ECOLOGIA BALKANICA
2020, Vol. 12, Issue 1 June 2020 pp. 179-189

Metal Pollution Assessment in Sediments of the Bulgarian Black Sea Coastal Zone

Valentina G. Doncheva, Ognyana D. Hristova, Boryana S. Dzhurova, Krasimira R. Slavova*

Institute of Oceanology, Bulgarian Academy of Sciences, Departments "Marine chemistry", "Marine geology and archaeology", PO Box 152, Varna 9000, BULGARIA
*Corresponding author: doncheva@io-bas.bg

Abstract. The present study was conducted to assess the pollution status of the coastal sediments of the Bulgarian Black Sea coastal zone using sediment pollution indices. Eleven sites and twenty-two stations from monitoring grid were selected for the collection of samples. The heavy metal concentrations were used to calculate: geoaccumulation index (Igeo); enrichment factor (EF); contamination factor (CF); modified degree of contamination (mCd); pollution loading index (PLI). In addition, ecotoxicological level of trace metals in sediments was also assessed by comparing with the numerical sediment quality guidelines (SQGs). Mean ERM quotient (mERM–Q) and mean PEL (m-PEL–Q) were applied for assessing the potential effects of multiple heavy metal contamination in sediments. The pollution level assessed by indices related to background level of the studied sites ranged from unpolluted to moderate and only in one case considerably polluted due to heavy metals, mainly Pb and Zn. Ecotoxicological risk was assessed as low and moderately low due to the presence of Pb, Cu, Ni. The northern Danube influenced area of the Bulgarian coastal zone was categorized according to the applied indices as slightly polluted with Zn and Pb. The sediments from the "hot spot" points were with higher accumulation of Ni, Cu and Pb.

Key words: Black Sea, metal pollution, coastal sediments, sediment quality indices, sediment quality guidelines.

Introduction

Black Sea ecosystem has been heavily impacted as a result of anthropogenic activities in coastal zones and watersheds. The Black Sea is a unique semi-enclosed basin that receives a great river inflow and has a single connection with the Mediterranean Sea through the narrow Bosphorus Strait. The Black Sea area is 461 000 km^2 and its drainage area extends over more than 2 200 000 km^2. Almost one-third of the entire land area of the continental Europe drains into it which has a detrimental effect on its health (Mee, 1992). Due to the slow rate of water renewal, the Black Sea is particularly vulnerable to pollution.

Sediments may act as sinks and sources of metals to the overlying water column and biota. Contaminated sediments can decrease water quality and ecological diversity, ecological functioning, and aesthetic properties of waterbodies (Davis & Fox, 2009). Sediments play a significant role as sensitive indicators for monitoring metal contamination in aquatic systems (Ariman & Bakan, 2008). Very limited

 Union of Scientists in Bulgaria – Plovdiv
University of Plovdiv Publishing House

information exists concerning trace metals in the sediments of the Bulgarian Black Sea coastal zone.

The main objective of this investigation was to assess the pollution status of the coastal sediments in the Western Bulgarian Black Sea part based on pollution indices.

Material and Methods

Sampling was carried out on 11 stations according to EU Water Framework Directive (EC, 2000) monitoring programme at 11 sites within the 1 nautical mile zone of the Black Sea western part during surveys in 2005 and 2016. The sediments were collected on the same network of monitoring stations during both surveys, but with slightly changed positions for some stations in 2016 (Fig. 1). Depths of the stations varied between 13 and 37 meters and the distance of the stations to the shore was in the range of 1 nautical mile.

