



Application of Chemcatcher® in Lake Shkodra as a Passive Sampling Technology for Lake Water[#]

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Abstract: A number of alternative methods monitoring water quality has been developed to complement and/or replace 'spot' sampling methods. A Chemcatcher® variant sampler based on diffusion of heavy metals through a porous CA membrane to a receiving phase is used. Heavy metals are there removed by chelating process in a chelating Empore™ disk, which has been developed for metals monitoring. The sampler reacts with dissolved and or weakly complexes species which are species that dissociate within the diffusive boundary layer of the sampler. The system collects the bioavailable forms of heavy metals; mimicking bio monitors and immobilise the contaminants in situ avoiding speciation changes. For the field application of Chemcatcher® there were selected three different stations of Shkodra Lake, Albania. AAS method using graphite furnace as atomizer was used for analysing heavy metals concentration after the deployment of Chemcatcher® samplers. Cluster Analysis and PCA model of data treatment were used to identify the chemical model via the relation of the objects (monitory stations) and their data (heavy metals content).

Key words: Chemcatcher®, Empore™ disk, CA membrane, AAS, PCA, Cluster Analysis

Introduction

The alternative methods of sampling procedure may be able to deliver the necessary information at lower cost and or more quickly than "grab" sampling. Due to concept of lower contaminations during transport and handling minimisation, the use of the passive sampler improved accuracy compared to bottle sampling. Björklund Blom (2002) The use of the chelating resin, Chelex 100, during water monitory showed a measurable, reproducible uptake of the soluble fraction of Cd, Pb and Zn at low concentrations Wu (1996). The membrane of the sampler reacts with dissolved and weakly complexes species which are species that dissociate within the diffusive boundary layer of the sampler. The system collects the bioavailable forms of heavy metals; mimicking bio-monitors and immobilise the contaminants in situ avoiding speciation changes. The free ion, or more generally, the labile fraction, is assumed to be the bioavailable fraction of metals in water and responsible for observed toxicity Royset (2005). The new methods provide information that may be similar to, or remarkably different from, the results that derived from the analysis of spot samples.

A Chemcatcher® variant sampler based on diffusion of heavy metals through a porous CA membrane as a receiving phase is used. Heavy metals are there removed by chelating process in a chelating Empore™ disk, which has been developed for metals monitoring. The aim of this study was the application of Chemcatcher® passive sampler for monitoring of heavy metal levels in water system of Shkodra Lake.

Material and Methods

Sampler preparation and field trial:

Metal configuration (chelating disk, cellulose acetate diffusion limiting membrane)

Chemcatcher® 2nd generation (made of polycarbonate)

Extraction procedure: 30 mL 2N HNO₃

Deployment period: 2 weeks

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Location: Shkodra Lake, Albania

Extraction procedure: 30 mL 2N HNO₃

Chemical analysis: AAS/ETA

Measurements of temperature, pH, DO, conductivity were made on the day of deployment and retrieval. AAS/ETA method was used determining the heavy metal (HM) content in HNO₃ solution used as eluent of HM's from passive sampler (*Chemcatcher® field trial*).

The calculation method of time weighted average concentration (TWA):

The method of calculation of HM's during the "in situ" monitoring is given in table 1. A Chemcatcher accumulates the trace metals in the receiving phase according to Equation:

$$M = M_o + R_s C_w t \quad (1)$$

Where M_o (μg) is the mass of analyte in the blank, M is accumulated analyte mass in the receiving phase, R_s is the sampling rate of the specific analyte L/h, C_w is the concentration ($\mu\text{g L}^{-1}$) of the analyte in water and t (h) is the deployment time. R_s is defined as the equivalent volume of water from which the analyte is completely removed per unit time, Vrana (2005) and is determined through laboratory calibration by plotting the metal uptake against exposure time. The C_w represents the time weighted average (TWA) concentration during the deployment time. R_s may vary with temperature and flow conditions around the sampler. The values R_s for calculations were taken from a calibration study Runeberg (2005).

