Int. J. Chem. Sci. : 2 (1), 2004, 101–107

AN EVALUATION OF HEAVY METALS CONTENT IN ORIKUM, DUKATI BAY ION SEA–ALBANIA

P. LAZO, F. LUBONJA, A. SHEHU and L. PJESHKAZINI

University of Tirana, Faculty of Natural Sciences, Department of Chemistry, TIRANA, ALBANIA
e–mail : *veralazo@albmail.com*

ABSTRACT

An evaluation of heavy metals and mercury content in seawater, sediment, biota and plant samples of Orikumi area, located in Dukati Bay, Ion Sea is given. Some geological considerations and normalisation procedures are used to explain the anthropogenic–input fraction of heavy metals in this bay. It is clearly demonstrated that the miss of industrial activities, notably affect to the purity of this area, pointed as an important tourist area of Albania.

Keywords : AAS, Heavy metals, Seawater, Sediments, Background levels, Normalisation

INTRODUCTION

Dukati Bay, positioned in South part of Vlora Bay is located just on the border of Ion Sea and Adriatic Sea. Heavy metals and Hg content in surface water, sediments, plants, and biota were measured during the period February–May 2003. Samples were collected on the end of February in five stations of Orikumi area. Whole digestion method was used for chemical analyses of sediment samples. 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 evaluated and on which dredging and dumping regulations are based[1,2]. All analytical results are reported on dry weight basis.

All the stations are located on suitable places such as beach, urban place, as well as near a military port and military area where a landfill of submarine alkaline batteries exist.

Description of the area[3]

Dukati Bay is located just on the border of Ion Sea and Adriatic Sea. Geological composition of terrestrial part consists mainly in carbonates formations on the West, followed by carbonates (about 90%), gritty and pudding stones (≈ 10%) on the East. Chemical analysis of carbonates of this area is given in Table 1.

Table 1 : The chemical analysis of carbonates of Karaburuni area[3] (% in dry weight)

Element	CaO	MgO	Al_2O_3	Fe_2O_3	SiO_2	SO3
Content (%)	55.8	0.2–0.4	0.12	0.00	0.02–0.4	0.00

MATERIALS AND METHODS

Seawater samples were conserved on 500 mL PET bottles. After filtration in green filter were acidified with 5 mL HNO_3 solution and stored at –5°C.

Sixteen surface (grab) sediment samples (4 for each station), 15 (three for each station) seawater samples, 5 plants and 2 biota samples was carried out in 5 different stations. The fractions smaller than 2 mm of sediment samples are well homogenized by grinding in agate mortar until all material is going through a 200 μm nylon sieve. Sub sample for mercury determination is dried at 50–60°C and sub sample for determination of other parameters is dried at 105°C. After drying, the samples for chemical analyses are stored in airtight plastic vials until required for future use.

Biota and plant samples was carefully washed with full distilled water for several times, till the water remain clear, dried at room temperature for 2 days, grinded by an electric grinder, dried again at 60°C for 3 hours.

Sample treatment and element determination

Analytical procedure of seawater samples

Seawater samples were first photo–oxidized for 20 min through a 110 W UV lamp (halogen lamp). After preconcentration on CHELEX (500 mL seawater and 1 g CHELEX was taken in a 1000 mL beaker and stirred for 4 hours thorugh a magnetic stirrer). Heavy metals from CHELEX were back extracted by 50 mL diluted HCl (pH = 1). Flame AAS technique is used for Zn determination; ETAAS system is used for Fe, Pb, Ni, Co, Mn, Cd and Cu determinations; CVAAS system is used for mercury determination[4]. All measurements were performed using Varian Plus 10 AAS instrument.

Analytical procedure of sediments

Total decomposition method using hydrofluoric acid in combination with concentrated oxidizing acids HNO_3 and $HClO_4$ is used[1,5,6]. Open teflon beakers were used for digestion procedure by heating at 250°C. Flame AAS system is used for Fe, Cr, Zn, Ni, Mn and Cu determinations, ETA–AAS system is used for Pb and Cd determinations and CVAAS system is used for Hg determination. IAEA–405 reference material is used for quality control of analysis in sediments.