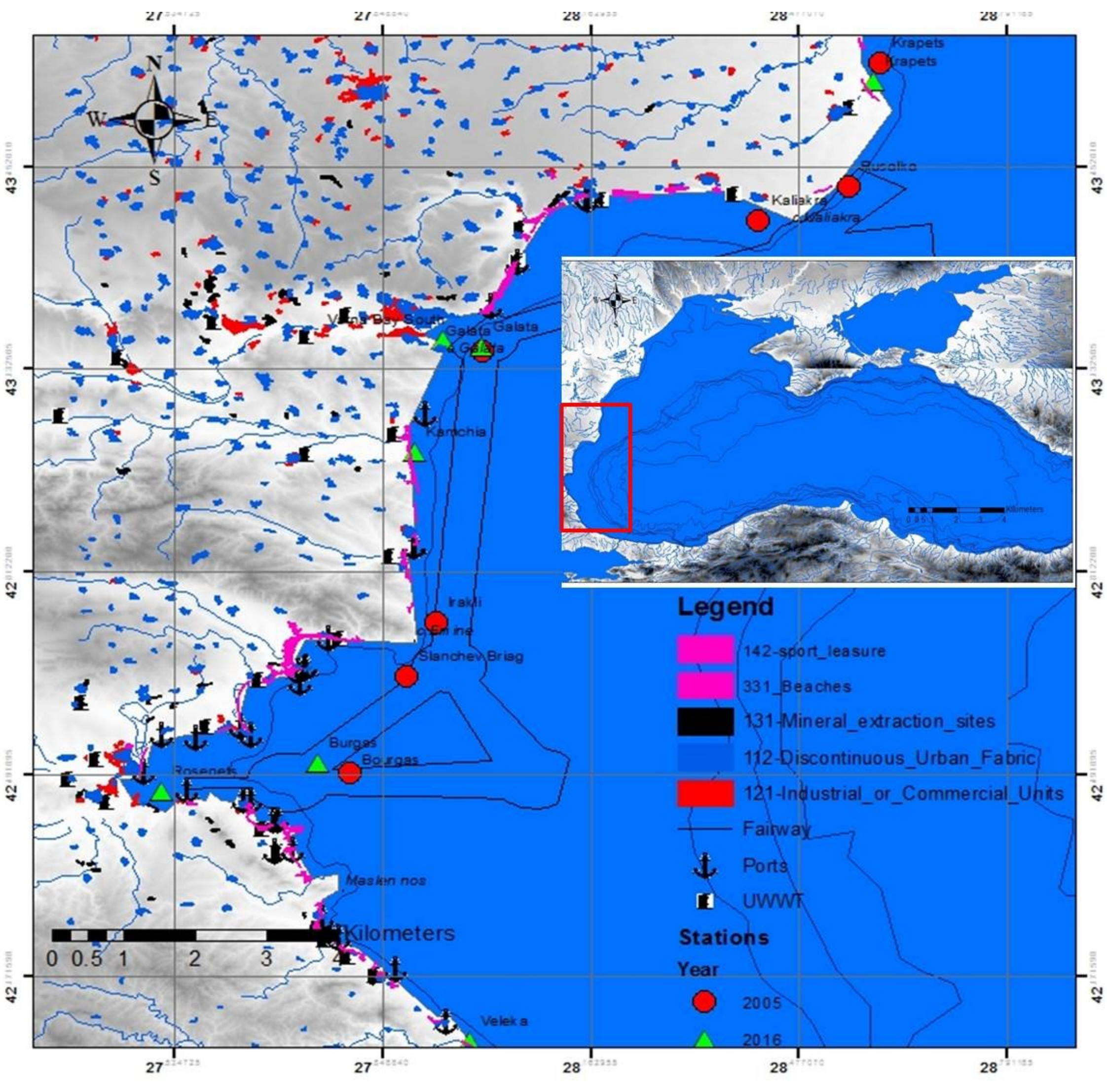

Fig. 1. Area of investigation with sampling stations (2005 and 2016) and anthropogenic pressures as Corine Land Cover (CLC) zones: Discontinuous Urban Fabric, Industrial or Commercial Units, Mineral extraction sites, Beaches, dunes, sand, Sport and Leisure facilities ("CLC Bulgaria", 2012); ports, fairway and UWWT.

The stations are in an area under the impact of different pressures. In the northern part (stations Krapets, Rusalka, Kaliakra) the influence of the Danube freshwater input along the Bulgarian Black Sea coast is the strongest. The local pressure comes from currents from the north, pollution from the waste treatment and maritime transport.

Station Kamchia is in front of the mouth of the biggest Bulgarian river Kamchia. Station Slanchev Bryag is in front of one of the biggest resorts but is in the protected sand bank "Cocketrice", an area with the highest biological diversity (Konsulova et al., 2010). Varna (st. Varna, st. Galata) and Burgas (st. Burgas, st. Rosenets) bays, and the Kamchia river mouth are exposed to direct or indirect influence of industrial and municipal discharges, port operations, tourism development and also inputs from diffuse sources.

Surface sediment samples (0-5 cm) were collected using a 0.1 m^2 Van Veen grab, placed in polyethylene bags, refrigerated and transported to the laboratory. The investigated parameters were Zn, Pb, Ni, Hg, Cu, Cd and Al. Data for 2005 were provided by the Black Sea Basin Directorate - Varna. The samples collected by IO - BAS in 2016 were analyzed in an accredited laboratories in Hungary (Biokor & Wessling) using ICP - OES technique.

The measured element concentrations were used to calculate the pollution indices.

To estimate enrichment of metal concentrations above background concentrations, the index of geoaccumulation (Igeo) as proposed by Müller (1969) was used:

$$Igeo = \log_2 Cn / 1.5 Bn,$$

where *Cn* is the measured concentration of the element *n* in the samples and *Bn* is the geochemical background value of the element *n* in the average crust. Background values and legal norms for the Bulgarian Black Sea sediments do not exist therefore the average crust value (Taylor, 1964) were used.

This index is basically a single metal approach to quantify metal pollution in sediments when the concentration of toxic heavy metals is 1.5 times greater than their lithogenic background values. The factor 1.5 was used to compensate possible variations of the background values which were attributed to lithologic variations in the sediment (Abrahim & Parker, 2008; Stoffers et al., 1986).

