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ASSESSMENT OF HEAVY METALS CONTENT IN VLORA BAY USING ATOMIC ABSORPTION SPECTROMETRY

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Abstract

The presence of heavy metals in the maritime waters has been constantly considered as an important issue in the environmental aspects. In this framework, herein we report some findings from measurements of concentration of so called heavy metals in the sea waters of the Vlora (Albania). We obtained that the concentrations of Cu. Fe, Cd, Mn, are in the range of their average values in other Adriatic places. Usually the concentration of those elements depends on the positions where measurement have been made, indicating that isolated sources of pollution are *likely to present. We observe a slight decrease of the construction of Cu and Mn following maritime local flows. Next we obtain that the concentration of Cu. Cd. Fe, Mn, Ni in the near coast line stabilize below 1m of depth supporting the idea that the sediments or the floor of the sea coast are not source and major factors of pollution with those elements are atmospheric process, water discharges and seawater flows.*

Keywords

Maritime Pollution, Heavy Metals, Atomic Absorption Spectrometry

1. Introduction

The bay of Vlora consist in a complex environment characterized by an open communication with the Adriatic Sea, river water discharges, and industrial activities including civil and military harbors (Pano.N et al, 2014) , (Kane S, Qarri F and Lazo P, 2015). In reference (Pano.N et al, 2014) is analyzed the dynamics of the sweaters that represent an interesting system with inner flows circulating clockwise as shown in the Figure 1. Small and medium size rivers discharge water in the Vlora bay. Vjosa river that discharge waters at the coordinates 40°38'40.7"N 19°19'07.7"E, about 30 km from Vlora (26 km distance) has its source on the northern Greece (https://www.balkanrivers.net) and goes through industrial zones or potential metal components sources in Albania parts of its flow. It is expected that its waters could affect the coastal waters of the bay. In short, all those specifics are expected to directly or indirectly affect the levels of concentration of metals and metalloids in the waters. In (Šmuc, N R. Dolenec.M, Kramar.S, and M. Ana , 2018) it is referred that various anthropogenic contaminants, especially heavy metals, are discharged and accumulated into marine coastal ecosystems and those data have been analysed for northern Adriatic Sea. In this framework, traces of the metals Cu, Zn, Pb,, Hg etc., are considered (Martin, S. Kwokal, D, Stoeppler, M. and Branica, M.1987) as more serious pollutants discharged by industrial and urban waste in Adriatic basin. Other analysis as in (S.P.C Tankere, P.J.Statham, 1996; Kljakovic Gaspic.Z, 2002) acknowledged that the level of some heavy metals the tissues of some maritime fish are low and generally the Adriatic Sea is not a contaminated environment regarding to the above dissolved elements. In this aspect, the study of the presence of such elements in the coastal waters in Vlora would exhibit twofold importance. It would be worthy as routine environmental study, comparative analysis regarding to other country's places measurement. From the other side, it has the relevance regarding to the concrete estimation of the anthropogenic sources effect of such mettle presence in the sea. Furthemore, the study of the maritime pollution and contamination for the Albanian Adriatic coasts is attracting the interests of many actors and agencies. Partial analysis have been undertaken in this framework as in (Çullaj A. et al., 2000), but up now there has not been established a large-scale process of measurement, data elaboration and mapping the metals and metalloid presence in the water. Bearing in mind that the tourism is very important part of the country’s economy, many researchers have been involved independently recently in the study of pollution from industrial activities as Hg for example (Denaj,A. et al, 2015). and (Lazo P, Bushati S, 2008) the presence of metalloids in the rivers, atmosphere and in the sea water.