Analytical procedure of biota and plants

HCl : HNO_3 = 3 : 1 digestion procedure[5] is used for biota and plant samples digestion in half pressure vessels. Digestion is carried out by putting the closed vessels for 5 days at room temperature; by gradually heating first at 80–90°C for 2 hours and then for 3 hours at 250°C. Flame AAS system is used for Fe, Zn, Ni, Mn and Cu determinations, ETA–AAS system is used for Cr, Pb and Cd determinations and CVAAS system is used for Hg determination.

Method of mercury determination

A 0.3–0.5 g sub sample is treated with a mixture of HNO_3 + HCl (9 : 1) on a hot plate at 70–80°C for 3 hours in closed PTFE vessels. After cooling, 1 mL of 5% $K_2Cr_2O_7$ is added and water up to 50 mL to Cold Vapor Atomic Absorption Spectrometry (CV–AAS) is used for Hg determination. Measurements were implemented using a home–constructed schema having sensitivity about 0.2 ppb Hg[4,7]. All reagents used for mercury analyses are "low in Hg" quality (from Merck).

Quality assurance of the data

A reference certified material (IAEA 405) was analyzed at the same time with sediment samples of studied area. It could be noticed that data obtained were in good agreement with certified values.

RESULTS AND DISCUSSION

The content of heavy metals in seawater

Five water samples (W1 to W5) collected from each station were analyzed. The content of heavy metals in seawater samples are given in Table 2.

Table 2 Content of heavy metals in seawater samples (μg/L, *ng/L)

St.	Sample	Cu	Zn	Fe	Hg*	Pb	Ni	Mn	Co	Cr	Cd
St. 1	W1	0.660	0.310	0.147	0.085	0.532	1.852	0.112	0.012	0.535	0.042
St. 2	W2	0.478	0.275	0.328	0.091	0.573	1.351	0.134	0.012	0.685	0.015
St. 3	W3	1.216	0.353	2.866	0.118	1.057	1.438	0.432	0.031	0.505	0.055
St. 4	W4	0.744	0.304	0.966	0.086	0.439	1.927	0.076	0.011	0.263	0.025
St. 5	W5	0.819	0.306	0.203	0.101	0.558	1.843	0.082	0.021	0.252	0.021

Heavy metal concentrations found in seawater samples were generally close to the results obtained from monitoring implemented during 1992–1996 in the framework of MED POL II Programme of Mediterranean Action Plan of UNEP[8], but lower than the values published by us for Durres and Vlora Bay–Adriatic Sea[9,10]

The content of heavy metals in surface sediment samples

At it is expected, the highest content of heavy metals in water and sediment samples were found only in station 3, the channel running from Orikumi Logoon area. From our results and also from other studies published[8, 11-13] for Albanian seacost sediments and Mediterranean Sea could be underline some high contents of Cr and low content of Fe compared to the sediments from other areas of Meditarranean Sea. Assuming that trace metals found in sediments through total digestion procedure are very low. It is due to carbonate sediments behaviour of the area[3]. These concentration level of heavy metals are normal concentrations for carbonate sedimentary rocks as reported from Williams[15].

Very high correlation of heavy metals in sediment samples and between sediment and seawater samples were found ($r > 0.9$). Different values of linear correlation coefficients ($r = \pm 0.n$, where $n = 1 \div 9$) were found for heavy metals in seawater, biota and plant samples. This high correlation values for heavy metals in sediment samples, may be due to only precipitation process of heavy metals from seawater and not related with geology of the area.