To identify anomalous metal concentration, geochemical normalization of the heavy metals data to conservative elements, such as Al, Fe, and Si was employed (Din, 1992; Windom et al., 1989). In this study, Al was used as a reference element to differentiate natural from anthropogenic components. The enrichment factor (EF) value of metal was defined as follows:

$$EF = \frac{(C_X / C_{Al})\,sample}{(C_X / C_{Al})\,background} ,$$

where $(C_x/C_{Al})_{sample}$ is the ratio of sediment sample concentrations of the heavy metal and Al concentrations; $(C_x/C_{Al})_{background}$ is the ratio of backgrounds of heavy metal and Al concentrations. The average crust concentration of Al (Taylor, 1964) was taken as background. Evaluation of pollution impact (2016) using enrichment factor regarding to Pb, Cu and Ni was done.

The pollution load index (PLI) and contamination degree based on computed contamination factors were used as a tool for assessment of the degree of overall contamination in surface sediment layer. The overall contamination of sediments was assessed based on contamination factor (CF), (Hakanson, 1980). The contamination factor (CF) was calculated according to the formula:

$$CF = \frac{measured\ concentration}{background\ concentration} .$$

Taylor's (1964) crustal abundance was used as background concentration.

Pollution load index (PLI) was evaluated following the method proposed by Tomilson et al. (1980). PLI could be calculated by the following equation:

$$PLI = (CF1xCF2x.....CFn)^{1/n},$$

where *n* is the number of metals and CF is the contamination factor.

Degree of contamination (Cd) given by Hakanson (1980) was based on seven metals and one organic contaminant. The modification of the method (mCd) to avoid these limitations was proposed by Abrahim & Parker (2008) who took into consideration all the CFs for a given set of pollutants divided by the number of the analysed pollutants, e.g. heavy metals - *n* (Abrahim & Parker, 2002):

$$mCd = \frac{\sum_{i=1}^{i=n} CF^i}{n}.$$

To evaluate sediment contamination and potential ecotoxicological effects associated with the observed contaminant concentrations, two sets of SQGs developed by National Oceanic and Atmospheric Administration (NOAA) for marine and estuarine ecosystems (Long & MacDonald, 1998; MacDonald et al., 2000) were used. The chemical concentrations corresponding to the 10th and 50th percentiles of adverse biological effects were called the effects-range-low (ERL) and ERM guidelines, respectively (Long et al., 1995). Another sediment quality guideline used to assess the ecotoxicology of sediments was the TEL and PEL approach. This approach is based on the relation between measured concentrations of metals and observed biological effects, such as mortality, growth or reproduction of living organisms. Threshold effect level (TEL) refers to the concentration below which adverse effects are expected to occur only rarely and probable effect level (PEL) indicates the concentration above which adverse effects are expected frequently to occur (Saleem et al., 2013).

The ratio of concentration to background gives a base to evaluate sediment quality but it provides little insight into the potential ecological impact of contaminants (Gao, 2012). Based on the fact that heavy metals always occur in sediments as complex mixtures, the mean PEL and ERM quotient method was applied to determine the possible biological effect of combined toxicant groups by calculating mean quotients for a large range of contaminants using the following equations:

$$m\text{-}ERM\text{-}Q = \frac{\sum_{i=1}^{n} Ci / ERMi}{n},$$

$$m\text{-}PEL\text{-}Q = \frac{\sum_{i=1}^{n} Ci / PELi}{n},$$

where Ci is the concentration of element i in sediments, ERMi and PELi are the guideline values for the element i and n the number of metals.

Results and Discussion

The mean concentrations of elements at different sites, background concentration in the continental crust (Taylor, 1964) and threshold effect sediment quality guidelines for metals (Long et al., 1995) are given in Table 1.

The Igeo method was applied to calculate the metal contamination levels. Müller (1979) defined seven classes of the geo-accumulation index: class 0 (Igeo ≤ 0; uncontaminated), class 1 (Igeo = 0-1; uncontaminated to moderately contaminated), class 2 (Igeo = 1-2; moderately contaminated), class 3 (Igeo = 2-3; moderately to strongly contaminated), class 4 (Igeo = 3-4; strongly contaminated), class 5 (Igeo = 4-5; strongly to extremely contaminated) and class 6 (Igeo > 5; extremely contaminated).

Based on Igeo, it was found that the studied samples could be considered uncontaminated with Ni and Cu. Among the five metals studied, Pb had the highest Igeo values. 54% of the stations were unpolluted and 46% were moderately to strongly contaminated. As the Igeo class of Pb at st. Krapets (2005) and st. Kaliakra (2005) was „moderately to strongly contaminated“ and for st. Rusalka (2005), st. Galata (2005), st. Rosenets (2016), st. Bourgas (2016) was „moderately contaminated“.

Sediments from only one st. Kaliakra showed moderately polluted status with respect to Zn.

Sediment quality classes were evaluated using the EF value. The EF values were interpreted as suggested by Birch (2003) where EF < 1 indicated no enrichment, EF < 3 was minor; 3 ≤ EF ≤ 5 was moderate; 5 ≤ EF ≤ 10 was moderately severe; 10 ≤ EF ≤ 25 was severe; 25 ≤ EF ≤ 50 was very severe; and EF > 50 - extremely severe.

