluorene, phenanthrene, anthracene,fluoranthen, pyren), alkylated PAHs (2-methylnaphtalene, 1-methylnaphtalene,2,6-dimethylnaphtaline), some PCBs (PCB 52, PCB 153, PCB 138) and aldrin. Other compounds identified and presented in the Figure 4 are alkylated benzenes. All of those compounds are collected from silicon material.

This method is low cost and successful for identification and analyses of organic micropollutants in natural waters. The new sampling approach presented a good blank levels and high sensitivity.

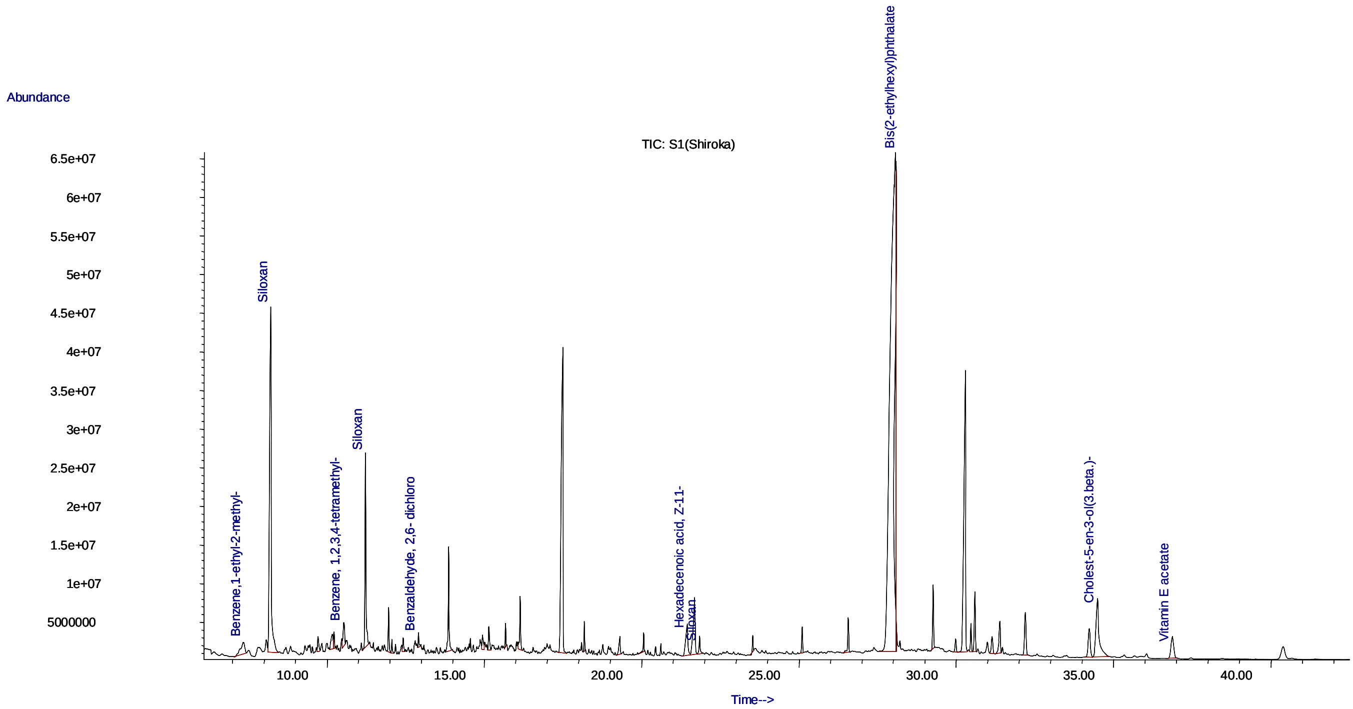

Figure 4. The total ion chromatogram of identified compounds in 1,5 cm silicon rod. (S1,Shiroka)

Compounds	S1 (Shiroka)	S2 (Zogaj)	S3 (Peshkimi)	S4 (Zues)
Naphtalin	2.81	2.90	3.29	5.36
2-Methylnaphtalin	1.21	1.19	1.19	2.62
1-Methylnaphtalin	0.55	0.56	0.53	1.25
Biphenyl	0.11	n.d	n.d	n.d
2,6-Dimethylnaphtalin	0.38	0.42	0.33	0.69
Acenaphthen	n.d	n.d	n.d	0.18
Fluoren	0.14	0.15	0.12	0.36
Phenanthren	0.44	0.97	0.39	0.90
Anthracen	0.04	0.32	0.02	n.d
PCB 52	n.d	0.19	0.18	0.16
Aldrin	5.17	n.d	n.d	n.d
Fluoranthen	0.25	0.48	0.24	0.18
Pyren	0.04	0.22	0.05	0.05
PCB 153	n.d	0.09	n.d	n.d
PCB 138	n.d	0.07	n.d	n.d

Table 2. Results of bare silicon rod 8 cm long analyses in TDU-GC- MS in ng/ 1.5 cm silicon rod.

