

DETERMINATION OF HEAVY METALS IN VILUNI LAGOON

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Abstract. The analysis of heavy metals (Pb, Cd, Cr, Cu, Zn, Ni, Mn and Fe) content in sediment samples of the Viluni lagoon is given. Monitoring of contaminant levels in sediment samples of the lagoon as well as metal analysis procedure were important for the evaluation of its environmental situation. Because the use of total concentration of heavy metals is not sufficient to obtain relevant information in environmental studies aimed to evaluate the impact of anthropogenic or natural pollution sources, a five-step sequential extraction procedure known as the 'Tessier' method was applied for this purpose. The state and mobility of heavy metals in sediments samples of the Viluni lagoon were studied. The most important species of metals present in sediments are in mobile forms and were determined after division into fractions, using appropriate chemical reagents such as: form A (easy exchangeable form and adsorbed to carbonates): ammonium acetate, $\text{CH}_3\text{COONH}_4$ (1M), pH = 5; form B (metals present in the reductive state bound to Fe/Mn oxides): 1:1 hydroxyl amine hydrochloride, $\text{NH}_2\text{OH}\cdot\text{HCl}$ 1M, acetic acid, CH_3COOH 25%; form C (bound to organic matter exchanging for acid-base effect at pH 1): chlorhydric acid, HCl 0.1 M; form D (bound to humic compounds): NaOH 0.5 M, HF (cc), HNO_3 (cc), H_2O_2 (cc); form E (bound as the sulphide): HNO_3 (8 M). Total heavy metals were found to be in very low content. The most part of Fe (about 78%), Zn (about 76%), Ni (about 60%), Pb (about 43%) and Mn (about 40%) are bounded with sulphide forms. About 36% of Mn are bounded to carbonates and are easily exchangeable forms. About 30% of Pb are bounded with Fe/Mn oxides and only 18% of its content exist in easy exchangeable or carbonates forms. The most part of Cu is bounded to organic matter exchanging for acid-base effect at pH 1 about 49.4% and about 14.7% are bound to humic compounds.

Keywords: AAS, metal analysis, heavy metals, sediments, extraction procedure, relevant extractant.

AIMS AND BACKGROUND

The problem of mercury and heavy metals pollutions in aquatic and sediments systems is an actual and global problem caused by urban and industrial discharges all over the world. This is clearly demonstrated that if we compare the content of heavy metals in contaminated area with the background level of these elements. The anthropogenic impact is relatively high for Pb, Hg, Cd, Zn and Cu, which are toxic at high content level.

The solid phase of an aquatic systems consist of a mixture of different solid parts coming by different ways like the erosion of rocks and lands, from atmo-

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spheric raining, discharges of wastes, etc., so the determination of heavy metals content in sediments is important for evaluation of the pollution level caused by these elements. The determination of heavy metals content in sediments is very important for evaluating the sources of pollution and the polluted area, too.

Chemical analyses of the whole sediment samples as well as five-step extraction method for metal analysis procedure were carried out. Total metal concentrations determine the true extent of metal levels in the sediments and it is the criteria by which the extent, if any, of contamination is evaluated¹⁻³. However, it is not sufficient to obtain relevant information to environmental studies aimed to evaluate the toxic potential of heavy metals due to their mobility, so the five-step sequential extraction procedure, known as 'Tessier' method, was applied for this purpose⁴⁻⁷.