According to the EF, contamination was assessed as generally "moderate" regarding Pb and "minor" for the other elements. The lowest EF values were determined between 0.6 and 2.3 for the most of analytes. The results range of EF values was between 2.8 - 7.5 for Pb, considered as a moderate severe enrichment. Maximum enrichment Pb level was found at Varna Bay station and minimum - at Veleka station.

According to Hakanson (1980) CF < 1 indicates low contamination; 1 < CF < 3 - moderate contamination; 3 < CF < 6 - considerable contamination; and CF > 6 - very high contamination.

In the present study, the contamination factors for Zn were low except st. Kaliakra where contamination was in the moderate category.

The contamination factor for Zn was in the low category at all sites in both sampling sessions (2005 and 2016), except st. Kaliakra where contamination was in the moderate category. In the present study, the contamination factors for Pb were low for 57% of the stations. Five stations (Rusalka, Galata, Varna Bay, Rosenets and Burgas Bay) showed moderate contamination and one (Kaliakra) – considerable contamination.

PLI < 1 indicates no pollution due to anthropogenic activities and PLI > 1 indicates pollution (Harikumar et al., 2009). In the present study, the pollution load index for all studied sites showed no human associated pollution with PLI < 1.

The classification of the sediments according to the modified degree of contamination (mCd) is the following: mCd < 1.5 - zero to very low degree of contamination; 1.5 < mCd < 2 - low degree of contamination; 2 < mCd < 4 - moderate degree of contamination; 4 < mCd < 8 - high degree of contamination; 8 < mCd < 16 - very high degree of contamination; 16 < mCd < 32 - extremely high degree of contamination; mCd ≥ 32 – ultra high degree of contamination.

mCd can make an integrated assessment of the overall contamination with metallic pollutants. It was found that the mCd values ranged from 0.3 to 1.9. The minimum values were observed at stations Krapets (2016) and Veleka and the maximum at Varna Bay. Four out of 14 observations had mCd values below 1.5, indicating 'nil to very low degree of contamination'. The rest of the stations indicated 'low degree of contamination' with mCd values from 1.03 to 1.5.

The sediment quality guideline (MacDonald et al., 2000) was used to categorize element concentrations in sediments based on the toxicity to benthic organisms.

When comparing the results of the present study with ERL and ERM values, it was observed that Cd, Hg, and Zn at 100% of sampling stations were below the ERL values (1.2, 0.15 and 150 mg/kg, respectively) which indicated that those metals were not likely to have adverse effects on animals that live in the sediment. One station (Krapets) had Pb concentration higher than ERL which indicated that Pb at this station was likely to have effects adverse on 50% of animal populations that live in that sediment. On the other hand, all the rest of the studied stations had Pb concentration below the ERL value which indicated that Pb in the studied area was not likely to have adverse effects on animals that live in the sediments, except st. Krapets. Ni at two sampling stations (Burgas and Rosenets) had a value over the ERL value. St. Rosenets had concentration of Cu above the ERL value.

When compared to the TEL-PEL SQGs, the concentrations of Cd, Hg, and Zn were lower than the TEL value at 100% of the sampling stations. Pb showed values higher than the TEL value at the sampling stations in the northern part – Krapets, Rusalka and Kaliakra. In the case of Cu, 36% of the samples fell in the range between TEL and PEL at Rusalka, Kaliakra, Galata, Rosenets and Burgas indicating that associated adverse biological effects might occasionally occur. Ni concentrations were over TEL value at two stations - Rosenets and Burgas.

Only four stations (29%) had ERM-Q > 0.1 and were categorized as non-toxic and the rest of the stations were categorized as medium low toxic and might have 30% probability of being toxic. The m- ERM-Q calculated for the rest sampling sites indicated low toxicity with 12% probability of being toxic.

Fifty percent of the stations (Krapets, Rusalka, Kaliakra, Galata, Rosenets and Burgas) had m-PEL–Q within the range 0.11 – 1.5 with 25% likelihood of toxicity or categorized as slightly toxic (medium low). The rest of the stations were with m-PEL–Q below 0.1 representing non-toxic level. The m- ERM-Q calculated for the sampling sites (based on metals Cd, Cr, Cu, Ni, Pb, Hg and Zn) ranged from 0.01 to 0.34 (mean value of 0.15), indicating that the combination of Cd, Cr, Cu, Ni, Pb and Zn might have 30% probability of being toxic.

The pollution status assessed by applying different indices with respect to the investigated metals is shown in Table 2. Stations at which no pollution is detected are not included.

Metal concentrations in costal marine sediments varied considerably. The highest variation exhibited Cu (Table 3) - the difference between minimum and maximum concentrations was about 60 times. The highest concentrations of Cu and Ni were measured at st. Rosenets located in Burgas Bay near a past mining activities area. Burgas Bay and Varna Bay were the “hot spots” along the Bulgarian Black Sea coast. The concentration of Zn ranged from 2 to 96 indicating 40 fold difference among the studied stations. The maximum concentration was found in the sediments at st. Kaliakra. Maximum Pb concentration was at st. Krapets. The minimum concentrations of all metals were established at st. Slanchev Bryag, situated in the protected sand bank "Cocketrice" zone (2005).

