Assessing and Spatio-Temporal Variations of Potentially Toxic Elements in the Sediments from Lower Danube River in 2011-2017 Period

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Abstract. The growing concern for most European rivers is due to pollution with potentially toxic elements (PTEs) and is of course a priority challenge for the Danube, a river that interconnects fresh water with the marine environment. The accumulation of PTEs from the Lower Danube River sediments and the potential negative effects of these chemicals on the water quality during and after the hydro-construction works carried out in the area to improve the navigation conditions have been studied in the present work. For seven years period (2011-2017), sampling campaigns from 10 monitoring sites were carried out. Sediment samples were taken from the Lower Danube River (km 375 - km 175) from the left and right banks, monthly during the construction period (2011 - 2015) and quarterly in the post-construction period (2015 - 2017). A total approximately of 1200 samples were analyzed and Cd, Cr, Cu, Pb, Zn and Ni content was determined to obtain the assessment of sediments that can influence water quality. Multivariate statistical analysis was applied to the complex data set obtained, the degree of accumulation and the distribution of these metals on the studied section was calculated. Also, the quality indicators of sediments were evaluated according to the legislation in force. The results showed that all concentrations of the monitored PTEs have recorded values over the normal values from the current legislation. On the whole, Zn has the highest concentration, while Cd has the smallest one. The order of the absolute average concentrations values found in this study is Zn > Cu > Cr > Ni > Pb > Cd. For the Zn and Cu elements, slightly higher values were recorded compared to other heavy metals (Pb and Cd), which means that historically contaminated deposits in sediments can be remobilized and transported to the upper layers of the sediment or even be diffused in water. Generally, due to different sediment types and input levels, there is a variable contamination throughout the Danube aquatic ecosystem. The statistical analysis applied to analytic data highlighted the action of anthropogenic sources on the Danube aquatic ecosystem, showing the interdependencies between monitored indicators and seasonal influence.

Keywords: Potentially toxic elements (PTEs), sediments, statistical analysis, Danube River

1.Introduction

As a result of the development of society, environmental pollution caused by the use and release of a wide range of chemicals, especially of potentially toxic elements (PTEs) has reached global proportions and in all environmental, those being found beyond the limits allowed by the law in force [1, 2]. Pollution with PTEs, among which heavy metals are most often incriminated, presents a great concern to researchers due to their toxicity and long-term persistence in ecosystems, thus contributing to the global pollution of riparian environments [3-5]. On the other hand, the uncontrolled discharge of PTEs into the environment has led to their accumulation in sediment and soil, thus becoming a secondary source of water pollution with potentially harmful effects on ecosystems and human health

[6]. In the ecosystem, metals are accumulated as non-biodegradable pollutants, and being among the most persistent pollutants they provide a fairly accurate history of river pollution [7]. It is recognized that the assessing the quality of an aquatic ecosystem is a complex procedure due to the variety of chemicals present, to which climate change is added. The sediment quality is a significant indicator of the pollution degree of a river basin [8, 9], being considered as a storage tank for a wide variety of pollutants and also a component part of the aquatic ecosystem that reflects all processes occurring in a river basin [10, 11].

The present study was undertaken in accordance with the requirements of the European Water Framework Directive to maintain and restore the good ecological status of freshwater bodies through implementation of Programme of Measures [12, 13]. Restoring the good ecological status often means that multiple environmental targets are to be achieved [14, 15].

The Danube River as one of the most important inland waterways in Europe and consequently the environmental problems and socio-economic development of its region are of great importance [12]. A special attention should be focused on the improvement of the navigation conditions dependent on the river flow and sedimentary regime, which is why hydro-construction works are required. [16, 17]. Hydro - construction works included dredging, embankments and construction of bottom sills, which mobilized the local historical sediments, their accumulation along the downstream river banks which could have a potential negative impact on the environment. Moreover, the hydrological constructions performed may affect anadromous migratory fish, such as sturgeon [10]. The dredging may have negative effects due to several causes: i) dredged materials cause habitat loss or alteration of sturgeon species; ii) during dredging operations, larvae, juveniles and adults may be killed; iii) the food for many fish species is destroyed because of zooplankton and phytoplankton alterations [10]. For environmental protection purposes, during the entire construction period, as well as before and after it, National Institute for Research and Development in Environmental Protection (INCDPM) performed the evolution of the environmental factors state in the intensive monitoring program [18]. Innovative monitoring systems were designed and used for identifying the possible impact of the constructions and to develop timely alternative solutions to intervene for reducing and controlling the foreseen risks.