Table 1. The calculation method of HM's in monitoring situ

Calculation method:	parameters
$C_w = \frac{Ms(t) - M_o}{R_s t}$	C_w Time weighted average concentration
	R_s Sampling rate [ml/h]
	M_o Mass of analyte found in the blank
	$Ms(t)$ Mass of analyte accumulated

R_s values taken from Runeberg (2005) are listed in Table 2.

Table 2. R_s values (taken from Runeberg, 2005)

Compound	Range R_s for 1 st generation <i>Chemcatcher®</i> [ml h ⁻¹]	Estimated range R_s for 2 nd generation <i>Chemcatcher®</i> [ml h ⁻¹]
	0 rpm, 4°C - 70 rpm, 18°C*	0 rpm, 4°C - 70 rpm, 18°C*
Cu	1.8 - 4.9	2.7 - 7.4
Ni	2.1 - 5.7	3.2 - 8.6
Zn	1.9 - 5.3	2.9 - 8.0
Pb	0.8 - 0.7	1.2 - 1.1
Cd	1.9 - 5.1	2.9 - 7.7

The R_s values are taken from the calibration data for Cu, Ni, Zn, Pb, Cd. The sampling rate (R_s) value is specific for each analyte and determined through calibration and is an expression of the volume of water which may be cleared for analyte per unit time.

Investigated area

Shkodra Lake is located on the border between Montenegro and Albania at 40° 10' North latitude, 19° 15' East longitude. 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 than 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 Aluminium 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 (2005).

Results

The time weighted average concentrations (TWA) or C_w values for heavy metals (Cu, Zn, Pb, Cd in $\mu\text{g/L}$) analyzed by AAS and calculated according the table 2 of R_s values for two monitoring periods (October 2007 (1) and January 2008 (2)) are listed in the Table 3 and are illustrated via histograms and graphics in the Figure 2.

Table 3. TWA in (ng/L), (N=3) each Cu, Cd, Pb and Zn (Deployment time [October 2007 (1) and January 2008 (2)] Analyzed via AAS

Station ID	Cd (ng/L)				Cu (ng/L)			
	C_{w1}	SDEV	C_{w2}	SDEV	C_{w1}	SDEV	C_{w2}	SDEV
Zogaj	19.02	1.01	26.03	1.34	98.97	3.25	96	5.42
Zus	7.42	0.57	14.75	0.76	123.4	3.22	117.51	2.33
Peshkatari	48.76	0.41	55.47	0.54	91.26	3.12	94.09	2.88

Station ID	Zn (ng/L)				Pb (ng/L)			
	C_{w1}	SDEV	C_{w1}	SDEV	C_{w1}	SDEV	C_{w1}	SDEV
Zogaj	122.13	1.92	137.64	2.79	10.05	1.31	12.67	1.57
Zus	51.16	1.78	42.02	1.38	6.06	1.26	7.38	1.36
Peshkatari	93.28	1.24	86.27	1.06	2.24	0.30	3.83	0.96

From the Figure 1, we can conclude that the Cu concentration in both three stations fluctuate in a very close interval 96 ng/L to 125 ng/L which show that there are no significant changes in concentrations for Cu in both three monitoring stations. The levels of two other elements Cd and Zn are different (7 ng/L to 55 ng/L for Cd and 42 ng/L to 137 ng/L for Zn) but from one station to another is evident a similar trend on their concentration changes. The lower concentration of this two elements are evidenced in the station Zus in comparison with two other stations which have very high values. The Pb concentration in both three stations is very low and from the station Zogaj to Peshkatari the concentration is going to be lower from 10 ng/L to 2.4 ng/L.

