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Heavy Metals Assessment in the Macrophytes of Viroi Lake

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Abstract

Macrophytes are considered as important component of the aquatic ecosystem since they serve as food source for aquatic invertebrates and can act as efficient accumulator of heavy metals. Current study assesses heavy metals in the sediments and macrophytes of the Viroi lake in Gjirokastra district (south of Albania) in order to find out their possible relationships. Heavy metals like Fe, Zn, Ni, Cr, Cu, Cd and Pb were analyzed in sediments and in dominant macrophytes of the lake. Contamination factors (CF) and degree of contamination (Cdeg) of the sediments with heavy metals were calculated. Obtained data showed that concentrations of heavy metals in the sediments were in following order Fe>Ni>Zn>Cr>Cu>Pb>Cd; and these sediments results with low or moderate contamination. The aquatic plants of the lake were not equally effective on removing of heavy metals. The concentrations of heavy metals in water plants were higher than the values of WHO standard. Furthermore, by using bioconcentration factor (BCF), were indentified aquatic plants as “accumulator” of heavy metals.

Keywords: macrophyte, water, heavy metal, contamination factor, bioconcentration factor.

1. Introduction

Heavy metals accumulation in plants and sediments of water ecosystem represent an important issue of environmental pollution. Monitoring of the contamination of sediments by heavy metals is of high importance because heavy metals can be accumulated to toxic levels in water ecosystems without any visible signs **[1]**. Most of the heavy metals accumulate in the biological environment in different ways, via the nutrient chain **[9]**. Heavy metals, such as Pb, Cd, Cr, Zn, and Cu are the most important pollutants in lake ecosystems due to their environmental persistence, toxicity, and capacity to bioaccumulate and biomagnify in food webs **[21]**. Heavy metals as Cr, Mn, Co, Cu, Fe and Zn play biochemical roles in the life processes of aquatic plants and animals, and their presence in trace amounts in the aquatic environment is essential **[5]**, while others heavy metals as Cd, Pb, and Hg have unknown biological function **[19]**. However, at high concentrations, these trace metals become also toxic **[5]**.

Macrophytes are considered as important component of the aquatic ecosystem not only as food source for aquatic invertebrates, but also act as an efficient accumulator of heavy metals **[12]**. The accumulation of heavy metals in the tissues of organisms of invertebrates can result in chronic illness and cause potential damage to the humans **[11]**, that at the top of the food chain, consume water species. Some plants play an important role in the remediation process, which makes it possible to remove several pollutants, including heavy metals from sediments and water. Aquatic plants like Lemna trisulca, Ceratophyllum submersum, Groenlandia densa and Apium nodiflorum have been exposed to bio concentrate heavy metals such as Fe and Cu up to 78 times their concentration in the water. Also Ni is the heavy metal that has been accumulated from these plants **[10]**. Plants can take up heavy metals by their roots, or even via their stems and leaves, and accumulate them in their organs. Plants take up elements selectively. Accumulation and distribution of heavy metals in the plant depends on the plant species, element species, chemical and bioavailiability, redox, pH, cation exchange capacity, dissolved oxygen, temperature and secretion of roots **[6], [14]**. The objective of this study was to assess the concentrations of some heavy metals in sediments and plants in water ecosystem, as well to find out the relationship between sediments and plants in the mobility of heavy metals in water ecosystem.

2. Material and Methods

2.1. The study area

Viroi lake has a surface area of 17 ha and is located in the north-west of Gjirokastra district and 3 km distance from the town itself in the south part of Albania, on the left side of national road Gjirokaster – Tepelene. It has a karstic water source called "Mother of Viroi", with a flow of 17 m^3 /second, and its yearly average temperature is 13-14°C

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Figure 1. Map of sampling plant and sediment samples

2.2. Sample collection and preparation

Sediment samples were collected during October 2013 at a depth of 0-15 cm in 4 sampling sites of the Viroi Lake. The samples were air-dried, sieved with a 2-mm sieve, and the fraction samples < 2 mm were used for further analysis. The total concentrations of Cd, Cr, Cu, Ni, Zn, Fe and Pb were determinate in sediment samples using the following procedure: 0.3 g of sediment samples were mixed with HNO_3cc acid and H_2O_2 33%, and the mixture of samples was kept in a microwave oven for 25 min at 180°C, then the concentrations of heavy metals were determinate by atomic absorption spectrometry (AAS) **[20].**