EXPERIMENTAL

A short view of Viluni lagoon. The Viluni lagoon is one of the major lagoons of Albania and represents a special geographical object in the system of the lagoons of the Albanian coast of the Adriatic sea. It is located in the northern segment of this coast, at delta of the Buna river. The Viluni lagoon (coordinates: 41°52' N and 19°26' W, longitude of about 3 km and width 0.9 km, surface of 1.96 km²) is famous for the variability of the plants and animals. Herbs and weeds of salty waters characterise this lagoon and one can meet different amphibians in the environment. The lagoon of Viluni constitutes an important environment in different aspects, despite the threatening factors caused by humans. Among the threatening factors we distinguish the devastation and degradation of the natural habitats. Also, thinking of a quick economical social development, especially during the last years, a special extraordinary exploitation of the natural and biological properties has occurred. The zone is becoming more populated and the damage of the beaches, devastation of woods, illegal hunting and fishing show their negative effects on the biological life as well as natural landscapes. The principal sources of pollutants are discharges from rivers containing high quantity of solid particles, agricultural chemicals (P, N, pesticides) and untreated urban wastes (N, P, HM).

All of these include a large number of threatened species from different representative groups which make regard to the Viluni lagoon to be considered as a scientifically important area that should be maintained (Fig. 1).

Sampling procedure. Ten sediment samples were collected and mixed together forming a composite sample as a representative sample for metal determination study of the area. Soil samples were collected 20 cm deep from the surface, air dried, sieved through a 2.0 mm screen, and then grounded and sieved through a

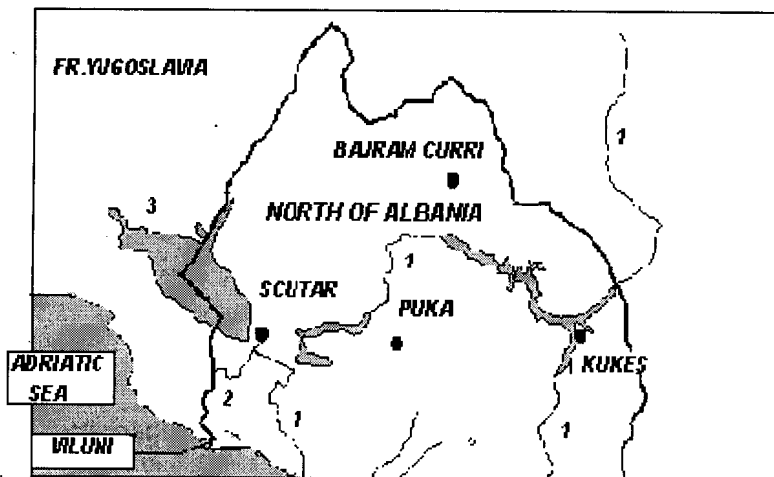


Fig. 1. The map of the north part of Albania

Legend: 1 – Drini river, 2 – Buna river, 3 – Scutari lake

0.063 mm screen. The homogenised samples were stored in airtight pure plastic bags until used for chemical analyses.

Materials and methods. The fractions smaller than 2 mm of the sediment samples were well homogenised by grinding in agate mortar until all material was going through a 200 μm nylon sieve. Sub samples for mercury determination were dried at 50-60°C and sub samples for determination of other parameters were dried at 105°C. After drying, the samples for chemical analyses were stored in airtight plastic vials until required for future use.

Sample treatment. The total digestion procedure^{1,2} was applied for sediments digestion. Flame AAS system was used for Fe, Cr, Zn, Ni, Mn and Cu determination, ETA-AAS system was used for Pb, Co and Cd analysis, CVAAS system was used for Hg determination. SD-M-2/Tm and IAEA 405 reference material were used for quality control of analysis in sediments.

Method for chemical analyses of heavy metals (except mercury). Total decomposition method with the use of hydrofluoric acid in combination with concentrated oxidising acids HNO_3 and H_2O_2 was applied^{1, 8-10}. Digestion was carried out into PTFE bombs, with 8 ml HNO_3 , 4 ml HF and 2 ml H_2O_2 . Sample solutions and blanks obtained were analysed for heavy metal concentrations by atomic absorption spectrometry. Flame technique was used for determination of metals present in sufficient concentrations, notably Fe, Cu, Cr, Ni, Mn, Zn and Pb in some cases, and graphite furnace technique was used for determination of trace metal levels of Cd, and Pb.