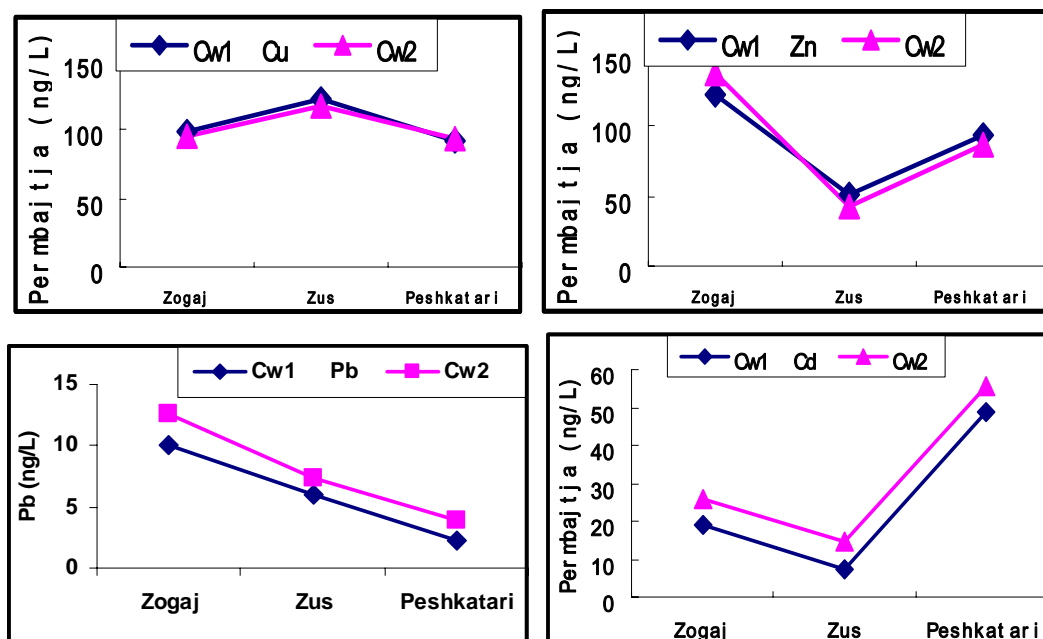


Figure 1. TWA values in ng/L (N=3) of Cu, Zn, Pb and Cd (Deployment time [October 2007 (1) and January 2008 (2)], analyzed via AAS).

Discussion

Based on the covariance and correlation coefficients of Cu, Pb, Zn and Cd. (see table 4 and 5), noticed that Pb and Zn have the highest covariance which show that their concentrations in both three stations have fluctuations, but Cu and Cd presents lower covariance than Pb and Zn .

Table 4. Covariance of elements Cu, Pb, Zn and Cd

<i>Covariance</i>	<i>Cd</i>	<i>Zn</i>	<i>Cu</i>	<i>Pb</i>
<i>Cd</i>	311.20			
<i>Zn</i>	170.44	1187.97		
<i>Cu</i>	-175.41	-325.45	151.24	
<i>Pb</i>	-350.67	637.78	30.73	1253.37

Table 5. Correlation coefficients of Cu, Pb, Zn and Cd

<i>Correlation</i>	<i>Cd</i>	<i>Zn</i>	<i>Cu</i>	<i>Pb</i>
<i>Cd</i>	1			
<i>Zn</i>	0.28	1		
<i>Cu</i>	-0.81	-0.77	1	
<i>Pb</i>	-0.56	0.52	0.07	1

Cu presents strong negative correlation with Cd and Zn. This evidence for the Cu presence in the three water stations was different origin from Cd and Zn. The concentration range for elements Cu, Pb, Zn and Cd are comparable with public values in other studies; Neziri (2006), and with ionic content values of heavy metals in lake water Shkodra published by Shehu (2008)

Factorial analyses (PCA) of the data

Factor analysis is used to uncover the latent structure (dimensions) of a set of variables. It reduces attribute space from a larger number of variables to a smaller number of factors and as such is a "non-dependent" procedure, to determine network groups by determining which sets of results cluster together. The PCA analyses were applied for the identification of chemical model which has to be studied. Through the investigation of a group of n- dimensional data taken as analytic information (in our case is 4 Cu, Zn, Pb and Cd) for a group of samples we have to know the individual properties of every sample in this way we can answer to a question or hypothesis and shows the relation of the objects and their data.