The macrophytes were collected during July 2013. The dominant plants were collected in the lake like *Ranunculus fluitans, Fontinalis antipyretica, Apium nodiflorum (L), Alisma plantago-aquatica,* and *Cyperus longus (L)*. The plants were separated into roots and shoots parts and were dried for 24 hours in 60^{o}C and than in 150^{o}C. Acid wet digestion in an open vessel method was used, which requires predigestion with HNO_3, followed by addition of $HClO_4$ and digestion at high temperature. The digestion was continued until the solutions became clear. The concentration of heavy metals Cd, Cr, Cu, Ni, Zn, Fe and Pb were determined by atomic absorption spectrometry (AAS) **[16].**

2.3. Assessment of ecosystem

The guidelines of ecological values were used for the evaluation of sediments by heavy metals **[17]** and WHO standard **[13]** was used for the level of heavy metals in plants. Assessment of heavy metals pollution in sediments was also defined by calculation of Contamination factors (CF) by using this formula:

CF = Cm of sample / Cm background; where:

Cm of sample = concentration of heavy metals in sample;

Cm background = heavy metals background values calculated as 90%.

Degree of contamination (Cdeg) was estimated by using following formula:

Cdeg = $\sum \boldsymbol{CF}$ [4], where CF are contaminations factors

Furthermore, by using bioconcentration factor (BCF), were indentified aquatic plants as "accumulator" of heavy metals. The Bioconcentration factors were calculated using this formula

BFC = P/E, where

P = represents the element concentration in plant tissues (mg/kg dry wt) and

E = represents the element concentration in the water (mg/L) or in the sediment (mg/kg dry wt).

A larger ratio implies better phytoaccumulation capability **[8].**

3. Results and Discussion

The heavy metals in sediments of the lake were measured in two periods. First- when lake was totally dried and the range of heavy metals concentration were Ni>Cr>Cu>Pb, whereas Cd not detected (Table 1) **[3].** In the second period the sample collection were made under the water. The range of heavy metals concentration were Fe>Ni>Zn>Cr>Cu>Pb>Cd (Table 2).

Table 1. Heavy metals in the sediments of lake (first period S1)

	Heavy metals				
	Ni (mg/kg)	**Cr** (mg/kg)	**Pb** (mg/kg)	**Cd** (mg/kg)	**Cu** (mg/kg)
Max	410.50	156.35	138.53	n.d	141.51
Min	25.45	8.64	42.52	n.d	8.67
Average	198.75	86.39	59.69	n.d	62.89
Stdev	113.27	39.27	20.43	n.d	40.15

Table 2. Heavy metals in second period (S2)

Stations	Heavy metals						
	Pb (mg/kg)	**Cu** (mg/kg)	**Ni** (mg/kg)	**Cr** (mg/kg)	**Cd** (mg/kg)	**Zn** (mg/kg)	**Fe** (mg/kg)
VL/S3_1	n.d	72,163	166,98	93,397	15,859	137,419	24706,19
VL/S3_2	55,296	75,587	125,43	96,426	11,311	146,53	24677,8
VL/S5_1	n.d	21,704	115,02	50,258	12,5447	67,397	13240,67
VL/S5_2	23,465	24,191	187,51	63,59	9,692	74,33	13763,73
Max	55.29	75.58	187.51	96.42	15.85	146.53	24706.19
Min	n.d	21.70	115.02	50.25	9.69	67.39	13240.67
Average	25.55	43.56	156.49	73.45	11.81	100	18030.42
Stdev	22.74	27.71	34.34	20.35	2.55	38.55	6084.91

The concentration of heavy metals in both periods showed the same trend. In the average values Ni vary from 198.75 mg/kg in (S1) to 156.49 mg/kg in (S2); Cr from 86.39 mg/kg (S1) to 73.45 mg/kg (S2);

Cu form 62.89mg/kg (S1) to 43.56 mg/kg (S2) and Pb form 59.69mg/kg (S1) to 25.55mg/kg (S2). Zn and Fe were determined in second period and founded concentration average values were 100 mg/kg for Zn and 18030.42 mg/kg for Fe. Cd was not detected in the first period but was detected in the second period in amount of 11.81 mg/kg, this can be due to the fact that Cd can be diluted in the water phase, meanwhile when the lake gets dry this heavy metal can be bound with the fractions <2mm of sediments.