Table 3 The mean concentrations of HM in sediment samples (in mg/kg DW, * ng/kg)

St.	Sample	Cu	Zn	Fe	Hg*	Pb	Ni	Mn	Co	Cr	Cd
St. 1	Sed 1	13.51	5.49	599.4	0.089	16.83	13.38	122.9	1.53	336.5	0.065
St. 2	Sed 2	1.21	5.61	595.6	0.107	28.42	11.10	157.3	0.94	595.61	0.056
St. 3	Sed 3	74.20	115.1	3694.2	0.632	90.74	73.69	688.1	7.77	3992.7	0.134
St. 4	Sed 4	10.45	9.49	591.0	0.096	21.31	10.34	179.7	1.12	591.08	0.064

Results of chemical analyses ; biota and plant samples

Accumulation of heavy metals from acquatic biota is a suitable tool for monitoring average load. We found only two different algae; one in station 3 (channel) and one other in station 3 (Radhima) in March 2003, so it seems to be difficult having any conclusion only with two samples. Neverthless, heavy metals content in biota is given in Table 4.

Table 4 Heavy metals content in biota samples (in mg/kg DW) (* Hg in μg/kg. DW)

Name	Station	Cu	Zn	Fe	Hg*	Pb	Ni	Mn	Co	Cr	Cd
Halidrys Siliquose	St. 3	3.40	17.02	217.1	0.14	0.53	0.64	124.44	0.105	5.18	0.08
Posidomic	St 4	2.609	9.75	353.7	0.18	0.65	0.69	173.04	0.093	3.39	0.13

Due to small number of samples and the fact that some algae species are able to accumulate heavy metals in their tissue and some other not, it was difficult to find any relation between heavy metals content in water and in biota. Most characteristics plants grown up only about 5 to 50 m far from the coast were collected. Heavy metals content in plant samples is given in Table 5.

Table 5 Heavy metals content in plant samples (in mg/kg. DW) (* Hg in μg/kg, DW)

Name	Station	Cu	Zn	Fe	Hg*	Pb	Ni	Mn	Co	Cr	Cd
Juncus acutus	St 1	1.24	9.28	8.9	0.155	0.669	0.641	79.56	0.025	4.84	0.103
Phlomis Fruticosa	St 1	7.38	23.96	438.3	0.213	0.803	0.469	168.55	0.083	3.76	0.101
Cardus pycnocephal.	St2	1.29	9.69	296.4	0.158	0.799	0.605	178.24	0.013	5.90	0.183
Graminae	St 3	10.38	33.21	683.4	0.174	0.514	0.862	273.03	0.113	3.85	0.105
Kladofora	St 3	4.47	22.33	2961.1	0.271	0.575	0.992	288.67	0.161	14.13	0.1432

Due to small number of samples and the fact that plants appear different abilities on heavy metals accumulation, it was difficult to find any relation between heavy metals content in sediment and plant samples of stations 1, 2 and 3, but as generally was found for the samples of other nature collected on the same station, the highest content of heavy metals concentration was found in samples grown up in station 3.

Normalization procedures in sediment samples

Special normalization procedures are necessary to carry out for the separation of anthropogenic and natural contaminants in sediments. We have tried to implement a geochemical normalization of the data obtained for our samples aiming to reduce the element variability. There are some normalization procedures recommended in the specialized literature[1, 2, 14], but some of them need data on background values of elements in sediments of them study area (calculation of so–called "index of geoaccumulation, I_{geo}" and "enrichment factor RE"). Because of lack of such data, we used metal : reference metal normalization procedure, selecting aluminium as reference metal, because it is not present in anthropogenic inputs from chemicals in this area, without industrial activity and far from urban centers, or agricultural activity. Another reason of selecting aluminium as reference metal, not iron or lithium, is the carbonates nature of the area, with very low content of Fe (less than 0.0%)[3] and the possibility of Li contamination from landfill of submarine alkaline batteries. Results of simple mathematical normalization using iron as reference element are presented in Table 6.