The Varimax rotation strategy is used for data analysis, which consist in a rotation maximize the variance in the new axis or taking a new successive model for each factor when their differences between each other are obvious, for achieving of new simple interpretation we have to take in consideration both two studied factors above: correlation and covariance coefficients. The data treatment was done with statistical program MINTAB by using "multivariate analysis". The results are showed in the figure 2 and 3. The monitoring objects (n=3 stations) were compared via 4 element study (m=4) observed in 6 different samples that belong respectively 2 samples for each station monitored in two different monitoring expeditions.

Factor Analysis: C1, C2, C3, C4

Principal Component Factor Analysis of the Correlation Matrix

Rotated Factor Loadings and Communalities

Varimax Rotation

Variable	Factor1	Factor2	Factor3	Factor4
C1	0.259	-0.880	-0.397	0.032
C2	-0.710	0.692	0.049	0.121
C3	0.886	-0.235	0.398	0.038
C4	0.256	0.300	0.919	0.004
Variance	1.4219	1.3983	1.1626	0.0171

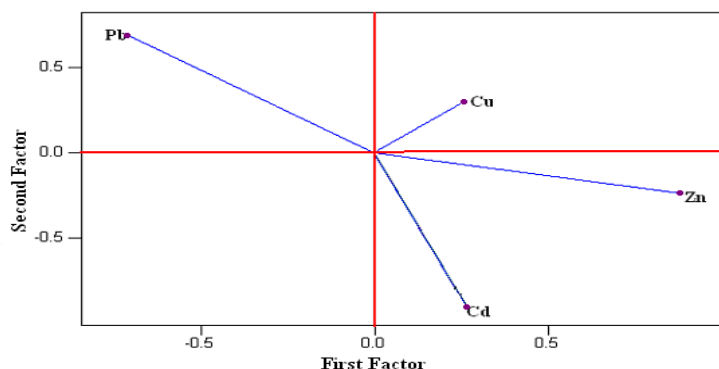


Figure 2. Results of PCA analyses

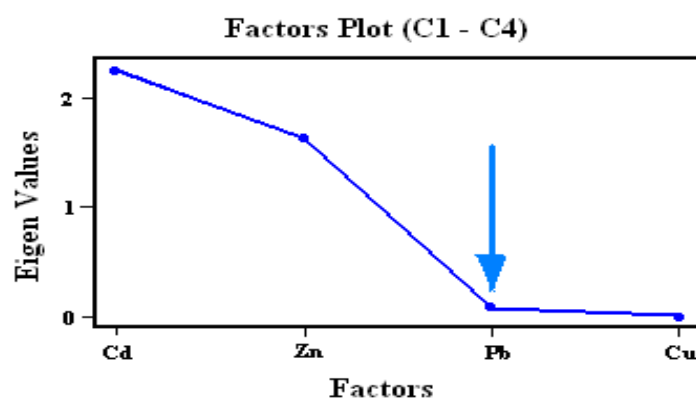


Figure 3. The plot of Eigen values

From the data listed above and graphically distribution of studied factors and showed in the Figure 2, is obvious that elements Cd and Zn have strong positive correlation with each other and other elements have weak correlation. The main factors that have to take in consideration in relation with environmental state of the studied stations results: Cd, Zn and Pb (See figures 2-3). The same result is taken from graphically presence of the TWA values of elements presented in the figure 2. Since the factor number and sample number is relatively small ($n=4$ elements and $m=3 \times 2=6$ samples; 3 monitoring stations in two different monitoring expeditions), the graphics excel results presented in the figure 2 and factorial analyses presented in the figures 2-3 are easily compared because of in this case is not necessary the reduction of studied factors.