In order to observe the long term impact that heavy metals on the sediments cause towards the biological receptors, mainly organisms like (algae, moss, earthworms, fish), two guidelines values were used for the assessment of heavy metals in sediment. These are ERL as effects range low and ERM as effects range median (Table 3). The values of heavy metals in the lake's sediments were often higher than the ERL (*Effect Range Low*) values, mainly for Cr, Pb, and Cu. With lower values then ERL for Zn while for Ni values were higher than ERM (*Effect Range Medium*). The values of Cd were higher than ERM. This means that the incidence of Cd metal in biological system is about 65.7%. The pollution of sediments is of natural and anthropogenic origin. Erosion and leaching of phosphate rock in the surrounding areas have an important contribution; this after phosphate rock can induce high concentrations of Cd, Zn, Cr, Cu and Pb in dominium phosphate **[6].** The major anthropogenic source of heavy metals is from atmospheric inputs.

The average values of heavy metals Ni, Pb, Cu and Cr were higher in the dry season of the lake than in the wet season, probably due to dilution by rainwater which influences concentration and heavy metal mobility**[15].**

Table 3. ERL and ERM guideline values for trace metals**(NOAA-USA, 1995)**

Chemical	Guidelines (mg/kg)		Percent incidence of effects		
	ERL	ERM	<ERL	ERL-ERM	>ERM
Arsenic	**8,2**	**70**	**5**	**11,1**	**63**
Cadmium	**1,2**	**9,6**	**6,6**	**36,6**	**65,7**
Chromium	**81**	**370**	**2,9**	**21,1**	**95**
Copper	**34**	**270**	**9,4**	**29,1**	**83,7**
Lead	**46.7**	**218**	**8**	**35.8**	**90,2**
Mercury	**0,15**	**0,71**	**8,3**	**23,5**	**42,3**
Nickel	**20,9**	**51,6**	**1,9**	**16,7**	**16,9**
Zinc	**150**	**410**	**6,1**	**47**	**69,8**

Table 4. Contamination factors and degree of contamination for heavy metals in sediments of lake

Cf	*Pb*	*Cu*	*Ni*	*Cr*	*Cd*	*Zn*	*Fe*
VL/S3_1	0	0,96	0,92	0,97	1,06	0,95	1
VL/S3_2	1,06	1,01	0,69	1	0,76	1,01	0,99
VL/S5_1	0	0,29	0,63	0,52	0,84	0,46	0,53
VL/S5_2	0,45	0,32	1,03	0,66	0,65	0,51	0,55
C_{DEG}(ΣCF)	**1,51**	**2,58**	**3,27**	**3,15**	**3,31**	**2,93**	**3,07**
Background as 90%	**52,11**	**74,55**	**181,35**	**95,51**	**14,86**	**143,79**	**24697,67**

The average values of heavy metals in second period were lower than in the first period. This is because of high temperature and evaporation, which cause the increase of heavy metals concentration in water and finally in sediments because metal ions transfer from water to sediment **[18].** Also the decomposition of water plants in dried lake can also increase the heavy metals concentrations. The calculated contamination factors and degree of contamination are shown in Table 4.

According to Hakanson (1980) [7], Cf has been classified into four groups: Cf<1 low contamination factor, 1≤ Cf<3 moderate contamination factor, 3≤ Cf<6 considerable contamination factor and Cf>6 very high contamination factor.

Based on obtained data the sediments of Viroi lake can be classified for all heavy metals in group 1 and 2 with low and moderate contamination.

Following classification was used based on Cdeg values: Cd < 8 low degree of contamination, 8 ≤Cd < 24 moderate degree of contamination, 24 ≤Cd <48 considerable degrees of contamination and Cd > 48 very high degree of contamination.

The calculated values of Cdeg for the sediments of Viroi Lake were lower than 8, which correspond to low degree of contamination.

In table 5 are shown the concentrations of heavy metals in water plants. The concentrations of heavy metals in the plants were significantly higher than WHO standard. The Iron (Fe) and Zinc (Zn) have the highest concentration than other determined heavy metals, whereas the Lead (Pb) was not detected in any plants. Lead frequently binds to phosphor in phosphate form (PO_4^{3-}). In these forms lead is extremely insoluble, and is present as immobile compounds in the environment. Lead compounds are generally soluble in soft, slightly acidic water [23]. Given that the sediments of Viroi lake are rich in phosphor, maybe this is the reason that Pb cannot be assimilate from plants. Furthermore, insolubility of Pb in the lake can be relates with the alkalinity of water [2].