Table 6. Results of mathematical normalization using aluminium as normalizing element for surface sediment samples (Me/Al ratio, fraction 0.063 mm)

St.	Sample	Cu	Zn	Fe	Hg*	Pb	Ni	Mn	Co	Cr	Cd
St. 1	Sed 1	0.011	0.0046	0.499	7.4E–05	0.014	0.011	0.102	0.0013	0.2804	5.4E–05
St. 2	Sed 2	0.009	0.0047	0.496	8.9E–05	0.024	0.009	0.131	0.0008	0.4963	4.7E–05
St. 3	Sed 3	0.062	0.096	3.078	0.00053	0.076	0.061	0.573	0.0065	3.3273	0.00011
St. 4	Sed 4	0.009	0.0079	0.492	0.00008	0.018	0.009	0.150	0.0009	0.4926	5.3E–05

From the data listed above, the values of Me/Al ratios are very small for all heavy metals of all stations. Some higher values compare with other stations, were found in station St 3. Station 3 presented as a polluted sample for most of elements compared with seawater samples, but it affected from Orikumi Lagoon, so these higher values of Me/Al ratio should be normal, too, also for this station.

CONCLUSIONS

Due to carbonates behaviour of the area, very low content of Fe was found, too, compared with other parts of Albanian seacost sediments. Some high contents of Cr, Ni and low concentrations level of Zn were found, compared to the sediments from other areas of Mediterranean Sea. High linear correlation coefficients of heavy metals in sediment samples, and between sediment and seawater samples were found. May be it is due only to precipitation process of heavy metals from seawater and not related with geology of the area.

The values of Me/Al ratios are very small for all heavy metals of all stations. Some higher values compared with other stations, were found in station St 3. It is related with the influence of Orikumi lagoon, so these higher values of Me/Al ratio should be normal, too.

REFERENCES

1. UNEP/IOC/IAEA : Manual for the geochemical analyses of marine sediments and suspended particulate matter. Reference Methods for Marine Pollution Studies No. 63, UNEP (1995).
2. M. Davies : Guidelines for the use of sediments for marine pollution monitoring programmes, Aberdeen, Scotland (no year of publication)
3. B. Ostrosi, A. Grazhdani, et al., Industrial Levels of Albanian Minerals, Monography, University of Tirana, Faculty of Geology and Miner Sciences, (1999) pp. 396–461, 582.
4. P. Lazo and A. Cullaj, Anal. Bioanal. Chem., **374(6)**, 1034 (2002).
5. UNEP/IAEA Reference Methods for Marine Pollution Studies No. 27, 31, 33, 34, 35, 37, 38 and 39
6. B. Welz, Atomic Absorption Spectrophotometry, VCH Publishers, Weinheim, (1985).
7. UNEP/IAEA Determination of total mercury in marine sediments and suspended solids by cold vapour atomic absorption spectrophotometry. Reference Methods for Marine Pollution Studies No. 26, UNEP (1985).
8. UNEP–MAP, Long–term Programme for Pollution Monitoring and Research in the Mediterranean Sea (MED POL – Phase II). Agreement between the Government of Albania and UNEP (1992).
9. P. Lazo, J. Environ. Protec. Ecol., **3**, 625 (2001)

10. Lazo, A. Cullaj and B. Baraj, J. Phys. IV France, **107**, 715 (2003).
11. V. Celo, D. Babi, B. Baraj, and A. Cullaj, Water, Air and Soil Pollution, **111**, 235 (1999).
12. A. Cullaj, V. Celo and D. Babi, J. Environ. Protect. Ecol., **1**, 81 (2000).
13. D. Babi, V. Celo, A. Cullaj and A. N. Pano, Fresenius Envir. Bull., **7**, 577 (1998)
14. D. H. Loring and R. T. T. Rantala, Earth Sci. Rev., **32**, 235 (1992).
15. L. Williams, D. B. Aulenbach and N. L. Clesceri, Aqueous Environmental Chemistry of Metals, Ann. Arbor Science Publishers, (1974), Chap. 2, pp. 77–127.

Accepted : 2.9.2003