



EVALUATION OF HEAVY METALS IN WATER AND SEDIMENTS OF ADRIATIC SEA

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SYNOPSIS

The study was carried out during the year 2007. The aim was to evaluate the content of heavy metals on water and the sediments on the seashore of Adriatic Sea. It was focused on two different areas of Adriatic coast, in Durres, (Porto-Romano, Bishti i Palles) and in Vlora (the bay closed to the ex industrial area). The sampling points on water and sediment were appointed according to the known methods. They were picked up in different distances from the sea coastal line. The samples were analyzed on the laboratory of the Agency of Environment and Forest in Tirana, Albania and GEO-test Company, Czech Republic. The heavy metals were analyzed by atomic absorption spectrometry.

The results showed that heavy metals are concentrated more in sediment than on water. The study demonstrated that Hg. Was in high values in water and sediment in Vlora area.

INTRODUCTION

The environment is everything that surrounds us, air, water, land and all living beings. It changes constantly as a result of natural and human activities. The balance between human and natural activities has been broken. Human and natural affects change the environment constantly. One of these changes is the pollution. Actually, the pollution is a global problem. The pollution is everywhere on air, land, water and these contaminate food and they cause the public health risk as well as.

There are official results about the chemical remnants on the environment and animal origin food. The evaluation of them is an immediate obligation to save our health, animals and contaminated ecosystems.

The reasons of the pollution are various, they have been the reason of lots of studies by different environmental organizations, associations etc. One of them is the United Nations Environment Programme (UNEP) that has diagnosed the most polluted areas in Albania, so called "hot spots" (UNEP 2000). There are the water polluted areas near the hot spots as well as. This means that the fish and all watery animals

are contaminated, too. The water pollution is result of releasing of fluid toxic substances, urban and industrial remains, or accidental discharges. The water organisms absorb and accumulate these components more than their concentrations in aquatic environment. (Nixon, E et al.1994). The main aim of this study is to evaluate the level of the pollution in water and sediment of Durres and Vlora coast.

MATERIAL AND METHODS

The study was carried out in the period April – July 2007. There were evaluated heavy metals such as Mercury (Hg), Chromium (Cr), Cadmium (Cd), and Lead (Pb).

The points of study were Durres coast (Porto Romano and Bisht Palle area) and Vlora coast (ex PVC factory). The samples were collected in 5 different points to every target area: 5 water and 5 sediment samples in Durres and the same in Vlora. There were collected 2 samples of water in every point of study. We measured the temperature in surface and the deep into water before collecting the samples.

The points of sampling in Durres were: outlet of hidrovor, - the new oil cistern port, Bisht Palla, - Ciklori, - Kallmi, - Currila;

In Vlora: - old port, - dipped ship, - in front of the ex PVC plant, - near the lighthouse, - fishing port. The water samples were taken using the equipment of water sampling (fig. 1). The water sample was of 500 ml, gathered in glass bottles.

The collecting of sediment samples was carried out in 5 points, one sample for each point, and they were collected with a motorboat. The sediment samples were taken by the Eckman grab (fig. 2, the weight of each sample was 200 g.

There was taken the proper notes of each collecting. The samples were labelled and conserved to a cold place after collecting. The sediment samples were inserted in plastic airtight sachets and they were transported to lab (Bernhard, M. 1976, 1986).



Fig. 1 Equipment of water sampling



Fig. 2 Eckman grab

Analytic procedures

The water samplings were conserved in sterile plastic bottles and treated with nitric acid with a concentration 1 ml/ 1 litre water. Before the analyzing the water was filtrated with green filter with the aim to separate all the inert material that can indicate in the result.(UNEP 1993). Seawater samples were photo-oxidized for 20 min. and they were preconcentrated for 72 hours in a Chelex column, cleaned with diluted HCl. There was used Cold Vapor Atomic Absorption Spectrometry (CVAAS) for the evaluation of Mercury, the evaluation of cadmium and lead were carried out by ETA-AAS system, the chromium was evaluated with the spectrometer PYE Unicam SP6. The measurements were defined with the AAS instruments variant +10 (UNEP/IOC/IAEA 1995).

Fraction sediment, smaller than 2 mm, were homogenized by grinding in agate until all material is going up 200 µm. Sub sample of mercury determination was dried at 50 – 60 °C and sub sample of the other parameter determination was dried at 105 °C. The fine grinding of sediment has a very important role in the examination of presence of heavy metals in sediments (Babi, D. and al.1998),.