Classification of stations according to the group theory (Cluster Analysis)

Using of the group theory realize the identification of the chemical models via relation of the objects and their data. The groups of the studied objects realized via comparison of their characteristic data, where a fixed number of objects with the same attributes are called "GROUP". The similarity of the objects was realized via comparison of their n -dimensional characteristic parameters or by comparison of successive mean values of characteristic spatial points that characterize every object. The graphically presence of similar points plotting may be evident by using different methods. **Manhattan method** (or object block) is used in our data treatment done with statistical program MINTAB by using "multivariate analysis".

The results are showed in the figure 4. Three monitoring stations were compared in two different expeditions. The monitoring objects ($n=3$ stations) were compared via 4 elements ($m=4$) observed in 6 different samples that belong respectively two samples for each station monitored in two different monitoring expeditions.

Cluster Analysis of Observations: C1, C2, C3, C4 (Cu, Pb, Zn and Cd)

Standardized Variables, Manhattan Distance, Single Linkage

Amalgamation Steps

Step	Number of Similarity clusters	level	Distance level	Clusters joined	New cluster	Number of obs. in new cluster
1	5	83.51	1.153	3 6	3	2
2	4	79.96	1.401	2 5	2	2
3	3	76.13	1.669	1 4	1	2

Final Partition

Number of clusters: 1

	Number of observations sum	Within cluster of squares	Average distance from centroid	Maximum distance from centroid
Cluster1	6	20.000	1.808	2.104

The grouping of sampling points is schematically showed in the Figure 5, the results obtained for the three stations during the two monitoring expeditions are very similar.

The results obtained for the station 3 in the first monitoring expedition are classified in the same group with the results obtained for the same station in the second monitoring field triad, the general similarity of the obtained results is 83.51%. The results obtained for the station 2 in the first monitoring expedition is classified in the same group with the results obtained for the same station in the second monitoring expedition and the general similarity of the obtained results is 79.96%, meantime for the station similarity is 76.13%.

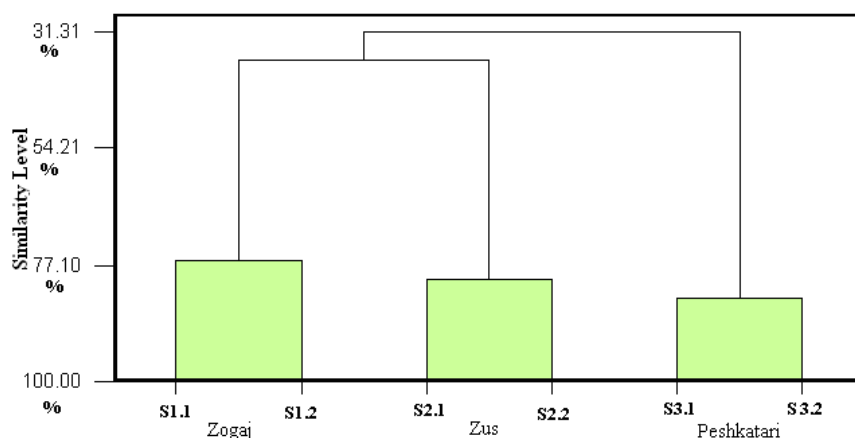


Figure 4. Cluster analysis of variables

Also, the stations S1 to S3 are changed from each other because of the distribution manner of elements Cd, Cu, Zn and Pb. The schematic presentation in figure 5 show that the station S1 has a similarity 36% with station S2 and they both (S1 and S2) present a low similarity 31% with S3 station, that result is comparable with listed results in table 3 where are showed the TWA values (ng/L), (N=3) for Cu, Cd, Pb and Zn.

Conclusions

Chemcatcher® inorganic version was successfully used in Lake Shkodra as a monitoring device for identification and quantification of freely dissolved fractions of heavy metals. The TWA data obtained from deployed samples in Lake Shkodra water were treatment by using statistical methods. The stations were classified via Cluster Analysis using similarity calculations for sampling stations. The experimental data were treated according to factorial analysis (PCA), and show the main factors that have to take in consideration in relation with environmental state of the studied stations results: Cd, Zn and Pb. The graphics excel results presented and factorial analyses are easily compared because of in this case is not necessary the reduction of studied factors.

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