As shown in Table 1, the average concentrations from nearly all the stations were lower than the average continental crust values. The exceptions were for Zn at st. Kaliakra and Cu at st. Rosenets which were both higher than the average continental crust value. This ratio measured concentrations / background value reflected in indices Igeo, CF, EF (Table 2). All single metal indices as Igeo, EF, CF indicated moderate contamination with Pb and Zn in the northern Danube influenced area of the Bulgarian coastal zone (stations Krapets, Rusalka and Kaliakra) and “hot spot” stations: Galata (close to Varna Bay), Rosenets and Burgas (in Burgas Bay).

The determined concentrations of Cd, Cu, and Pb at the sampling locations within the Bourgas Bay were significantly higher than those determined in the sampling sites outside the bay as a result of industrial and former mining activities in the area (Slaveykova et al., 2009). The highest Cu concentration was observed in macrophytes in Rosenets area (Strezov & Nonova, 2005).

Indices PLI and mCd indicated null overall pollution except st. Varna with low degree of contamination.

According to the low range values (ERL or TEL), adverse effects on sediment dwelling organisms were likely to occur regarding Pb, Ni and Cu concentrations at the stations in the northern part (Krapets, Rusalka, Kaliakra) and the "hot spot" stations Galata, Rosenets and Burgas. Concentrations higher than ERM or PEL were not established at the other stations indicating that adverse effects on benthic fauna were not expected to appear.

The classification of sediments according to ERMQ and PELQ showed that there was 30% or medium low probability of sediments to present toxicity in amphipod survival bioassays at the stations Kaliakra, Galata, Burgas and Rosenets and 25% probability in the northern part, the Danube current affected stations (Krapets, Rusalka and Kaliakra) and the "hot spots" (Galata, Burgas and Rosenets).

Upper range values (ERM or PEL) represent concentrations above which adverse effects are expected to appear.

Although some studies were carried out in the Bulgarian Black Sea coastal zone to assess the spatial variation of metal levels in sediments mainly in the past Andreev & Simeonov (1988; 1990); Jordanova et al. (1999); Simeonov & Andreev (1989); Simeonov et al. (2000); Stoyanov & Dimitrov (1991); none of those had assessed the status of metal pollution and the effect of pollution on benthic organisms especially in the recent period using pollution indicators.

The values were compared with other parts of the Black sea region (Table 3). Metal levels in the Bulgarian coastal zone are generally lower than those in the other Black sea regions. The maximum copper concentration at Rosenets station is comparable with the intense copper mining areas of Turkey – Rize. Average Ni and Pb concentrations are higher than the measured concentration in "hot spot" sediments from the Bulgarian Black Sea coastal zone (Simeonov et al., 2000).

Table 1. Average concentrations of metals in surface sediments from the Bulgarian Black Sea coastal zone, background concentration in the continental crust and Sediment Quality Guideline – ERL, ERM, TEL, PEL (mg/kg dry weight).

Station	Zn (mg/kg)	Pb (mg/kg)	Ni (mg/kg)	Hg (mg/kg)	Cu (mg/kg)	Cd (mg/kg)	Al (mg/kg)
Krapets	44.20	31.25	9.50	0.05	9.50	0.20	8799
Rusalka	67.00	30.40			21.50	0.14	
Kaliakra	96.10	45.80			40.30	0.14	
Varna Bay		11.00	8.00	0.05	9.60	0.25	9721
Galata	65.10	21.35	31.10	0.05	21.25	0.20	26210
Kamchia		6.20	10.70	0.05	8.70	0.25	13410
Irakli	14.30	7.60	10.60	0.01	6.70	0.08	
Slanchev Bryag	2.29	2.43	2.27	0.01	1.09	0.23	
Rosenets		29.90	42.20	0.05	66.90	0.25	43930
Bourgas	23.00	16.50	28.40	0.03	19.85	0.19	47800
Veleka		5.00	8.90	0.05	9.40	0.25	11620
Min-Max	2.29÷96.1	2.43÷57.5	2.27÷42.2	0.05÷0.02	1.09÷66.9	0.08÷0.25	8799÷47800
All Grps	45	20	18	0.04	19	0.20	23070
Continental crust (Taylor, 1964)	70	12.5	75	0.008	55	0.2	82300
ERL	150	46.7	20.9	0.15	34	1.2	
ERM	410	218	51.6	0.71	270	9.6	
TEL	124	30.2	15.9	0.13	18.7	0.68	
PEL	271	112	42.8	0.7	108	4.21	

Table 2. Pollution status of Bulgarian Black Sea coastal zone stations, established by applying individual metal indices.