Generally, the assessment of the Danube River pollution is one of the key elements of ecology and people's health from its region. Particularly the risk of pollution during some hydrotechnical construction had been take into account, many specialists from connected scientific fields addressing various aspects of the problem through several studies based on integrated monitoring data [19]. These data were the result of the successive monitoring programs, considered very important in terms of providing representative and reliable estimates of the data in time and space. At cross-border level, monitoring the quality of the Danube ecosystem is carried out by the ICPDR, through the Transnational Monitoring Network (TNMN), which provides a comprehensive water quality database [20, 21]. This study has been designed to continue and to integrate previous research on the region of the Lower Danube [22 – 30]. Compared to those studies, this paper addresses entire period of seven years monitoring, so that comprised both the hydro-construction period and the post-construction period. The accumulation of potentially toxic elements in sediments from the Lower Danube River (km 375-km 175) during 2011-2017 were carried out and is here presented, taking into account the database obtained following the intensive monitoring program and the links between multiple pressures on the aquatic ecosystem and the interdependencies of the monitored indicators.

2.Methods and materials

The sediments monitoring sites are located along the lower area of the Danube River (Fig. 1), between Calarasi (km 375) and Braila (km 175), where hydro-technical works were carried out to meet the recommendations of the Danube Commission to maintain minimum navigation water depths during dry seasons [31].

The sediment samples were collected from 10 locations from the Lower Danube River area, according to figure 1 and table 1, and the following indicators were monitored: copper (Cu), cadmium

(Cd), chromium (Cr), lead (Pb), nickel (Ni) and zinc (Zn) content. Sediment were sampled monthly from each of the 10 locations during the construction monitoring stage (52 months during 2011-2015) which yielded 104 samples per section, comprising of the left and right banks sampling points. During the post-construction monitoring (2016-2017), the sampling was carried out quarterly yielding 16 samples per section for each of the 10 locations (8 sampling campaigns). In total, 1200 sediment samples were collected and analyzed.

Table 1. Sediment sampling locations

Monitoring area	Location	Length (km)	Geographical coordinates	
			longitude	latitude
MA-1 (Bala Area)	S1	347	27°34'9.549"	44°11'24.35"
	S2	345		
	S3	344		
	S4	343		
MA-2 (Epurasu Island)	S5	340	27°37'2.349"	44°11'59.10"
	S6	341		
	S7	334		
MA-3 (Lupu Island)	S8	197	27°54'27.93"	45°4'0.316"
	S9	196		
	S10	195		

Sampling was carried out from about 1 m from the shore (Danube river bank) and from at least 0.5 m Danube water depth. Samples were collected using a *Petersen* sediment sampler when the sampling was possible and a *Burkle* auger core sampler for more densely aggregated sediments. Approximately 500 g of sediment was collected for each sample in 500 mL clean PTFE recipients and stored in the dark at 4°C during transport to the laboratory. Prior to analysis, the samples were dried at room temperature. After drying, to obtain representative sediments samples, they were milled, sieved and in order to bring them into the solution, mineralization of about 0.5 g of the sample from the 63 μm fraction.

Figure 1. Sampling locations on the Lower Danube River, between Calarasi (km 375) and Braila (km 175)

To determine the concentration of the elements, sediment samples was subjected to microwave assisted pressured digestion by 3:1 HCl (37%):HNO3 (65%) with a maximum temperature plateau of 200°C for 10 minutes. The obtained clear solutions were quantitatively filtered and brought to 100 mL calibrated flask with diluted nitric acid solution in ultra-pure water.

Microwave digestion of sediment samples was performed on a Milestone ETHOS Microwave System. Elements concentration in digested samples were determined using flame (FAAS) and graphite furnace (GFAAS) atomic absorption spectrometry (Solaar M5, Thermo).

All solutions were prepared using ultra-pure water from a Micropure Ultrapure water system (TKA, Germany) and Suprapur® nitric acid (65 %) purchased from Merck, Germany. Samples were filtered using 0.45 μm acid hardened cellulose membrane filters (Whatman, Merck, Germany).