The concentration of heavy metals in the plants were in the follwing order according to the analysed plant: B1BM (Fe>Zn>Ni>Cu>Cd>Cr and Pb not detected); B2BM (Fe>Zn>Cu>Ni>Cr>Cd and Pb not detected); B2BB (Fe>Zn>Cu>Ni>Cr; Cd and Pb not detected); B3B1R (Fe>Zn>Cu>Cr>Ni>Cd and Pb not detected); B3B1K (Fe>Zn>Cu> Cr>Ni; Cd and Pb not detected); B3B2R (Fe>Zn>Ni>Cr>Cu ;Cd and Pb not detected); B3B2K (Fe>Zn>Cu>Ni>Cr; Cd and Pb not detected). The heavy metals were determined in root and shoot part of the plants Alisma plantago-aquatica and Cyperus longus L. Obtained concentration values of heavy metals as Cu, Cd and Fe were higher in root parts and the others (Ni, Zn and Cr) were accumulated more in shoot parts of Alisma plantago-aquatica. Whereas, for Cyperus longus plant, all determined heavy metals were accumulated more in the root parts.

The heavy metals Cd, Cr, Fe, Pb, Cu, Zn and Ni in plants, must have a concentration higher than 100 mg/kg, 1000 mg/kg, 10000 mg/kg, 1000 mg/kg, 1130 mg/kg, 1320 mg/kg and 4683.76 mg/kg respectively, in order to be defined as hyperaccumulator plants **[22]**. Therefore, based on our data these plants cannot be classified as hyperaccumulators, but they can help water ecosystem to remove heavy metals.

The BCF factor was calculated to understand the possible role of water plants in phytoremediation process. In the Table 6 are presented the calculated BCF factors values of different plants. The BCF factors were lower than 1, except Zn to B1BM (1.43) and Cu to B2BB (1.01). Based on these results can be concluded that the analyzed plants were not hyperaccumulators and the most important they cannot be considered as potential plants to the phytoremediation process of heavy metals from sediments.

Table 5. Concentration of heavy metals in water plants

Codes	Plants	Cr mg/kg	Cu mg/kg	Cd mg/kg	Pb mg/kg	Ni mg/kg	Zn mg/kg	Fe mg/kg
B1BM	*Ranunculusfluitans*	5,75	28,7	9,94	n.d	42,25	143,33	174,27
B2BM	*Fontinalis antipyretica*	2,549	20,88	0,269	n.d	10,2	56,38	253,71
B2BB	*Apium nodiflorum (L)*	16,4	44,09	n.d	n.d	17,73	76,87	3193,24
B3B1R	*Alisma plantago-aquatica***(root)**	5,16	15,3	0,0064	n.d	2,048	53,83	158,42
B3B1K	*Alisma plantago-aquatica***(shoot)**	6,323	10,91	n.d	n.d	5,82	64,66	102,72
B3B2R	*Cyperus longusL.* **(root)**	22,36	20,37	n.d	n.d	25,2	74,11	4885
B3B2K	*Cyperus longus L.* **(shoot)**	4,13	9,74	n.d	n.d	6,85	21,96	170,21
WHO STANDARD		**1.30**	**10**	**0.02**	**2**	**10**	**50**	**20**

Table 6. BCF factors of water plants

BCF plant/sediments							
	Cr	**Cu**	**Cd**	**Pb**	**Ni**	**Zn**	**Fe**
B1BM	0,075	0,65	0,84	0	0,26	1,43	0,0096
B2BM	0,034	0,47	0,022	0	0,065	0,56	0,014
B2BB	0,22	1,01	0	0	0,11	0,76	0,17
B3B1R	0,07	0,35	0,00054	0	0,013	0,53	0,0087
B3B1K	0,086	0,25	0	0	0,037	0,64	0,0056
B3B2R	0,3	0,46	0	0	0,16	0,74	0,27
B3B2K	0,056	0,22	0	0	0,043	0,21	0,0094
Average	0,12	0,48	0,12	0	0,098	0,69	0,069

4. Conclusions

The sediments of Viroi Lake were rich in Ni e Cd with higher values than ERM (Effect Range Medium), showing that the incidence of Cd metal in biological system was about 65.7%.

In the aquatic plants of the lake were found higher concentration of heavy metals than WHO standard, but these plants cannot be classified as hyperaccumulator plants based on BCF factor values. Therefore, these plants cannot be considered as potential plants to the phytoremediation process of heavy metals from sediments.

6. References

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