For the solution of sediments was used the common procedures with HCL. For the examination of Cr was used the system AAS with fire. For the examination of Cd and Pb were used the system ETA-AAS, and for the examination of Hg, system CV-AAS (UNEP/IOC/IAEA. 1995)

The methodology for the examination of Mercury on the sediment

The procedures for the examination of Hg were based on the recommended methodologies. On portion of 0.3-0.5 g of sample was treated and mixed with HNO₃ + HCl in the portion 9:1 in one warm dish in the temperature 70-80°. It was conserved in the closed container PTFE for three hours. After the refrigeration in the solution was aded 1 ml K₂Cr₂O₇ and 50 ml water. One portion of solution was used for the examination of Hg with Cold Vapor Atomic Absorption Spectrometry (CV-AAS) (UNEP/IOC/IAEA. 1995).

RESULTS AND DISCUSSION

There were collected and analyzed 10 samples of water in 5 different points, in Durres and Vlora bay, to determinate the levels of the heavy metals in them. There were analyzed 4 heavy metals: mercury (Hg), chromium (Cr), cadmium (Cd) and lead (Pb). The data are shown in the below tables and figures. It is seen the level of the heavy metals changes in each sample (Tables 1, 2, and Fig. 3, 4,). The level of mercury in water varied from 0,010 µg/l to 0, 109 µg/l in Durres bay; it is determined from 0,007 µg/l to 0,242 µg/l in Vlora bay. This level is high, compare with other parts of our coast, but they are in norms, compare with other results in Mediterranean Sea (UNEP 1989; 1996; EEA, 2005). The difference between the samples is high because pollution sources are situated in these parts. The pollution of the water by mercury

could be result of the terrestrial pollution or of the geomorphologic structure. The samples 1 (Durres) and 2a (Vlora) are the highest polluted ones; so they represent the pollution of the areas where they were collected. There is determined a high level of mercury in the samples 1a, 2, 3, 3a, as well. On the other hand, samples 4a in Durres and Vlora have the lowest level of mercury. These results indicate us that the pollution is not only of terrestrial origin, but the geomorphologic origin, too. The comparing of mean values of Hg in the sea water in Durres (**0.082** and Vlora(**0.14** µg/l), with the values reported from the study for the Mediterranean sea 52 µg/l) Vega, M. 2005), show that the result for Durres and Vlora are in the same level with Mediterranean sea.

-Cadmium is a heavy metal affect on the quality of the sea water (ATSDR. 1989); its level in water is from 0.095 µg/l to 0,179 µg/l (Durres) and 0,094 µg/l - 0,193 µg/l (Vlora). The irregular distribution of this element show that it's origin can be from different source of contamination. They can be from terrestrial flooding or as a result of geomorphologic structure of the area around the Durres and Vlora bay. The comparing of the result of this study with the results of Mediterrenean sea (0.002-0.90 µg/l. Vega, M. 2005), the mean values in this study (**0.14** µg/l Durres and 0.15 µg/l in Vlora , show that this values are in the limits of the mean values of Mediterrenean sea or lower then its.

-Pb is a toxic metal and it's presence over the norm caused the poisoning and damage of aquatic fauna (Taylor & Francis. 1998);. Its presence is from 0.105 µg/l to 0.568 µg/l on the Durres bay and from 0.004 µg/l në 0.153 µg/l on Vlora bay. The presence of Pb on these level compared with the result in other part of our coast are lower (Lazo P. 2003), but compared with the result reported for Mediterranean sea are lower. Vlerat mesatare n[Durrs 0.26 µg/l dhe Vlor[0.086 µg/l jan[m[t[ul[ta se vlera mesatare e Pb n[detin Mesdhe 0.016 – 20.5 µg/l (;UNEP 1989; 1996; Jetic, L.M. 1990; Vega, M. 2005; EEA 2005).

-It is noticed that Chromium levels are high in samples picked up in the bay of Durres. This high level it is thought to be related to its presence in around area, its transition from superficial and underground waters on the sea and geomorphologic structure of the area. Its level varies from 0.569 µg/l till 3.876 µg/l (Durrës) and from 0.103 µg/l - 0.889 µg/l (Vlorë). These values are higher than they have been evaluated in different parts of Adriatic Sea. This high variance demonstrated inconstant content of chromium in water and its origin, as well as.

It is known the presence of chromium oddments in Porto Romano, like a stuff for the ex industry of the area. This oddment continues to be present actually, and it could be one of main sources of the pollution of sea water of area.

