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AN ASSESSMENT OF HEAVY METAL CONTAMINATION IN SURFACE SEDIMENTS OF THE MONTENEGRIN COAST USING GEOACCUMULATION INDEXES AND STATISTICAL ANALYSIS

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ABSTRACT

The aim of the study was to determine the levels and distribution of heavy metals in the sediments in the Montenegrin coast, and also to assess the extent of anthropogenic impact using geo-accumulation index (Igeo) and metal pollution index (MPI). Surface samples were taken from 10 locations. Grain size and trace element (Fe, Mn, Zn, Cu, Co, Ni, Pb, Cd, As and Hg) variations were analyzed, and MPI as well as Igeo calculated to understand the contamination level of the study area.

Key words: Sediment, Geoaccumulation index, Metal Pollution Index

INTRODUCTION

Pollution of the natural environment by trace metals has become a world-wide problem in recent years. Trace elements from natural and anthropogenic sources continuously enter the aquatic ecosystem where they pose a serious threat because of their toxicity, long time persistence and bioaccumulation (Loring, 1991). The impact of anthropogenic perturbation is most strongly felt by estuarine and coastal environments adjacent to urban areas. Like many other areas, the Montenegrin coast is also under a great impact of anthropogenic factors and the activities on shore. The Mediterranean Sea is an area where sediments have different geochemical composition: metal concentrations vary according to the area and are dependent on different inputs from the coastal environment. Sediments show a high capacity of accumulating and eventually integrating the low concentrations of trace elements usually found in water. In this paper, Co, Ni, Pb, Cd, Fe, Zn, Cu, Mn, As and Hg total concentrations have been determined in fraction (<63 μm) of ten surface sediments from Montenegrin coast (Southern Adriatic Sea), in order to increase the knowledge on metal levels in this area, which has not been studied in detail. The aim of this study was to determine the spatial and temporal variations of trace metal contamination on Montenegrin coast. We also evaluated the influence of anthropogenic activity on the composition of the surface sediments using metal pollution index (MPI) and geoaccumulation index (*I*geo) of metals. Geoaccumulation index has been calculated to assess sediment contamination and establish whether metals concentrations represent background levels for the Mediterranean Sea (Loska et al., 1997; Rubio et al., 2000; Ruiz, 2001).

MATERIALS AND METHODS

Study area

Samples were collected at ten selected locations in Montenegrin coastal area: Sveta Stasija, Kukuljina and Herceg Novi in the semi-enclosed Boka Kotorska Bay, and on the coastline of open sea at Žanjice, Mamula, Bigova, Budva, Bar, Rt Đeran and Ada Bojana, situated in the proximity of different geochemical, hydrological and human impacts (Figure 1).

Boka Kotorska Bay is on the northern coast of Montenegro with a mouth 2.95 km in width and an in-land length of 28.13 km, surrounded by mountains, with 75000 inhabitants on the Bay coast. Sveta Stasija is located in a small Kotor bay near Kotor, a city where a previous galvanization plant discharged used galvanization baths directly into the sea, between 1965 and 1991. Herceg Novi was/is a favored tourist city with a marine, shipyard and food industry. The beach Žanjice with hotels and cottages is situated close to the entrance of the Bay. Budva is an urban, tourist and industrial city suited in the middle of the Montenegrin coastline with 18000 inhabitants. The harbor of Bar is on the south of the Montenegrin coastal area with 15000 inhabitants. Bar was an important industrial harbor in former Yugoslavia, the biggest on the eastern side of Adriatic, especially for crude oil and oil products traffic, and still is. The problem of pollution in the vicinity of these sites increases in the fall periods because of the summer tourist seasons and increased discharge of wastewater directly into the sea.

