Thalassia Salentina
Thalassia Sal. 36 (2014), 35-42
ISSN 0563-3745, e-ISSN 1591-0725
DOI 10.1285/i15910725v36p35
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HEAVY METALS CONTAMINATION OF THE SEDIMENTS IN THE VIROI LAKE OF GJIROKASTRA DISTRICT ALBANIA

RIASSUNTO

La valutazione dei metalli pesanti presenti nei sedimenti degli ecosistemi idrici ha un ruolo importante nel determinare lo stato dell'inquinamento e la qualità di questi ecosistemi. Abbiamo preso 21 mostre da 7 posti di studio diversi e cinque metalli pesanti Cu, Cr, Ni, Pb e Cd sono stati analizzati nei sedimenti del lago di Virua, nella regione di Argirocastro, nel Sud d'Albania. Il contenuto totale dei metalli pesanti si è definito nelle frazioni <2mm tramite il spettofotometro ad assorbimento atomico. I valori medi dei metalli pesanti erano, Ni 198, 75 (± 113.2), Cr 86.36 (± 39.2), Cu 62.89 (± 40.1), Pb 59.69 (± 20.4), mentre il Cd non è stato definite. Questi valori seguono l'ordine Ni>Cr>Cu>Pb. Questi valori erano superiori ai valori raccomandati dal Consensus - basato negli orientamenti della qualità dei sedimenti di Wisconsin. Il livello dell'inquinamento dai metalli pesanti è stato calcolato basandosi sul fattore dell'arricchimento (Ef) e l'indice del geoaccumulazione. Il fattore di arricchimento (Ef) dei metalli nei sedimenti variava da 1.016 a 4.51. Questi valori dimostrano un arricchimento da minimo a moderato dei sedimenti in presenza di questi metalli. L'indice del geo-accumulazione (Igeo) variava da -0.56 a 1.59, il chè testimonia che questi sedimenti sono praticamente da non inquinati a mediamente inquinati . Nonostante ciò sono necessari degli studi ulteriori per specificare i metalli pesanti, la loro mobilità nella catena alimentare dell'ecosistema idrico.

SUMMARY

The assessment of heavy metals in the sediments of water ecosystems has an important role in determination of pollution status and in the quality of these ecosystems. Twenty one sediment samples were taken in seven sampling points and five heavy metals Cu, Cr, Ni, Pb and Cd were analyzed in the sediments of the Viroi lake in Gjirokastra district in the south of Albania. Total content of heavy metals was determined in fractions <2mm by atomic absorption spectrophotometer. The mean concentrations of heavy metals in the sediments were, Ni 198, 75 mg/kg, Cr 86.36 mg/kg, Cu 62.89 mg/kg, Pb 59.69 mg/kg, while Cd was not detected. These values followed the sequence Ni>Cr>Cu>Pb. These values were higher than the values recommended in Consensus-Based Sediment Quality Guidelines of Wisconsin. Level of sediment pollution with heavy metals is evaluated based on calculation of enrichment factor (Ef) and geo-accumulation Index (Igeo). Enrichment Factor (Ef) of heavy metals in sediments ranged from 1.016 to 4.51. These values showed that the sediments have minimal enrichment to moderate enrichment with these heavy metals. Geo-accumulation index (Igeo), ranged from -0.56 to 1.59, showed that these sediments are unpolluted to moderately pollute. Therefore, further studies on the speciation of heavy metals in order to evaluate their mobility in the food chains of water ecosystem are needed.

INTRODUCTION

Sediment is the loose sand, clay, silt and other soil particles that settle at the bottom of body of water (DAVIES and ABOWEI, 2009). Data from sediments can provide information on the impact of distant human activity on the wider ecosystem. Sediment analysis is important in evaluating qualities of total ecosystem of a body of water in addition to water sample analysis practiced for many years because it reflects the long term quality situation independent of the current inputs (ADEYEMO *et al.,* 2008) and it is the ultimate sink of contaminants in the aquatic system (DAVIES and ABOWEI, 2009). Monitoring of the contamination of sediments by heavy metals is very important, because heavy metals may accumulate to toxic levels in water ecosystems without any visible signs. This study aims to analyze concentrations of heavy metals in sediments of Viroi lake in Gjirokastra district in south part of Albania and to evaluate the degree of sediments pollution with these metals.

MATERIAL AND METHODS

The study site

Viroi lake have a surface area of 17 ha. It is located in northwest and 3 km faraway from Gjirokastra district in south part of Albania, on the left of national road Gjirokaster – Tepelene. It has a karstic source called "Mother of Viroi", with a flow of 17 m^3/second and the yearly average temperature is 13-14°C. The area is characterized by continental climate with hot summer which affects the partial drying of this lake, thus causing direct impact in human and natural activities in the sediment of lake (Fig. 1).