2. Method and Data Analysis

Generalized method of sampler preparation and treatment are considered especially in the guide of the field of research (K. Danzer., 1996, Ponnada. S, 2013, Smith, R). From geographic point of view, we schematized the stations of measurement in a zone where no considerable natural waters discharges are present. It corresponds to the points between points [$40^{0}27.952^{,}$ $19^{0}27.461$’, $40^{0}25.288^{,}$, $19^{0}29.271$] situated in stations distanced about 1km to each other. The first station is located nearby a small fishing port and the last one is the end point of the city coast. We realized another set of measurement in a Laguna northern of the bay. The measurements were realized in a calm water, during springtime where the temperature of the waters has been around 15^{o} C. The stations were located at distance 50 m from the coastline and samplers tare taken in three vertical points: at surface and close under-surface straits at 10 cm -60 cm largeness, and in a intermediate depth of -120 cm quote, with a horizontal Van Dorn water sampler. The idea behind this measurement was to get known about direct surface situation where atmospheric or low discharges would be dominant factor and more homogenized part of the waters under this strait. However, the number of the data collected was not satisfactory enough for a deep quantitative analysis, so this work in its whole consists in a modest measurement, and mostly observation. Based on the first goal of the study consisting in empirical evidence we have pursued standard rules in sampling and homogenization of the specimens. Practically a good level of homogenization is reached by taking samplers in 500 ml volume of water as usually applied in such measurement and also recommended in standard guides, or metioned in references as [(Çullaj A. et al., 2000), Angeline. E, et al, 2016).]. Next, regarding to the start of a more analytic view aimed in the analysis of the pollutant factors, we considered the reference (Pano. N et al, 2014) wherein we acknowledged that the sea flows circulate along the coast in clockwise direction referred to the figure 1. If there has no source of metal in the area under study, succeeding the direction of those flows it is expected that the water of open sea would modify the concentration of constituents imposing a slight gradient forward to the flow direction. If average concentration of a metal in the seawater is lower than the concentration on the coast where discharged or other sources are present, the gradient observed in the pathway of such flows would result positive. For a reliable reading of the phenomenon we needed a 2D grid measurement which is not finished in this study and is under process now. So, we will restrict this analysis herein in the empiric evidences and some comments. Notice that the average depth of the sea in this quote goes from 2m -10m and in our selected measurement points it was generally around 2-3 m. Therefore, the recorded data consisted in measurement on a coastal strait of surface waters. The effects of small part of materials as sediments and other point sources are expected to be small in the absence of active sources of pollutants. Finally, the analysis has been carried out using Flame Atomic Absorption Spectrometry and Induced Plasma Spectrometry and the data elaboration steps were held according to the standard guides of such measurement (Method 3015a Microwave Assisted Acid Digestion of Aqueous Samples and Extracts) and do have nothing new to mention here.