Station	Igeo	EF	CF	ERL	TEL
Krapets	Pb moderately to strongly contaminated	Pb moderate	Pb considerable	Pb medium low	Pb medium low
Rusalka	Pb moderately contaminated		Pb moderate		Pb, Cu medium low
Kaliakra	Zn moderately contaminated, Pb moderately to strongly contaminated		Zn moderate, Pb considerable	Cu medium low	Pb, Cu medium low
Varna Bay		Pb significant			
Galata	Pb moderately contaminated	Pb moderate	Pb moderate		Cu medium low
Kamchia		Pb moderate			
Slanchev Bryag			Cd moderate		
Rosenets	Pb moderately contaminated	Pb moderate	Pb, Cu moderate	Ni, Cu medium low	Ni, Cu medium low
Bourgas	Pb moderately contaminated	Pb moderate	Pb moderate	Ni medium low	Ni, Cu medium low

Table 3. Comparison of sediments concentrations of heavy metals (mg/kg dry weight) with the data from literature sources.

Region/Authors/Period	Cd	Cu	Ni	Pb	Zn
West Black Sea (Unsal et al., 1998)	0.001÷0.225	2÷47		5÷143	12÷238
Whole Black Sea 1989 (Kiratli & Ergin, 1996)		29÷68	38÷130	14÷35	50÷108
Whole Black Sea 1997-1998 (Topcuoglu, 2000)	0.6÷0.9	23÷75	38÷130	14÷35	57÷127
West Black Sea 2008 (Ozkan & Buyukisik, 2012)	0.18÷0.53	40÷72	57÷93	20÷38	83÷184
South-Western (Bulgarian) Black Sea (Andreev & Simeonov, 1988)		22÷46	31÷38	23÷36	76÷105
Bulgaria Hot Spots (Simeonov et al., 2000)	0.01÷4.29	3÷786	1÷28	1.55÷118.8	14.77÷265.54
Romania 2006-2011 (Alexandrov et al., 2012)	0.01÷9.63	0.53÷147.84	0.40÷211.73	0.10÷300.78	
Midia Port (Catianis et al., 2016)	0÷2	5÷145	12÷44	2÷92	21÷222
Odessa (Dyatlov, 2015)	0.2÷17	0.1÷65.2	12.6÷79		
Range of metals in this study	0.08÷0.25	1.09÷66.9	2.27÷42.2	2.43÷57.5	2.29÷96.1
Romania 2006-2011 (Alexandrov et al., 2012)	1.03	27.54	36.54	26.71	
Rize (Alkan et al., 2015)	0.3÷0.5	33÷54	7÷9	14÷19	78÷96
Rize (Topcuoglu et al., 2003)	<0.02	67.8		67.8	483.1
Eastern Black Sea (Baltas et al., 2017)		576.31		97.33	357.2
Romania (Secrieru & Secrieru, 2002)	0.75	32.2	66.4	15	64.6
Ukraine (Wilson et al., 2008)	2.1	117		614	114
Georgia (Wilson et al., 2008)	2.7				3.35
Bulgaria Hot Spots (Simeonov et al., 2000)	0.81	80	12.96	15.96	58.97
Mean concentration in this study	0.20	18.96	18.01	19.75	44.57

Factor analysis was applied to summarize the spatial pattern of metal distribution. The only one extracted factor explains 94% of the total variance and eigenvalue of 2.9 with statistically significant loadings of Ni, Pb and Cu. The highest scores of this factor are found in the "hot spot" stations Galata, Burgas and Rosenets. Therefore, Factor 1 is attributed to anthropogenic pollution.

Conclusions

Several environmental indices were used for assessment of heavy metal contamination levels in the sediments of the studied area. The level of the most trace metals was not extremely high in the surface sediments of the Bulgarian Black Sea coastal zone and did not present a serious threat to the local fauna and flora**.** The northern Danube influenced area of the Bulgarian coastal zone was categorized according to the applied indices as slightly polluted with Zn and Pb. The sediments from the "hot spot" stations were with higher accumulation of Ni, Cu and Pb.

Although the results were preliminary, they did not reveal high pollution levels in the Bulgarian coastal zone.

Acknowledgments

This study was carried out as part of the TC Project RER7009/IAEA „Enhancing Coastal Management in the Adriatic and the Black Sea by using Nuclear Analytical Techniques".

References

Alkan, N., Alkan, A., Akbaş, U., & Fisher, A. (2015). Metal pollution assessment in sediments of the southeastern Black Sea coast of Turkey. *Soil and Sediment Contamination: An International Journal*, *24*(3), 290-305. doi: 10.1080/15320383.2015.950723.

Alexandrov, L., Anton, E., Boicenco, L., Coatu, V., Cristea, M., Diaconeasa, D., & Zaharia, T. (2012). *The Initial Assessment of the state of the marine environment under Article 8 of the Marine Strategy Framework Directive*, 215 p. Retrieved from rmri.ro. (in Romanian)

Abrahim, G., & Parker, R. (2002). Heavy metal contaminants in Tamaki Estuary: impact of city development and growth, Auckland, New Zealand. *Environmental Geology*, *42*(8), 883–890. doi: 10.1007/s00254-002-0593-0.