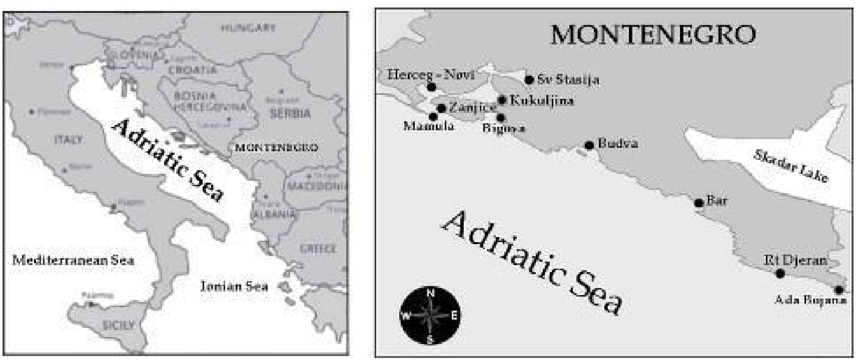

Figure 1. The map of researched area

Sampling method, sample preparation and trace metals analyses

Approximately 500 g of surface sediment samples (~5 cm depth) were collected at low tide from ten stations strategically distributed along the Montenegrin coastline (Figure 1). Sampling was carried out in autumn 2005. Sediments were collected using an internal diameter plastic gravity corer, put into clean plastic bags and taken to the laboratory. Once in the laboratory, the sediment samples were frozen and then lyophilized in a Martin Christ apparatus. Finally, samples were sieved to assure a maximum particle size of 65 μm and kept in the refrigerator at 4 ˚C until analysis.

Table 1. Metal concentration (μg g^{-1} dry weight) and recovery in certified marine sediment (IAEA-158)

Element	Certified value	Found value	Recovery (%)
Co	9.0 ± 1.35	10.1 ± 1.5	112
Ni	29.4 ± 4.12	31.0 ± 0.72	105
Pb	38.0 ± 7.7	35.0 ± 3.9	92
As	11.4 ± 1.71	12.6 ± 0.91	110
Cd	0.37 ± 0.09	0.45 ± 0.005	120
Hg	0.132 ± 0.017	0.12 ± 0.018	90
Fe	25.8 ± 2.58*	24.0 ± 1.9*	93
Zn	138 ± 13.2	131 ± 7.8	95
Mn	350 ± 3.8	326 ± 4.1	93
Cu	47.9 ± 5.27	45.5 ± 4.7	95

*g kg^{-1}

Total metals (Co, Ni, Pb, Cd, Fe, Zn, Cu, Mn, As and Hg) were determined using atomic absorption spectrometer equipped with a deuterium-are background corrector and Perkin Elmer MHS-10 hydride generator were used after acid digestion of sediments in a microwave oven. Dry sample (about 0.5 g) were digested with 2 ml of HNO_3 (65%), 6 ml HC1 (37%) in a microwave digestion system (CEM. Corporation, MDS-

2100) for 30 min and diluted to 25 ml with deionized water and stored in polyethylene bottles until analysis. A blank digest was performed in the same way.

The accuracy of the method was checked by analysis of the IAEA 158 Certified reference material, with satisfactory results. Analytical results indicate a good correlation between the certified and determined values (Table 1) and metal recovery being practically complete for most of them (recovery was from 90-120%).

Metal Pollution Index

The overall metal contents were compared, using the metal pollution index (MPI). MPI was calculated using the following formula:

$$\mathrm{MPI} = (M1 \times M2 \times M3 \times \cdot \cdot \cdot \times Mn)/n,$$

where Mn is the concentration of metal n expressed in $\mu g \cdot g^{-1}$. In this case, number of metal (n) =10. When MPI > 1, the soil ecosystem is considered to be polluted and when MPI < 1, it is regarded as unpolluted (Usero et al., 2005).

Geo-accumulation index (Igeo)

Geoaccumulation index (I*geo*) has been calculated for analyzed metals. It was originally defined by Müller (1981) in order to determine and define metal contamination in sediments, by comparing current concentrations with pre-industrial levels (Buccolieri et al., 2006). It can be calculated by the following equation:

$$\mathrm{I}geo = \mathrm{Log}_2\,[(\mathrm{C}n) / 1.5\,(\mathrm{B}n)],$$

where C*n* is the measured concentration of the examined metal “*n*” in the sediment and B*n* is the geochemical background concentration of the metal “*n*”. Müller has distinguished seven classes of geoaccumulation index (Müller, 1981), Table 2.