Analytical quality assurance was performed by the random duplicate sample method and with a *river Elbe sediment certified reference material* (CRM LGC 6187, UKAS reference materials, United Kingdom) periodically during each run. Further information regarding the sampling areas and the quality indicators may be accessed on the monitoring project homepage *http://www.afdj. ro/en/content/romomed*.

Statistical methods, such as Principal Component Analysis (PCA) and Cluster Analysis (CA) were used at the database obtained from the intensive monitoring program. Sediment quality assessment was performed by comparing the analyzed values with the limits (quality standard criteria) imposed by the Ministerial Order 161/2006 [32], which in turn implements the guidelines of *Directive 2000/60/EC of the European Parliament* [13].

3.Results and discussions

The information regarding the central tendency and distribution of each potentially toxic elements (Cu, Cd, Cr, Pb, Ni and Zn) in sediments from the studied area was obtained by applying the multivariate statistical analysis techniques using the statistical software package JMP 10, and the values were assessed according to the national legislation in force.

Table 2 presents a descriptive analysis of the potentially toxic elements concentration using the following variables: minimum, median, maximum, mean, standard deviation, standard error mean and reference values according to the applicable legislation.

The results showed that all PTEs have recorded concentration values over the normal values from the national legislation. Generally, Zn has the highest concentration (217.43 mg·kg^{-1}), while Cd has the smallest one (1.33 mg·kg^{-1}).

Table 2. Statistical analysis of potentially toxic elements in sediments

	Cu (mg·kg^{-1})	Cr (mg·kg^{-1})	Pb (mg·kg^{-1})	Cd (mg·kg^{-1})	Ni (mg·kg^{-1})	Zn (mg·kg^{-1})
Min	2.65	1.85	0.42	0.02	10.08	28.29
Median	32.47	37.18	19.22	0.39	36.43	91.59
Max	126.52	99.87	84.75	1.33	99.67	217.43
Mean	35.18	38.94	20.20	0.38	37.90	94.91
St Deviation	16.06	19.63	11.74	0.16	11.95	26.62
St Error Mean	0.47	0.58	0.34	0.01	0.35	0.78
Normal values*	40	100	85	0.8	35	150

*Normal values of potentially toxic elements in sediments according to M.O. 161/2006 [32].

The order of absolute average values observed in this study is Zn> Cu> Cr> Ni> Pb> Cd. For Cu, Zn and Ni elements, slightly higher values were recorded compared to other heavy metals, which means that historically contaminated deposits in sediments can be remobilized and transported to the upper layers of the sediment or can diffused in water. Another possible explanation for the higher zinc concentration may be its predisposition to form highly soluble complexes, a process that may involve a high risk for biota aiding the PTE mobility, while Cd and Pb complexes exhibit average mobility in the environment, and Ni has low mobility, probably also because of the inert complexes that may exist. Generally, due to different sediment types and input levels, there is a variable contamination throughout the aquatic ecosystem.

To find the direct relationships between the studied elements, the *Pearson* correlations matrix was applied. Table 3 shows the matrix of correlation coefficients between the potentially toxic metals concentrations.

Table 3. Correlation matrix for potential toxic elements studied

	Cd	Cr	Cu	Pb	Zn	Ni
Cd	1.0000					
Cr	0.1169	1.0000				
Cu	0.4698	0.3122	1.0000			
Pb	0.3066	0.2329	**0.5658**	1.0000		
Zn	0.4754	0.3141	**0.7702**	**0.4966**	1.0000	
Ni	0.4178	0.2886	**0.5287**	0.4437	**0.5692**	1.0000

Pearson correlation coefficients for concentrations of potentially toxic elements from the sediment samples (table 3) showed a direct relationship between studied metals. These statistical values have highlighted the pronounced heterogeneous nature of metals concentrations dispersion at the sediments in the monitored area because the correlations were predominantly low, with only a few statistically more significant correlations.

Table 4 contains selected significant loading values for the first 3 Principal Components (PC).