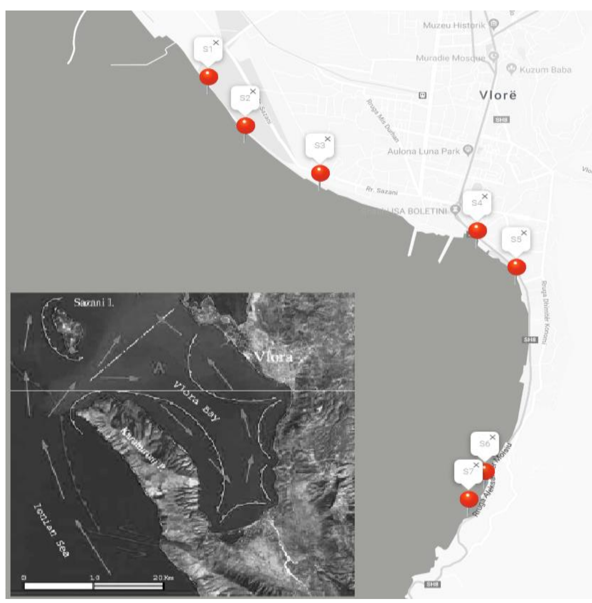

Figure 1: *Positions of sampling Stations*

3. Results

By direct analysis using FAAS the level of concentration of the metals Cu, Ni, Cd, Mn have been identified. Each of them shows specifics that we are referring shortly herein. The concentration of the Cu metal has been estimated with good certainty for all stations 1-7 and tree depth quotes surface (10m) undersurface (60 cm) and mid-depth at 120 cm. Initially we checked for representative values for all points considered as a unique place. We observed that the values taken in all stations were not like to be drawn from a give distributions. Therefore, the zone explored has not a representative value for concentration of Cu in statistical sense. It can be related to the water currents, unidentified or hidden sources which remained to be examined in the future by using more dense data points. Up here we can report results as point measure and findings and arithmetical average that does not contain statistical properties of the mean. The quoted variance coefficient $k_{i,v} = \frac{\Delta C}{C_{mes}} * 100$ with C the point concentration of the metal for each depth, diminish from station 1 to 6 in a monotonic way, Fig1 supporting the idea that the average has not representative property. We obtained a high deviation in station 7 therefore in calculating approximately the mean we excluded it and restrict the report fort station 1-6, Fig 1.

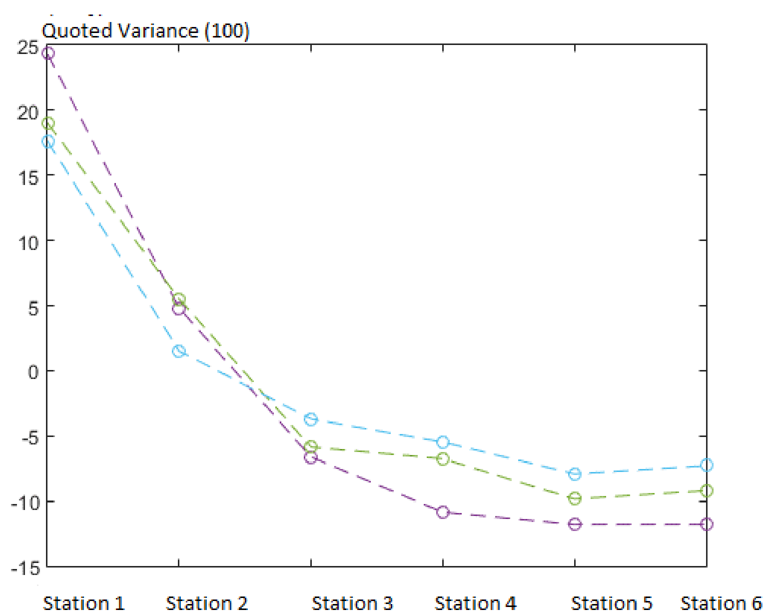

Figure 2: *The Deviation Coefficient among Stations*

Arithmetical values are displayed in table 1. Some scholars don't highlight differences between statistical values which are specifically representative of the simply arithmetical which have only empirical information. In our consideration this is underlined to avoid subjective statement and misunderstanding on the reading. So, if the distribution approached to the densities of values obtained, or the nearest distribution that is likely to characterize were found not stationary, the average values are qualified as 'arithmetical'.

Table 1: *Arithmetical Values*

First station [40º27.952', 19º27.461']		Last Station [40º25.288', 19º29.271']	
Depth	Surface: 10 cm	Under-surface: 60cm	Normal depth120 cm
Average of all stations	0.0391 mg/l	0.0379 mg/l	0.0372 mg/l
STDEV	0.0066 mg/l	0.0048 mg/l	0.0041 mg/l

If approaching normal distribution for our data records from stations 1-7 that belongs to urban area of the bay, the assessment for the values are given in the table 2.

Table 2: *Arithmetical values for Cu concentrations*

Depth	Parameter	Value in mg/L	Low boundary	Upper boundary
10cm	Mean	0.0379	0.032845	0.042955
	Stdev	0.004817	0.003007	0.011814
60cm	Mean	0.0379	0.032845	0.042955
	Stdev	0.004817	0.003007	0.011814
120cm	Mean	0.037233	0.032953	0.041514
	Stdev	0.004079	0.002546	0.010004

In the case of Ni, we observe that its concentration is higher in some stations that testify the presence of local source. Figure 2 shows that in the geographic zones between station 5 and station 6 the level of Ni concentration is higher than elsewhere. A high value of concentration is obtained in the surface points far from those two stations. The system shows some dynamics according to the depth form surface too. It is clearly deduced from intersections of the empiric curves of level of Ni in certain depth, Figure 2. Stations 5 and 6 are just in the urban area of the bay, and in nearby of station 6 it is situated the port of the city. It resulted that major sources of Nicel presence in the waters analyzes is related to the urban wastes, and discharges. The average empirical vales are found around 0.1280µg/L or 0.124 µg/kg.