Table 2. Müller’s classification for the geoaccumulation index (Müller, 1981)

Igeo value	Class	Quality of sediment
<0	0	Unpolluted
0–1	1	Unpolluted to moderately polluted
1–2	2	Moderately polluted
2–3	3	Moderately to strongly polluted
3–4	4	Strongly polluted
4–5	5	Strongly to extremely polluted
>5	6	Extremely polluted

This classification is a methodological approach based on the geochemical data. It allows mapping a study area and discriminating different sub-areas according to their degree of contamination. In addition it is feasible to obtain a proper comparison between various marine areas in terms of their heavy metal quality.

RESULTS AND DISCUSION

Heavy metals concentrations in sediments and basic statistics

The concentrations of heavy metals investigated (Co, Ni, Pb, Cd, Fe, Zn, Cu, Mn, As and Hg) in sediment samples collected during 2005 from Montenegrin coast are summarized in Table 3. The mean concentration of heavy metals in sediment is represented in decreasing order as follows: Fe > Mn > Ni > Zn > Cu > Co > As > Pb > Cd > Hg.

Rt Djeran and Ada Bojana, are locations with the highest concentrations of metals in sediments. At these locations, the concentration some elements are significantly higher compared to other locations. For example, the location of the Rt Djeran, concentration of iron has a maximum recorded value of 34 637 µg/g, manganese 729 µg/g, zinc 62.4 µg/g, nickel 335 µg/g, copper 24.7 µg/g, cobalt 14.5 µg/g, arsenic, 17.7 µg/g. These high values of metals in these locations can be explained by the river laden wastewater and industrial water (Solana, etc.) through a system of Skadar Lake and river Bojana and Drim bring large amounts of sediment laden many pollutants, as if that many stationary industrial facilities and hospitals are on the coast, contributing to this area quite adversely anthropogenic influence (Filipović, 1981; Joksimović, 2010; Joksimović & Stanković, 2011), Table 3.

Table 3. Metal concentrations (µg g^{-1} dry weight) in sediments

	ELEMENTS (µg g^{-1})										
Location	Fe	Mn	Zn	Cu	Co	Ni	Pb	Cd	As	Hg	MPI
Ada Bojana	21222.7	754.7	46.2	20.7	26.2	228.6	3.6	0.4	<0.1	0.00	3.04
Rt Djeran	34637.0	729.1	62.4	24.7	14.5	335.0	6.4	0.4	17.7	0.06	2.88
Bar	62164	657.1	22.4	14.7	11.4	15.7	5.2	0.1	3.1	0.03	2.03
Budva	1243.2	132.4	5.1	3.23	5.2	2.7	2.6	0.2	2.6	0.003	1.39
Bigova	713.7	183.0	4.0	5.6	13.8	10.5	1.3	0.3	3.5	0.03	1.68
Mamula	1594.2	282.3	7.7	4.7	5.0	12.7	5.1	0.4	4.5	0.03	1.84
Zanjice	10507.5	497.1	19.8	7.7	6.6	16.4	3.9	0.8	19.6	0.03	2.21
H. Novi	6090.0	772.3	23.8	11.8	9.0	32.3	3.7	0.8	3.8	0.08	2.28
Kukuljina	11711.5	325.9	45.2	14.4	10.2	745	9.5	0.5	5.2	0.00	2.48
Sv. Stasije	9263.3	208.7	25.1	6.6	3.9	18.2	7.0	0.8	4.8	0.06	2.13

The results showed that there are significant differences in the concentrations of metals in sediments of the investigated locations. The values of the concentrations of the trace elements in sediments from the Boka Kotorska Bay are higher in relation to certain locations that are under the influence of the open sea, but not greater than the concentration in sediments obtained from the locations Rt Djeran and Ada Bojana (Joksimović & Stanković, 2011).

All sites in the present study recorded degree of contamination metals in sediment. The MPI values at all locations were between 1.39 and 3.04. Locations that have had the highest MPI values were Ada Bojana and Rt Djeran (open sea) and Kukuljina (bay), which is in complete agreement with the earlier claims, as these are locations with the highest content of trace elements in sediment. Although MPI values indicate that the pollution is present, comparison with other countries of the Mediterranean Sea (Usero et al., 2005, Rodríguez-Barroso et al., 2009, Uluturhan, 2010) shows that the Montenegrin coast has the least content of trace elements in sediment.