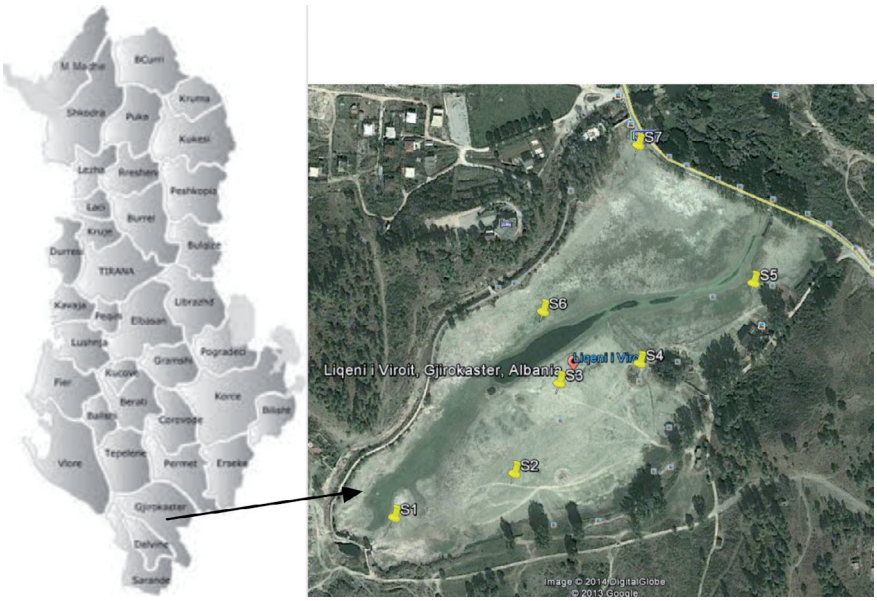

Fig. 1- The study area in Viroi lake

Sampling methods and sample analysis

Sediment samples were collected during August 2012 at a depth of 0-15 cm in 7 sampling points, of the Viroi lake, with three replicates, in total 21sediment samples. All sediment samples were air dried, sieved with a 2 mm sieve and the fractions samples < 2mm were used to analyze the total concentration of Cd, Cr, Cu, Ni and Pb. For the determination of the heavy metals 0.3g sediment samples were mixed with 8 ml HNO_3cc acid and 2 ml H_2O_2 33%. The mixture of samples was carried in microwave for 25 minutes in 180°C. The concentrations of heavy metals were determined by atomic absorption spectrophotometer (AAS).

Data statistic elaboration

Level of sediments pollution with heavy metals is evaluated based on comparison with the values recommended in Consensus-Based Sediment Quality Guidelines of Wisconsin, calculation of enrichment factor (Ef) (LI YU e*t al*., 2008) and geo-accumulation Index (Igeo) (HUU *et al*., 2010). Enrichment factor is calculated using the following formula:

Ef=metal content in a given soil/metal content in earth crus**t** (1)

In this study, contents of Cd, Cr, Cu, Ni, Pb in earth crust are taken from Rudnick and Gao (2005).

While, geo-accumulation index is calculated using the equation:

Igeo= log2 (metal content
in a given soil/metal content in the earth crust *1.5) (2),

when 1.5 is used to compensate for possible variations of the reference data due to lithogenic effects.

RESULTS AND DISCUSSIONS

Total contents of heavy metals in the analyzed sediments are shown in (Tab. 1).

Tab. 1- Total heavy metals contents in sediment samples

Sampling sites	Ni mg/kg	Cr mg/kg	Pb mg/kg	Cu mg/kg
VL/S1_1	45,70	42,72	45,58	23,38
VL/S1_2	45,22	43,19	52,98	17,82
VL/S1_3	25,45	37,21	48,20	8,67
VL/S2_1	161,94	75,88	57,08	42,67
VL/S2_2	189,77	77,12	51,62	48,89
VL/S2_3	193,02	88,58	45,44	46,50
VL/S3_1	156,24	58,54	51,08	82,20
VL/S3_2	183,06	70,90	59,18	102,40
VL/S3_3	191,05	70,41	74,36	98,64
VL/S4_1	318,30	116,37	46,71	68,51
VL/S4_2	61,26	112,95	138,53	40,72
VL/S4_3	286,49	115,30	42,52	66,30

VL/S5_1	181,88	97,62	46,22	34,65
VL/S5_2	167,81	99,91	50,57	30,49
VL/S5_3	149,82	85,09	57,11	34,71
VL/S6_1	404,26	154,26	59,04	141,51
VL/S6_2	410,50	156,35	75,23	138,74
VL/S6_3	406,56	153,69	73,28	139,86
VL/S7_1	214,02	8,64	55,27	48,35
VL/S7_2	211,41	80,55	63,93	62,61
VL/S7_3	170,11	68,28	59,58	43,18
Mean	**198,75**	**86,36**	**59,69**	**62,89**
STDEV	**113,27**	**39,27**	**20,43**	**40,15**
Maximum	**410,50**	**156,35**	**138,53**	**141,51**
Minimum	**25,45**	**8,64**	**42,52**	**8,67**

Heavy metals content, expressed on mg/kg, were as follow: Cr (8,64-156,35), Ni (25.45-410.50), Cu (8.67-141.51) and Pb (42.52-138.53), whereas Cd was not detected. The higher values of Ni, Cr and Cu are shown in station VL/S6 and for Pb in VL/S4.