Abrahim, G., & Parker, R. (2008). Assessment of heavy metal enrichment factors and the degree of contamination in marine sediments from Tamaki Estuary, Auckland, New Zealand. *Environmental Monitoring and Assessment*, *136*(1-3), 227–238. doi: 10.1007/s10661-007-9678-2.

Andreev, G., & Simeonov, V. (1988). Occurrence and distribution of some elements in sediments from the Black Sea. *Toxicological & Environmental Chemistry*, *18*(2-3), 221-228. doi: 10.1080/02772248809357314.

Andreev, G., & Simeonov, V. (1990). Distribution and correlation of elements in waters, suspensions, sediments and marine organisms from the Black Sea. *Toxicological & Environmental Chemistry*, *28*(1), 1-9. doi: 10.1080/02772249009357586.

Ariman, S., & Bakan, G. (2008). Sequential Extraction of Heavy Metal in Sediments at River and Marine of Mid-Black Sea Coast, Turkey. 22-26 Jun 2008, *35th International Symposium on Environmental Analytical Chemistry*, ISEAC 35, Gdansk-Poland.

Baltas, H., Sirin, M., Dalgic, G., Bayrak, E., & Akdeniz, A. (2017). Assessment of metal concentrations (Cu, Zn, and Pb) in seawater, sediment and biota samples in the coastal area of Eastern Black Sea, Turkey. *Marine pollution bulletin*, *122*(1-2), 475-482.

Birch, G. (2003). A scheme for assessing human impacts on coastal aquatic environments using sediments. In Woodcoffe, C. D., Furness, R. A. (Eds.), *Coastal GIS 2003*. Wollongong University Papers in Center for Maritime Policy, 14, Australia.

Catianis, I., Ungureanu, C., Magagnini, L., Ulazzi, E., Campisi, T., & Stanica, A. (2016). Environmental impact of the Midia Port-Black Sea (Romania), on the coastal sediment quality. *Open Geosciences*, *8*(1), 174-194. doi: 10.1515/geo-2016-0018.

Corine CLC Bulgaria (2012). *Corine Land Cover Bulgaria 2012*. Retrieved from eea.government.bg (in Bulgarian)

Davis, C., & Fox, M. (2009). Sediment fingerprinting: review of the method and future improvements for allocating nonpoint source pollution. *Journal of Environmental Engineering*, *135*(7), 490-504. doi: 10.1061/(ASCE)0733-9372(2009)135:7(490).

Din, T. (1992). Use of aluminum to normalize heavy metal data from estuarine and coastal sediments of straits of Melaka. *Marine Pollution Bulletin*, *24*, 484–491. doi: 10.1016/0025-326x(92)90472-i.

Dyatlov, S. (2015). Heavy Metals in Water and Bottom Sediments of Odessa Region of the Black Sea. *Journal of Shipping and Ocean Engineering*, *5*, 51-58. doi: 10.17265/2159-5879/2015.02.001.

EC. (2000). Directive 2000/60/EC of the European Parliament and of the Council establishing a framework for Community action in the field of water policy. *Official Journal of the European Communities, L327,* 1-72. Retrieved from: eur-lex.europa.eu.

Gao, X., & Li, P. (2012). Concentration and fractionation of trace metals in surface sediments of intertidal Bohai Bay, China. *Marine Pollution Bulletin*, *64*, 1529–1536. doi: 10.1016/j.marpolbul.2012.04.026.

Hakanson, L. (1980). An ecological risk index for aquatic pollution control a sedimentological approach. *Water Research*, *14*(8), 975–1001. doi: 10.1016/0043-1354(80)90143-8.

Harikumar, P., Nasir, U., & Rahman, M. (2009). Distribution of heavy metals in the core sediments of a tropical wetland system. *International Journal of Environmental Science & Technology*, *6*(2), 225-232. doi: 10.1007/BF03327626.

Jordanova, A., Strezov, A., Ayranov, M., Petkov, N., & Stoilova, T. (1999). Heavy metal assessment in algae, sediments and water from the Bulgarian Black Sea coast. *Water science and technology*, *39*(8), 207-212. doi: 10.2166/wst.1999.0423.

Kiratli, N., & Ergin, M. (1996). Partitioning of heavy metals in surface Black Sea sediments. *Applied Geochemistry*, *11*(6), 775–788. doi: 10.1016/ S0883-2927(96)00037-6.

Konsulova, T., Trayanova, A. & Todorova, V. (2010). Sand bank Koketrays – a case study on the effect of marine protected area designation as a key approach to the Black Sea biodiversity and habitats conservation. *Acta zoologica bulgarica*, *62*(1), 89-97.

Long, E., & MacDonald, D. (1998). Recommended uses of empirically derived, sediment quality guidelines for marine and estuarine ecosystems. *Human Ecological Risk Assessment 5*, 1019–1039. doi: 10.1080/10807039891284956.

Long, E., McDonald, D., Smith, S., & Calder F. (1995). Incidence of adverse biological effects within ranges of chemical concentrations in marine and estuarine sediments. *Environmental Management, 19*, 81–97. doi: 10.1007/BF02472006.