The degree of correlation between trace metals and other major constituents is often used to indicate the origin of the elements. In this study, correlations between the element pairs were statistically tested (Zwart, 2005). The relationship between parameters is show on Person's correlation coefficient matrix in Table 4. There were significant statistical relationships between same elements. Zink show correlation with many elements, like Pb, Ni, Co, Mn and Cu, manganese, copper and chromium are in correlation with Ni and Co. The toxic elements, Fe, As and Cd are not correlated with any elements, except Hg which is correlated with Pb and Cd.

The obtained results for I*geo* show that Ada Bojana and Rt Djeran are locations that are moderately polluted with cadmium and manganese, while the I*geo* value for nickel puts Ada Bojana in the moderate to heavy polluted area and Rt Djeran as area heavily polluted with this metal (Table 5). The nickel contamination in these areas is due to anthropogenic impacts from land, including waste water, port activities, the use of anti-corrosive paints for ships and boats (Yasar et al., 2001). It is also interesting that toxic elements such as mercury, lead and arsenic, as well as essential elements copper and zinc, have I*geo* values that classify all investigated areas as practically unpolluted.

Table 4. Correlation between metals in the sediments sampled

	Pb	**Ni**	**Co**	**Mn**	**Cu**	**Zn**	**Cd**	**Fe**	**As**	**Hg**
Pb	1.00									
Ni	0.22	1.00								
Co	0.03	***0.75***	1.00							
Cr	0.11	***0.71***	***0.68***							
Mn	0.04	***0.59***	***0.71***	1.00						
Cu	0.35	***0.89***	***0.82***	***0.80***	1.00					
Zn	***0.59***	***0.87***	***0.69***	***0.62***	***0.92***	1.00				
Cd	0.25	-0.02	-0.09	0.22	0.00	0.20	1.00			
Fe	0.05	-0.18	0.09	0.28	0.17	-0.06	-0.50	1.00		
As	0.18	0.32	-0.12	0.21	0.22	0.33	0.33	-0.18	1.00	
Hg	***0.70***	0.06	-0.20	0.13	0.22	0.41	***0.55***	-0.11	0.17	1.00

Marked correlations are significant at $p < 0.05$

Comparing the results of the geoaccumulation index with other authors (Buccolieri, et al., 2006), we conclude that the obtained values are significantly lower when compared to the existing literature and that they occur at positions where the usual concentration of metals has been increased.

Table 5. Geoaccumulation indexes of heavy metals in Montenegrin sediments

I*geo*	Ada Bojana	Rt Đeran	Bar	Budva	Bigova	Mamula	Žanjice	H. Novi	Kukuljina	Sv. Stasije
Fe	–0.82	–0.11	–2.60	–4.91	–5.72	–4.55	–1.83	–2.62	–1.67	–2.02
Mn	**0.75**	**0.70**	**0.55**	–1.76	–1.30	–0.67	**0.14**	**0.77**	–0.46	–1.11
Zn	–1.03	–0.60	–2.07	–4.21	–4.56	–3.62	–2.25	–1.98	–1.06	–1.91
Cu	–0.54	–0.28	–1.0.3	–3.21	–2.42	–2.67	–1.96	–1.35	–1.06	–2.18
Ni	**2.73**	**3.28**	–1.13	–3.67	–1.72	–1.44	–1.07	–0.09	**1.11**	–0.92
Pb	–3.13	–2.29	–2.59	–3.59	–4.59	–2.63	–3.01	–3.08	–1.73	–2.17
Cd	**0.15**	**0.15**	–1.85	–0.85	–0.26	**0.15**	**1.15**	**1.15**	**0.47**	**1.15**
As	–7.91	–0.43	–2.95	–3.21	–2.77	–2.41	–0.29	–2.65	–2.21	–2.32
Hg	–4.28	–1.70	–2.70	–6.02	–2.70	–2.70	–2.70	–1.28	–1.12	–1.7

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