Tab. 2 - Comparisons between heavy metals of this study and metals according Consensus-Based Sediment Quality Guidelines of Wisconsin

	Metal Consensus-Based sediment value (mg/kg dry wt)	Mean values of heavy metals in the sediments of Viroi lake (mg/kg dry wt)
Cadmium	0,99	not detected
Chromium	43	86,36
Copper	32	62,89
Lead	36	59,69
Nickel	23	198,75

The mean concentrations of heavy metals in the sediments of Viroi lake were higher than the values recommended in Consensus-Based Sediment Quality Guidelines of Wisconsin (CBSQG) [WISCONSIN DEPARTMENT OF NATURAL RESOURCES, 2003], as it is shown in (Tab. 2). Only Cd was not detected. CBSQG applies to biologically active zone associated with deposited sediments in flowing (streams and rivers) and static (lakes and ponds) water bodies and wetland soils and sediments (OLUBUNMI *et. al.*,

2010). In the absence of other study, these values as preliminary data, may be naturally higher or can have the contributions of the anthropogenic origins.

The results of the calculation of Enrichment Factor (Ef) of heavy metals in sediments in Viroi lake is shown in (Tab. 3). Enrichment factor (Ef) can be used to differentiate between the metals originating from anthropogenic active (OLUBUNMI *et. al.*, 2010). As the EF values increase, the contributions of the anthropogenic origins also increase (SUTHERLAND, 2000).

Level of sediments pollution is determined based on the following categorization of Ef index (HUU *et al.*, 2010)

1) Ef ≤1 no enrichment
2) 1 < Ef ≤3 minimal enrichment
3) 3 < Ef ≤5 moderate enrichment
4) 5 < Ef ≤10 moderately severe enrichment
5) 10 < Ef ≤25 severe enrichment
6) 25 < Ef ≤50 very severe enrichment
7) Ef > 50 extremely severe enrichment

Tab. 3 - Ef in the sediments of Viroi lake

Heavy metals	Ni mg/kg	Cr mg/kg	Pb mg/kg	Cu mg/kg
Mean values	198,75	86,36	59,69	62,89
Ef	4,51	1,016	3,51	2,15
Category of pollution	III	II	III	II

Enrichment factor of heavy metals in sediments of Viroi lake showed that Cr (1.016) and Cu (2.15) have minimal enrichment but Ni (4.51) and Pb (3.51) have moderate enrichment.

Index of Geo-accumulation (Igeo) has been used widely to evaluate the degree of metal contamination or pollution in terrestrial, aquatic and marine environment (TIJANI *et al.,* 2009).

The degree of metal pollution in the sediments of Viroi lake is assessed in terms of seven contamination classes based on the increasing numerical value of the index as follows: (HUU *et al.*, 2010)

1) Igeo <0 = means unpolluted
2) 0<=Igeo<1 means unpolluted to moderately polluted
3) 1<=Igeo<2 means moderately polluted
4) 2<=Igeo<3 means moderately to strongly polluted
5) 3<=Igeo<4 means strongly polluted
6) 4<=Igeo<5 means strongly to very strongly polluted
7) Igeo>=5 means very strongly polluted.

Tab. 4 - Igeo in the sediments of Viroi lake

Heavy metals	Ni mg/kg	Cr mg/kg	Pb mg/kg	Cu mg/kg
Mean values	198,75	86,36	59,69	62,89
Igeo	1,59	-0,56	1,22	0,73
Category of pollution	III	I	III	II

The values of Igeo as it is shown in (Tab. 4) result that, sediments of Viroi lake were unpolluted with Cr (-0.56), unpolluted to moderately polluted with Cu (0.73) and moderately polluted with Ni (1.59) and Pb (1.22). In comparison with other studies in Albania about the pollution level of rivers sediments (GJOKA *et.al,* 2010), the values of heavy metals in Viroi lake were lower for Cr, Cu and Ni but higher for Pb. Thus, can be assumed that Pb element in these sediments can be originated from human activities, urban waste, air polluted with emitted Pb by vehicles that drive in the national road near to the study area.

CONCLUSIONS

This study gives the preliminary data about heavy metals in sediments of Viroi lake. The mean concentrations of Ni, Cr, Cu, and Pb were higher than the values recommended in Consensus-Based Sediment Quality Guidelines of Wisconsin, whereas Cd was not detected. The enrichment factors calculated for the heavy metals showed that the enrichment of the heavy metals ranged from minimal enrichment to moderate enrichment. The Geo-accumulation Index calculated showed that the pollution status ranged from unpolluted to moderately pollute. Further research has to be carried out to determine the concentrations of heavy metals in soil around lake, sediments, water and water plants of Viroi lake to determine mobility of heavy metals in food chain and to evaluate the origin of higher concentrations of heavy metals in sediments.

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