In Table 4 it can be seen that the pronounced non-uniformity of the values does not seem to indicate other major common sources of contamination, the first component being associated with common alluvial intake for the entire region. The results of the loading matrix on the principal components showed that the first component comprised the variability of all elements from data sets, the second component took over the variability of Pb, Cd and Cr and the third component was associated with Cd and Cr concentration as main constituents

Table 4. Loading matrix

Parameters	PC1	PC2	PC3
Cu	0.8694		
Zn	0.8646		
Ni	0.7577		
Pb	0.7096	-0.5678	
Cd	0.6400	0.5097	-0.4465
Cr	0.4558	0.2683	0.8321

To reduce the dimensionality of the data set, PCA statistic method was performed using a matrix composed of the concentrations obtained for each metal and the possible patterns or element sources in the sediments database was identified. Figure 2 shows the eigenvalues associated with the principal components and the percentage of variability accounted by each PC.
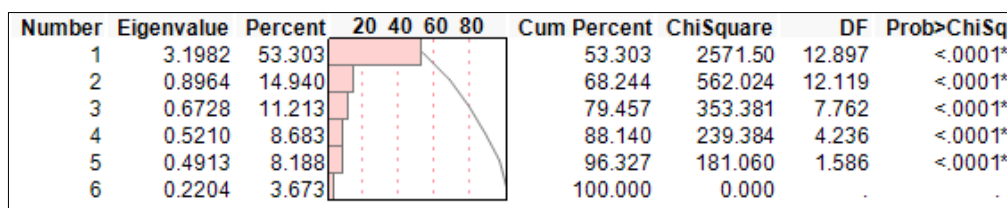
Number	Eigenvalue	Percent	20 40 60 80	Cum Percent	ChiSquare	DF	Prob>ChiSq
1	3.1982	53.303		53.303	2571.50	12.897	<.0001*
2	0.8964	14.940		68.244	562.024	12.119	<.0001*
3	0.6728	11.213		79.457	353.381	7.762	<.0001*
4	0.5210	8.683		88.140	239.384	4.236	<.0001*
5	0.4913	8.188		96.327	181.060	1.586	<.0001*
6	0.2204	3.673		100.000	0.000	.	.

Figure 2. Eigenvalues and percentage of data variability accounted by each PC

The first principal component represents (PC1) 53.30 % from the variability of the entire data set, the second principal component (PC2) supplemented by 14.94 % the coverage of the original variance and the third principal component (PC3) contributed with 11.21 %. This fact indicated that the first component collected much of the information from the samples, which contained potentially toxic elements from the common source of alluvia supplied by the river. All the three principal components accounted for approximately 79.45 % of the entire variability of the data set, highlighting the major trends of the monitored ecosystem. The relative slow decay rate of the variability contribution of each individual PC may be another indication of the mostly uncorrelated evolutions of the monitored indicators caused by a high degree of heterogeneity.

For a more detailed assessment of the relationship between PTEs and for identification of anthropogenic and natural sources, Cluster Analysis (CA) has been used. The results are illustrated by a hierarchical dendrogram as shown in Figure 3. It is known that as value on the group of distances is lower, the more important the association is.
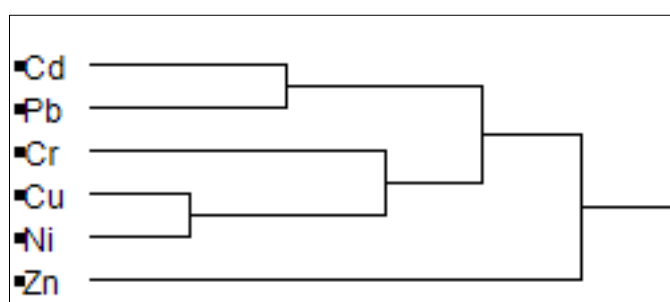

Figure 3. Dendrogram of potentially toxic elements

Depending on the degree of association between PTEs, two distinct clusters could be identified (Figure 3): the first group includes Ni, Cu and Cr, supporting the hypothesis of a common origin and the second group formed by Cd, Pb and Zn, which probably derives from anthropogenic activities. Overall, the clusters seemed to indicate the presence of both natural and anthropogenic potentially toxic elements sources of origin.

The statistical distribution of the data was compared to an equivalent normal distribution, with an average confidence level of 95 %. Histograms for concentration of Cu, Cr, Pb, Cd, Ni and Zn are shown in Figure 4. The assessment of histogram confirmed that the original data sets for the analyzed potentially toxic elements are normally distributed. Over all, the assessed ecosystem is not severely affected by the presence of PTEs in sediments, resulting also in the heterogeneous distribution of the elements represented in histograms.