We observe that the level of Mn is more homogenous in all stations. A low decreasing trend is identified in the direction Station 1-Station 7 which support the idea that the seawater inner flows in the bay according to the direction given in (Pano.N et al, 2014) seem to reduce the concertation of Mn. This trend is observed in the three quotes of the depth, testifying that vertical gradients doesn't hide the forward decrease of the concertation against the flows. However, the level of the Mn concertation was not in the alarm zone.

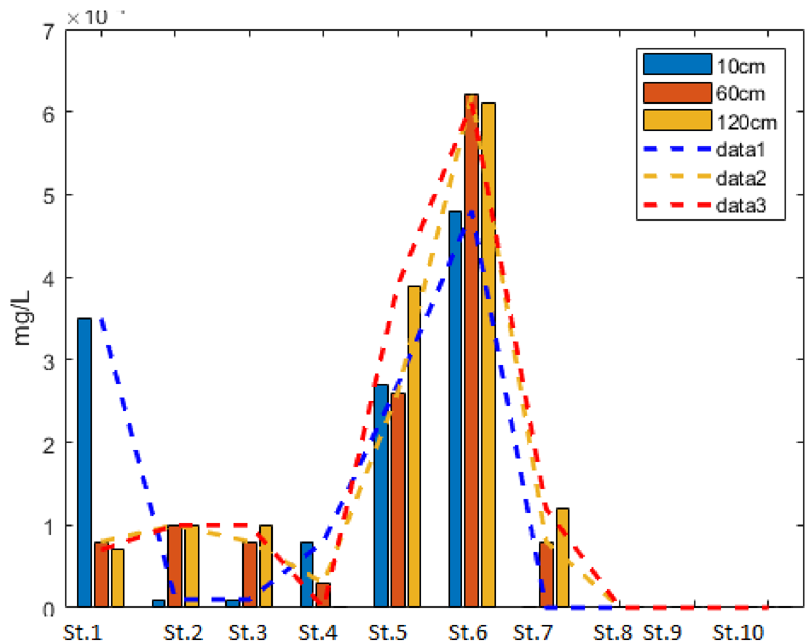

Figure 1: *Behavior of Concentration for Nickel. Stations 8,9,10 belongs to Laguna of Orikumi*

It is smaller than in some other area of northern Adriatic and this is related to very low level of industrial activities on the area. we observe that the level of cadmium increases in the opposite direction of the assumed flows. However, it is important to note that in the pathway of flows is the military harbor, so the decrease trend toward station 1 des not means that the bay has less metal presence than opened Adriatic Sea. Up now we can admit that there are not significant Cd pollutants in the urban area. of the bay. Next, the level of Cd metal in a closed sea water environment (Laguna) is obtained remarkably lower, Figure 4. From station 1 to 7 the trend is increasing for all vertical coordinates. If there are sources, they could be in the direction of station 7 that is located in the front line of the circulating seawater flows.

The obtained data of the descriptive statistics on the three depth levels is shown in table 4. It is noticed that Cu has a mean concentration value higher than other elements. This value tends to decreased depending to the depth levels. The same argumentation stands also for Mn, while for Cd and Ni mean concentration values are increasing with depth.

In general, the standard deviation values for all the elements is lower in the 60cm depth quote. Based on this, we may say that the heterogenicity of all the values is lower in 60cm quote than the other depth quotes studied, 10cm and 120cm respectively.

we also notice that at the three depth levels all the studied elements present a kewness less than -1 or greater than 1, so the data are highly skewed.