All measurements were carried out using a Varian SPECTRAA 10 Plus instrument equipped with a GTA-96 graphite furnace. Instrument parameters for measurements of each element were optimised according to the specialised literature¹⁰⁻¹¹ and manual of apparatus¹². Chemical modifier, $\text{NH}_4\text{H}_2\text{PO}_4$, was used for Cd and Pb determinations with ETA-AAS. Single-element calibration standards were prepared from 1000 mg element l^{-1} Merck standard solutions. All reagents used were purchased from Merck (p.a. quality).

Quality assurance of the data. Two reference certified materials (CRM) were analysed at the same time with sediment samples of the studied area, SDM/2-TM and IAEA 405 purchased from IAEA Monaco. It could be noticed that the data obtained were in good agreement with the certified values.

The 'Tessier' method for metal analysis^{4-7,13,14}. The most important species of metals present in sediments were in mobile forms and were determined after division into fractions, using appropriate chemical reagents as given in Fig. 2.

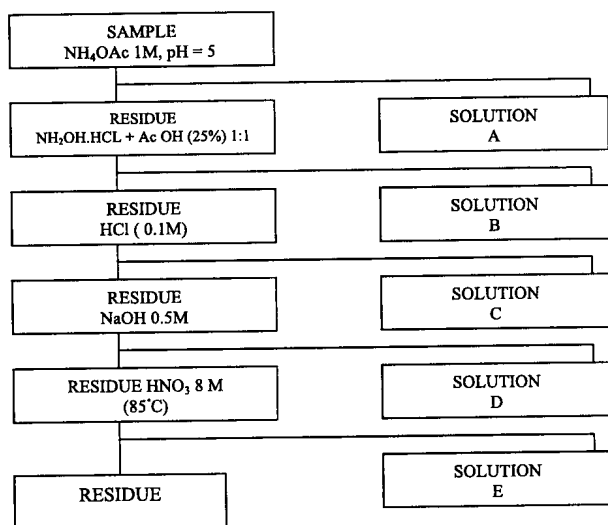


Fig. 2. Schematic diagram of the 'Tessier' method used for metal analysis

RESULTS AND DISCUSSION

Results of chemical analyses of sediment samples. Table 1 shows the mean content of heavy metals in sediment samples of the Viluni lagoon area.

Table 1. Results of chemical analysis of sediment samples (in mg/kg, DW)

Zn	Fe	Cu	Mn	Ni	Pb	Cd
56.4	26420.78	19.8	509.4	302.9	16.3	0.2

From the data of Table 2, it is seen that the Viluni lagoon has low concentration of Cu, Ni, Zn and Pb metals, and normal concentration of Fe, Mn and Cd.

Table 2. Heavy metals content (in mg/kg, DW) in each sediment fraction ($N=5$)

Parameters	Total	Step A	Step B	Step C	Step D	Step E
Fe (mg/kg, DW)	26420	6880	3520	1640	1355	21470
RSD	8.7	11.3	11.3	8.5	13	0
Mn (mg/kg, DW)	509.4	144.4	71.1	14.5	2.6	158.7
RSD	2.10	4.50	12.10	48.20	17.60	2.20
Ni (mg/kg, DW)	275.4	9.3	34	38.6	8.2	136
RSD	9.80	8.60	6.10	23.00	9.00	0.90
Zn (mg/kg, DW)	56.4	1.4	4.3	5.7	0.4	38.4
RSD	13.7	5.0	2.0	3.6	27.0	1.3
Cu (mg/kg, DW)	19.8	1.2	4.4	15	4.5	4.7
RSD	6.5	8.3	9	4	2.2	1.1
Pb (mg/kg, DW)	3.3	2.9	4.9	1	0.5	7
RSD	220	48.9	13.9	21	1.7	23.6
Cd (mg/kg, DW)	0.2	n.d.	n.d.	n.d.	0.3	n.d.
RSD	125	n.d.	n.d.	n.d.	11	n.d.