Sediment quality assessment was also performed by comparing the obtained PTEs values to the limits from the chemical quality standards set by Ministerial Order 161/2006 [32] that implements the guidelines of Directive 2000/60/EC of the European Parliament [13].

In the monitored area of the Lower Danube River, PTEs concentrations showed moderately increased values, indicating mixed geogenic and anthropogenic influences, which most likely originate from historical deposits of sediments. As an unintended consequence of the hydro-technical works, which involved dredging, embankments and construction of bottom sills, the historical sediment layer re-suspension occurred, distributing the newly re-suspended sediments downstream along the banks with a potential impact on the environment.
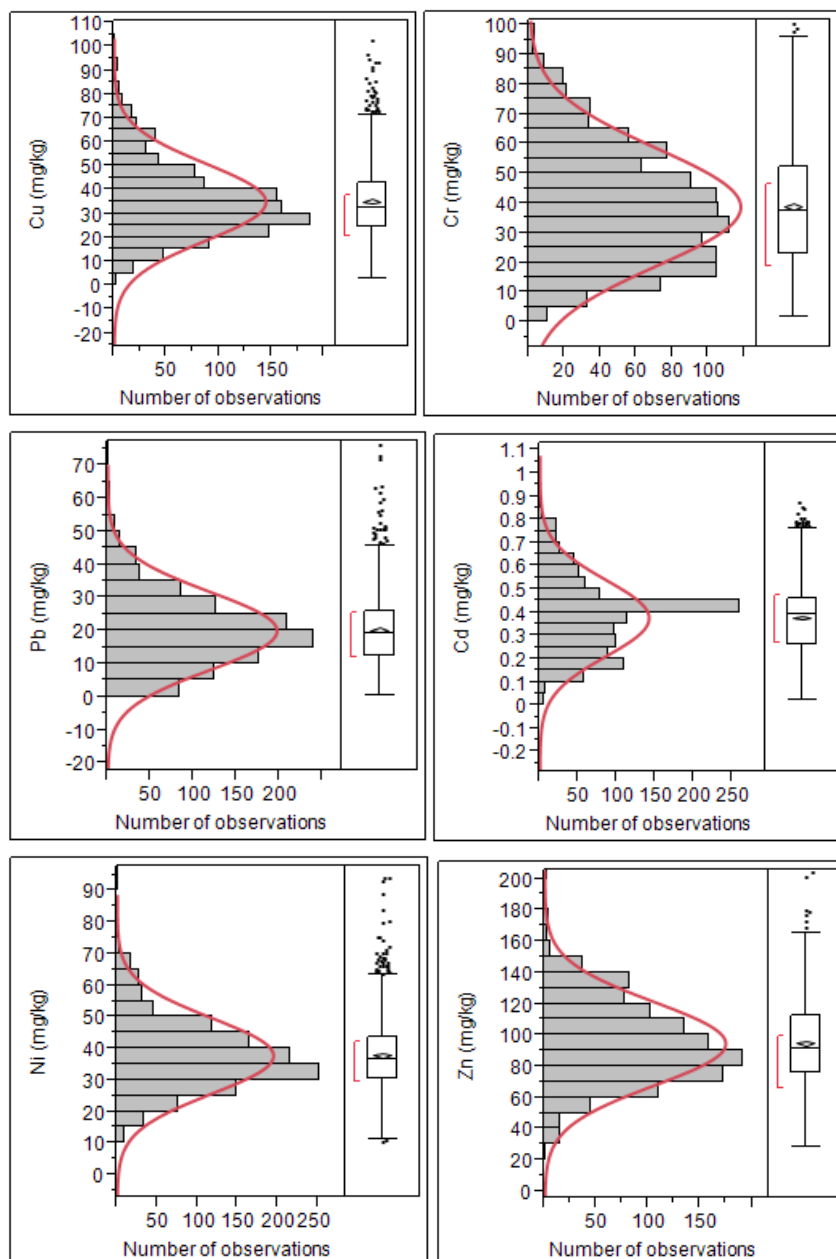
Figure 4. Histograms of Cu, Cr, Pb, Cd, Ni, Zn concentration in sediment samples

From Figure 5 it is observed that the spatio-temporal variation of metals in sediments collected from the lower Danube section have registered a moderate increased values during the monitored period regarding the presence of all potentially toxic elements. In section MA-2, immediately downstream of the dredging and embankments activities the PTEs have slightly higher concentration values than in the other monitored sections (Figure 5).