Heavy metal concentrations founded in this sample 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 (UNEP – MAP 1992)

Table 1. Heavy metals content in sea water (Durrës bay)

Nr. of samples	Hg	Cd	Pb	Cr
	µg/l			
1	0.109	0.179	0.568	2.972
1.a	0.108	0.168	0.543	3.654
2	0.102	0.156	0.364	2.785
2.a	0.107	0.16	0.321	2.069
3	0.101	0.167	0.174	3.876
3.a	0.106	0.148	0.162	2.986
4	0.094	0.115	0.105	0.811
4.a	0.01	0.095	0.106	1.057
5	0.057	0.132	0.124	0.764
5.a	0.025	0.112	0.11	0.569
Mean	0.082	0.14	0.26	2.15
Ds	0.037	0.028	0.18	1.27

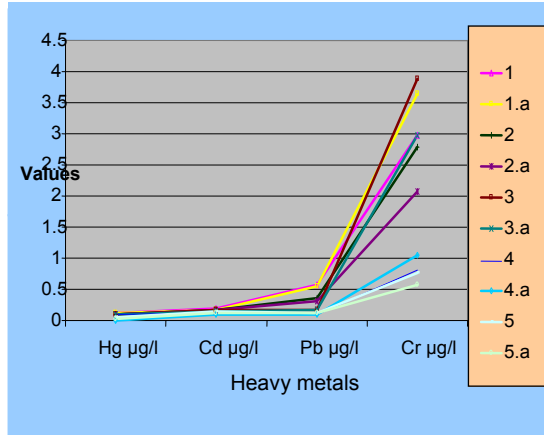


Fig. 3 Heavy metals distribution (Durrës bay)

Table 2. Heavy metals content in sea water (Vlora bay)

Nr. of samples	Hg	Cd	Pb	Cr
	µg/l			
1	0.242	0.187	0.129	0.756
1.a	0.221	0.193	0.153	0.889
2	0.198	0.179	0.098	0.512
2.a	0.287	0.177	0.156	0.876
3	0.201	0.175	0.135	0.891
3.a	0.169	0.154	0.143	0.874
4	0.017	0.094	0.021	0.117
4.a	0.007	0.102	0.018	0.109
5	0.009	0.103	0.007	0.103
5.a	0.018	0.101	0.004	0.108
Mean	0.14	0.15	0.086	0.52
Ds	0.11	0.041	0.065	0.37

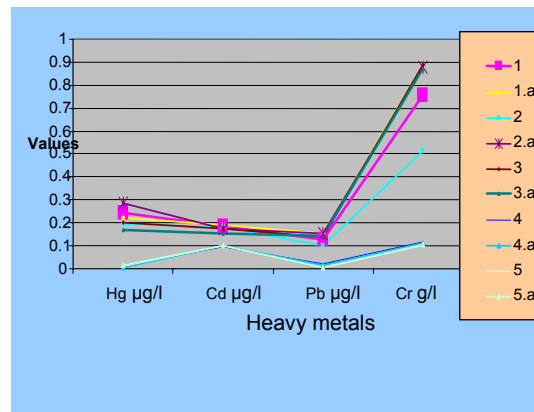


Fig. 4 Heavy metals distribution in sea water (Vlora bay)

Sediment evaluation

Sediments have been evaluated in 5 points, in different distances and depth to the seashore. The presences of the heavy metals in sediments are higher then in water, because of their process of accumulation on ground (Tables 3, 4 and Fig. 5, 6).

Table 3. Heavy metals content in sediments (Durrës bay)

Nr. of samples	Hg mg/kg	Cd mg/kg	Pb mg/kg	Cr mg/kg
1	0.107	0.051	12.328	231.12
2	0.105	0.53	20.352	323.4
3	0.294	0.012	58.64	352.17
4	0.062	0.032	22.24	126.16
5	0.101	0.079	21.13	114.21
Mean	0.13	0.14	26.94	229.41
D S	0.091	0.22	18.15	109.36

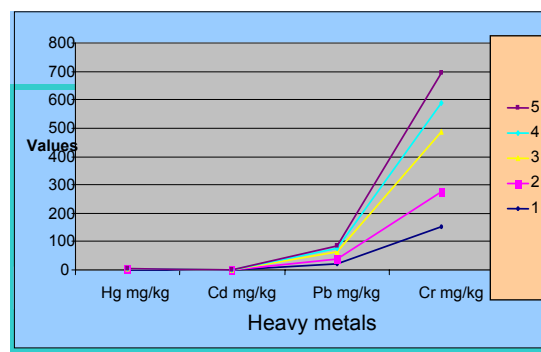


Fig. 5 Heavy metals distribution in sediments (Durrës bay)

Table 4. Heavy metals content in sediments (Vlora bay)

Nr. of samples	Hg	Cd	Pb	Cr
	mg/kg			
1	1.73	0.24	21.8	154.14
2	2.007	0.21	17.33	122.09
3	1.23	0.32	25.51	211.15
4	0.42	0.13	10.12	101.02
5	0.24	0.11	10.23	106.00
Mean	1.13	0.2	16.99	138.88
Ds	0.77	0.084	6.87	45.42

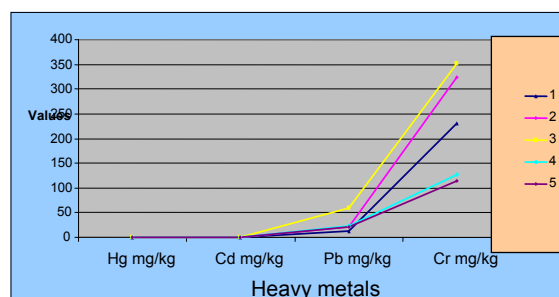


Fig. 6 Heavy metal distribution in sediments (Vlora bay)