MacDonald, D., Ingersoll C., & Berger, T. (2000). Development and evaluation of consensus-based sediment quality guidelines for fresh-water ecosystems, Archives of *Environmental Contamination and Toxicology 39*, 20–31. doi: 10.1007/s002440010075.

Mee, L.D. (1992)**.** The Black Sea in crisis: the need for concerted international action. *Ambio, 21*(4), 278–286.

Müller, G. (1969). Index of geoaccumulation in the sediments of the Rhine River. *Geojournal*, *2*, 108–118.

Müller, G. (1979). Schwer metalle in den sedimentn des Rhiens-Verenderrungen seit. *Umsechan 79*, 778–783.

Ozkan, E., & Buyukisik, B. (2012). Geochemical and Statistical Approach for Assessing Heavy Metal Accumulation in the Southern Black Sea Sediments. *Ekoloji*, *21*(83), 11–24. doi: 10.5053/ekoloji.2012.832.

Saleem, M., Iqbal, J., & Shah, M. H. (2013). Study of seasonal variations and risk assessment of selected metals in sediments from Mangla Lake, Pakistan. *Journal of Geochemical Exploration*, *125*, 144-152.

Secrieru, D., & Secrieru, A. (2002). Heavy Metal Enrichment of Man-made Origin of Superficial Sediment on the Continental Shelf of the North-western Black Sea. *Estuarine, Coastal Shelf Sci. 54*, 513-526. doi: 10.1006/ecss.2000.0671.

Simeonov, V., & Andreev, G. (1989). Interpretation of Black Sea sediments analytical data by the clustering approach. *Toxicological and Environmental Chemistry*, *24*(4), 233-240. doi: 10.1080/02772248909357495.

Simeonov, V., Massart, D., Andreev, G., & Tsakovski, S. (2000). Assessment of metal pollution based on multivariate statistical modeling of 'hot spot' sediments from the Black Sea. *Chemosphere*, *41*(9), 1411-1417. doi: 10.1016/S0045-6535(99)00540-8.

Slaveykova, V., Karadjova, I., Karadjov, M., & Tsalev, D. (2009). Trace metal speciation and bioavailability in surface waters of the Black Sea coastal area evaluated by HF-PLM and DGT. *Environmental science and technology 43* (6), 1798-1803. doi: 10.1021/es802544n.

Stoffers, P., Glasby, G., Wilson, C., Davis, K., & Watter, P. (1986). Heavy metal pollution in Wellington Harbour. *New Zealand Journal of Marine and Freshwater Research*, *20*, 495–512. doi: 10.1080/00288330.1986.9516169.

Stoyanov, A., & Dimitrov, D. (1991). The ratio of Corg/Me as a biochemical parameter of surface sediments from a Bulgarian shelf. In *Marine chemistry investigations*,. Moscow, 194 p. (in Russian)

Strezov, A., & Nonova, T. (2005). Environmental monitoring of heavy metals in Bulgarian Black Sea green algae. *Environmental monitoring and assessment*, *105*(1-3), 99-110.

Taylor, S.R. (1964). Abundance of Chemical Elements in The Continental Crust: A New Table. *Geochimica et Cosmochimica Acta*. *28*, 1273-1285. doi: 10.1016/0016-7037(64)90129-2.

Tomilson, D.C., Wilson, J.G., Harris, C.R., & Jeffrey D.W. (1980). Problems in assessment of heavy metals in estuaries and the formation of pollution index. *Helgol Meeresunlters*, *33*, 566-575. doi: 10.1007/BF02414780

Topcuoglu, S. (2000). Black Sea ecology pollution research in Turkey of the marine environment. *International Atomic Energy Agency Bulletin*, *42*(4), 12–14.

Topcuoglu, S., Ergul, H. A., Baysal, A., Olmez, E., & Kut, D. (2003). Determination of radionuclide and heavy metal concentrations in biota and sediment samples from Pazar and Rize stations in the eastern Black Sea. *Fresenius Environmental Bulletin, 12*, 695-699.

Unsal, M., Cağatay, N., Bekiroğlu, Y., Kıratlı, N., Alemdağ, Y., Aktaş, M., & Sarı, E. (1998). Heavy metal pollution in the Black Sea. *Tarım ve Koyişleri Bakanlığı Trabzon Su Urunleri Araştırma Enstitusu*. Project No: YDABCAG-456/G-457/G; 51 p. (in Turkish)

Wilson, J., Komakhidze, A., Osadchaya, T., Alyomov, S., Romanov, A., & Tediashvili, M. (2008). Evaluating ecological quality in the north-eastern Black Sea coastal zone. *Mar. Poll. Bull. 57*, 202-207. doi: 10.1016/j.marpolbul.2008.04.020

Windom, H. L., Smith, Jr., R. G., & Rawlinson, C. (1989). Particulate trace metal composition and flux across the southeastern US continental shelf. *Marine Chemistry*, *27*, 283–297. doi: 10.1016/0304-4203(89)90052-2.

Received: 10.04.2020
Accepted: 08.05.2020