Table 3: *Sampling Stations for the Analyzed Heavy Metals*

Deepth	Elements	Descriptive Statistics							
		Mean	Median	St. Dev.	Kurtosis	Skewness	Min.	Max	Range
10cm	Cu	0.0412	0.0367	0.0082	-1.0252	1.0089	0.035	0.0539	0.0189
	Ni	0.00017	0.00008	0.00019	-1.3234	0.6932	0	0.00048	0.00048
	Cd	0.0129	0.0122	0.0023	2.821	1.7247	0.0111	0.0175	0.0064
	Mn	0.0106	0.0105	0.0003	-1.2047	0.516	0.0103	0.0111	0.0008
60cm	Cu	0.0374	0.0355	0.0046	3.108	1.8575	0.0345	0.0468	0.0123
	Ni	0.00018	0.00008	0.00021	4.3315	2.0806	0.00003	0.00062	0.00059
	Cd	0.0134	0.0124	0.0029	0.0304	1.2447	0.011	0.0184	0.0074
	Mn	0.0106	0.0106	0.0002	-0.7497	-0.2656	0.0102	0.0109	0.0007
120cm	Cu	0.0319	0.0353	0.0145	5.7189	-2.2542	0.0001	0.0452	0.0451
	Ni	0.0002	0.0001	0.00022	1.1151	1.4305	0	0.00061	0.00061
	Cd	0.0116	0.0119	0.0039	4.0891	-1.7712	0.0034	0.0158	0.0124
	Mn	0.0091	0.0106	0.004	6.945	-2.6318	0	0.011	0.011

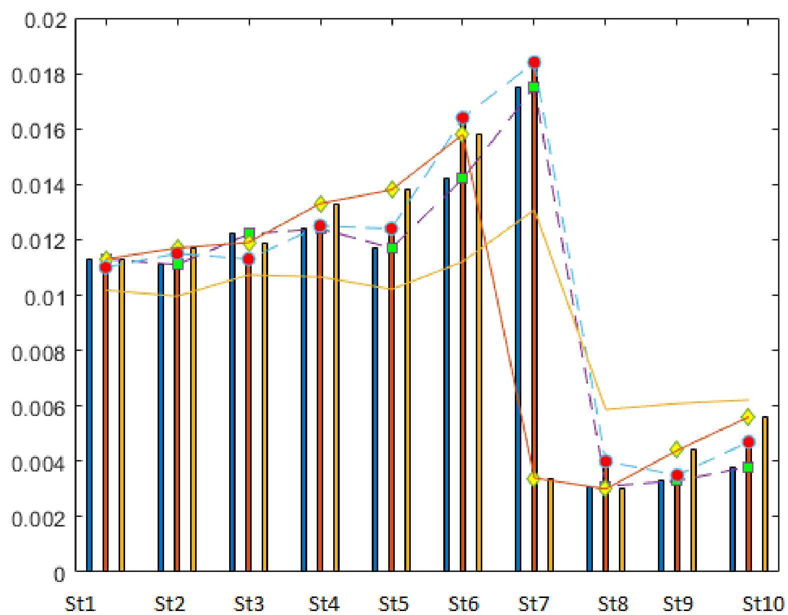

Figure 2: *Concentration of Cadmium*
Blue Bar, 10 cm, Red Bar, 60 cm, Yellow Bar, 120 cm

4. Conclusion

Concertation of some heavy metals as Cu, Ni, Cd, Mn etc., in the bay of Vlora are in normal values of non-contaminated waters. The average concentration of Cu in more homogeneous strait measured (at 120 cm depth) is 0.0372 ±0.0041 mg/l, whereas the averaged level for all quotes give the values 0.03686 mg/l and the empirical deviation is 0.01 mg/l. There are low -intensity emitting sources on the area, mostly related to the urban wastes and other anthropogenic low-level pollutants. For Mn the level of average concentration is around 0.0126±0.003 mg/l whereas for Mn we obtained the level 0.0101 ± 0.0023 mg/l. Nickel has been estimated in a very low values for the major part of stations.

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