It is clear that all target samples demonstrated high level of heavy metals, as we can see in the above tables and figures (Tables 3, 4, Fig. 5, 6). Hg varies from 0.101 mg/kg to 0.294 mg/kg (Durrës) and from 0.244 mg/kg to 2.007 mg/kg (Vlorë); these values are sometimes higher than they derived from other monitoring studies carried out in Adriatic and Mediterranean seas. Mean value of Hg (0.133 mg/kg) in sediments is lower in Durres, compared with mean value of Northern Adriatic Sea (0.24-0.60 mg/kg) (UNEP.1989 b, 1994, 1996 d; Vega, M. 2005). The result shows that there is the same situation from the last reporting of the other studies in Adriatic Sea (Babić D 1998; Cullaj et al 2000).

Mean value of Hg (Vlorë) (1.128 mg/kg) is higher than mean value in other part of Albania Adriatic coast (Celo. V 1999). For several points of sampling of Vlora bay there are reported the same conclusion also from the Czech company GEO-test.

(Prúša. J 2006). This contamination thought to be as a result of existing of resource of pollution in this area. A former plant of PVC has existed in it, the geomorphologic structure of the area and related to continuously flow bringing of Vjosa river can consider as potential sources of contamination of the sea water and the sediments. Table 4 shows clearly that pollution is not limited only near the former plants of caustic soda and PVC area, but there is evident the tendency of pollution distribution on the other parts of the bay. Winds, waves, and marine streams, can explain the migration of Hg in southwest part of the bay as well and the possible redistribution of it through migration and deposition in the deeper layers of sediments.

-The mean value of Cadmium (Cd) is 0.140 mg/kg (Durrës) and 0.20 mg/kg (Vlorë); mean values of Lead was 26.93 mg/kg in Durrës and 16.99 mg/kg in Vlorë. These values are higher, related to mean values reported from different studies carried out in Adriatic Sea (Cd - 0.047 mg/kg; Pb - 8.76 mg/kg); but these values aren't higher than their mean values in Mediterranean Sea (Cd 0.158 mg/kg and 25 mg/kg Pb) (Jeftic, L.M. , 1990; UNEP.1989 b, 1994, 1996 d; Vega, M. 2005). It is thought there aren't any source of these heavy metals pollution, but the risk of their presence depend of mineralogical consist of sediments, municipality discharges, industrial activity and flow bringing of Vjosa river in Vlora bay..

Chromium level is higher compared with the other heavy metals. Its mean values varies from 114.21 mg/kg till 352.17 mg/kg (Durrës) and 101.023 mg/kg - 211.152 mg/kg (Vlorë). The mean value (229 mg/kg, Durrës) is higher than mean values of it in Adriatic seashore (200 mg/kg) (UNEP.1989 b, 1994, 1996 d; Vega, M. 2005; EEA., 2005), but the compare with mean values on the Mati and Ishem river estuaries they are approximately the same or lower than in Durres bay (Celo. V 1999). This mean value is many times higher then in different points of (Hidrovorë). It show that chromium stocks in Porto Romano area have served such as main source of sediments pollution of Durres bay.

It's thought Chromium high level in Vlora is referred to be because of geomorphologic structure of area. The pollution of ex plant area is higher because of the its activity.

Statistical analysis of data (Stat Plus program, Anova 2007) demonstrated that differences are more evident between groups that within group. It is seen an evident correlation between Hg-Pb, (coefficient $r > 0.93$) and Hg-Cd, Cd-Pb, Cd-Cr and Pb-Cr mean coefficient 0.97.

CONCLUSIONS

Hg results in high levels, in water and sediments, in both areas. Hg values in water are higher in Vlora that Durres (0.287µg/l - 0.109 µg/l). Its level in marine sediments of Durres and Vlora is some times higher than values of different studies carried out in the other parts of Adriatic and Mediterranean Seas.

Mean values of Cd and Pb are higher in water and sediments in both of studied areas than they referred in different studies of Adriatic Sea, but lower that they referred to Mediterranean Sea.

Mean value of Cr in water is higher than Adriatic Sea referred values, in both of areas. High value of Chromium it is thought to be because of the stuff stocks of it in these areas.

High correlation exists between Hg-Pb ($r > 0.93$) and Hg-Cd, Cd-Pb, Cd-Cr and Pb-Cr with a mean coefficient $r = 0.97$.

It is thought there aren't any source of these heavy metals pollution, but the risk of their presence depend of mineralogical consist of sediments, municipality pours, industrial activity and flow bringing of Vjosa river.

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