Metal analysis. The five-steps 'Teisser' method was used for heavy metals analysis. The results of analysis of total content of heavy metals and the content that belongs to each form are represented in Table 2 and are illustrated in histograms in Fig. 3. The percentage values of extractable part against each heavy metal

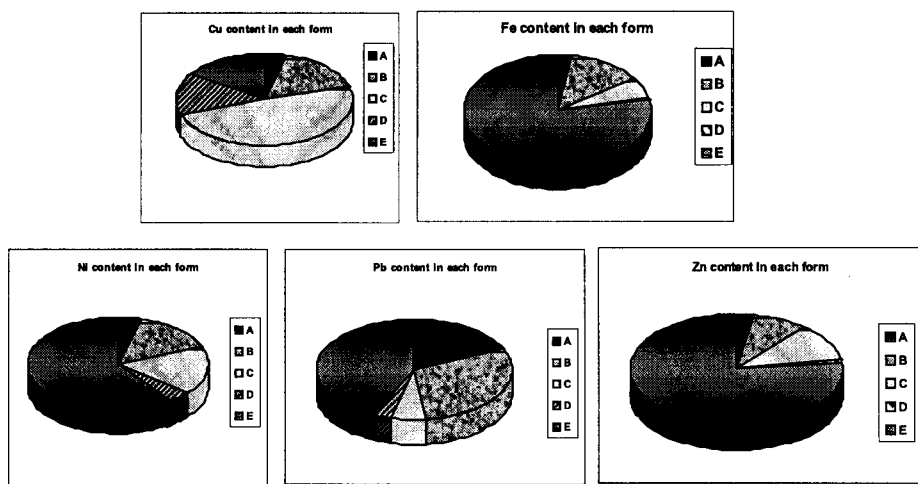


Fig. 3. Histograms of heavy metals distribution in each form of sediment sample

concentration was used to study the distribution of heavy metals in each fraction. The results are shown in Table 3.

Table 3. The percentage values of each extractable part against the total extractable part

Step	Fe	Mn	Zn	Cu	Ni	Pb	Cd
A	2.5	36.9	2.7	3.9	4.1	18.0	n.d
B	12.8	18.1	8.5	16.2	15.0	30.0	n.d
C	5.9	3.6	11.4	49.4	17.0	5.8	n.d
D	0.5	0.7	0.8	14.7	3.6	2.9	n.d
E	78.2	40.6	76.6	15.6	60.2	42.9	n.d

CONCLUSIONS

Total heavy metals were found to be in very low content. Considerable levels of most of them (Fe, Zn, Ni, Pb) found to be bounded as sulphides forms (phase E). Mn and Pb are found to be bounded in exchangeable form and adsorbed to carbonates (phase A). Cu was found to be bounded to organic matter (phases C and D). From the data listed in Table 2, it is clearly demonstrated that some RSD values of some elements in some extraction steps (like Mn and Ni in step C; Pb in steps A, B and E; Cd in step A) are relatively high. It may be related to different extraction rate of these elements in the so-mentioned extraction step.

The most part of Fe (about 78%), Zn (about 76%), Ni (about 60%), Pb (about 43%) and Mn (about 40%) are bounded with sulphide forms. About 36% of Mn content are bounded to carbonates and easy exchangeable forms. About 30% of Pb are bounded with Fe/Mn oxides and only 18% of Pb content exist in easy exchangeable or carbonates forms. The most part of Cu was found to be bounded to organic matter (phases C and D), about 49.4 and 14.7%, respectively.

The sequential extraction procedure used in this work permits the evaluation of the distribution of heavy metals among the various chemical forms in which they are present in sediments. So, it is possible to distinguish the metal fraction bound to organic matter that present as sulphides and the mobile part of them. This allows a more reliable analysis of metals and, consequently, the evaluation of environmental risk due to mobility and availability of the different forms of the metals in sediments.

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