Chemcatcher (inorganic version)

From the the application of Chemcatcher there were identified a number of bioavailable heavy metals accumulated in the reciving phase EmporeTM disc. The results are listed in the table 3 as absolute concentration (μg/disk). Those results are available for comparison of pollution levels in monitoring stations.This alternative method gave to as some qualitative data for (Fe, Cr, Co and Mn) as preliminary results to indicate where further investigation is necessary. The results presented in the figures 3 -6 show high concentrations of Fe, Cr, Co, Mn in sampling station Zogaj and low concentrations in Peshkimi station. The method needs the further calibration for studied analytes and comparison with classical analytical anlysis of water.

Concentration [μg/disk] ***Station ID***	**Fe**	**Cr**	**Co**	**Mn**
Zogaj	430.34	8.103	6.163	13.476
Zus	347.32	4.603	6.636	9.233
Peshkimi	337.56	4.090	4.827	8.423

Table 3. The heavy methals concentration in μg/disc

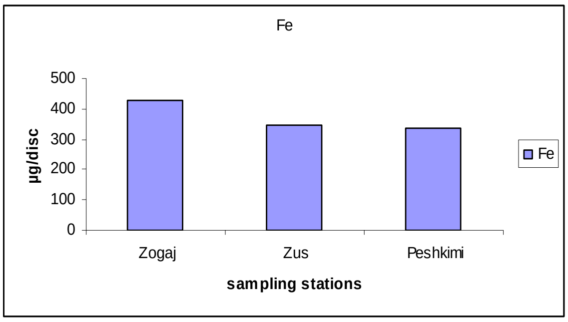

Figure 5. The absolute concentrations of Fe

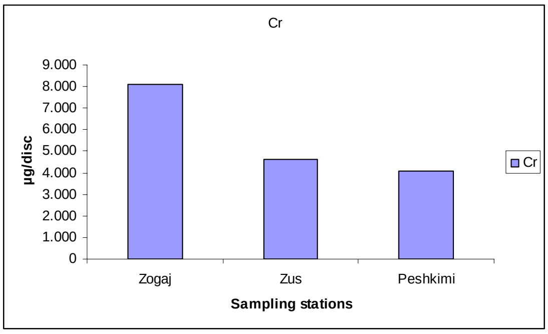

Figure 6. The absolute concentrations of Cr

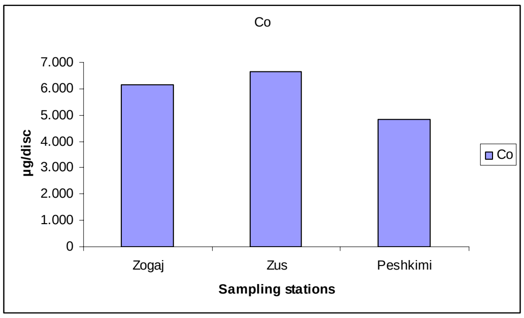

Figure 7. The absolute concentrations of Co

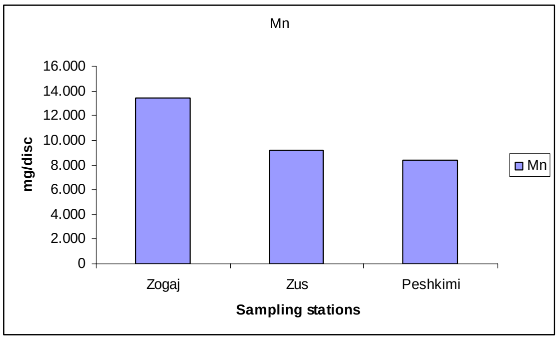

Figure 8. The absolute concentrations of Mn

CONCLUSIONS

The passive sampling has a number of advantages compared with spot sampling as it provides a measure of average conditions in a body of water over extended periods of time, low cost of analyses and the collecting phase can subjected to bioassays.

There were identified a number of organic pollutants as PAHs, PCBs in lake Shkodra by using bare silicon rod as new sampling method. The bare 8 cm silicon rod is a novel and inexpensive “in situ” sampling method of organic compounds from natural waters. The new approach needs the further calibration in order to quantify the identified organic compounds.

Chemcater reacted perfectly with dissolved and weakly complexes species which are species that dissociate within the diffusive boundary layer of the sampler. The system collects the bio- available forms of heavy metals; mimicking bio-monitors and immobilise the contaminants in situ avoiding speciation changes. From the application of Chemcatcher in lake water there were identified some bioavailable heavy methals as Fe, Cr, Co, Mn. The method needs the further calibration for studied analytes and comparison with classical analytical anlysis of natural water.

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