Copper showed considerable concentration variations, from 21.72 mg·kg^{-1} at MA-3 to 54.52 mg·kg^{-1} at MA-2 (Figure 5a), probably due to hydro-technical activities superimposed on upstream pollution. At all sampling sites, concentrations are lower in relation to normal values according to M.O. 161/2006 (40 mg·kg^{-1}), except at MA-1 and MA-2 in the 2014 period.

Figure 5 depicted that in the analyzed sediments, the total concentration of Cr ranged from 18.71 mg·kg^{-1} (at MA-3) to 57.79 mg·kg^{-1} (at MA-1) (Figure 5b) and total concentration of Pb varies from 8.24 mg·kg^{-1} (MA-3) to 32.44 mg·kg^{-1} (MA-1) (Figure 5c). Total concentration of Ni in sediments

ranged from 31.65 mg·kg⁻¹ (at MA-3) to 50.89 mg·kg⁻¹ (at MA-1) (Figure 5e) and total concentration of Zn varies from 69.13 mg·kg⁻¹ (MA-2) to 113.33 mg·kg⁻¹ (MA-2) (Figure 5f).

Figure 5. Spatio-temporal variations of monitored parameters: a) Cu; b) Cr; c) Pb; d) Cd; e) Ni; f) Zn. QS - Ministerial Order 161/2006 [32]

The average Pb concentrations were generally low and did not posed a significant environmental risk considering the already known diffuse and localized sources of Pb pollution, such as industrial activities (mining and smelting) and leaded gasoline emissions which generally pose a high environmental risk (Figure 5c). Total Cd concentrations increased along the monitored area, varying from 0.24 mg·kg⁻¹ at MA-3 to 0.57 mg·kg⁻¹ at MA-2 (Figure 5d), but this low concentration value indicates that Cd does not pose an ecological risk in the studied area. The higher Cd concentrations at MA-2 may be a result of the reduction of river flow, leading to re-settling of historical sediments and Cd accumulation. From MA-1 down to MA-3, the average PTEs content was lower in relation to normal values according to M.O. 161/2006.

The present values of total PTEs concentrations are similar to those found in earlier studies on the Lower Danube River [28].

Figure 6 shows that in the monitored areas the hydrological regime of the Danube is relatively uniform, with the exception of section MA-2 where very low values for water flow are observed.
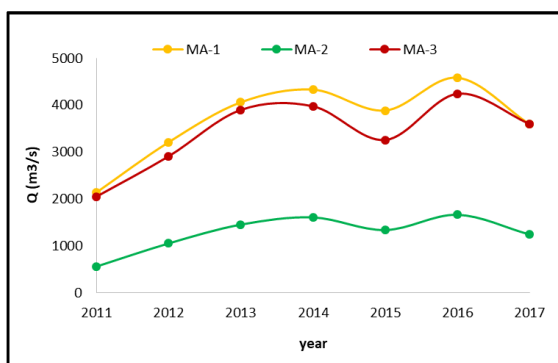
Figure 6. Spatio-temporal variations of Danube River water flow, between Calarasi and Braila

The integrated results obtained following the intensive monitoring program presented in this study, as well as other works and studies carried out by INCDPM specialists, show that the sediments are affected by historical pollution, the construction works carried out did not have a major negative impact on environmental factors, the quality of sediment being characterized by natural and anthropogenic influences, agriculture, industry, climate change etc. [22-30]. Increased attention should be paid to the frequent monitoring of heavy metals content for a significant impact on the quality of water and sediment in the Lower Danube River and for a long-term positive environmental protection of the final collector, the Black Sea basin. The assessment of loads in the Danube River contributes greatly to estimates of the influx of polluting substances to the Black Sea, and provides vital information to support policy development [21].

This study is a useful tool in protecting water resources in the context of providing information for a Danube Basin Management Plan that can help improve the quality of life and the environment. The protection and improvement of the water quality and of the environment in the Danube River Basin is essential for achieving sustainable development and is vital for the long-term health, well-being and prosperity of the Danube Region population.

4. Conclusions

The evaluation and the spatio-temporal variations of the potentially toxic elements, Cd, Cr, Cu, Pb, Zn and Ni in sediment layers from Lower Danube River in 2011-2017 period were performed and the correlation between the PTEs concentration and compliance with the actual quality standards was assessed. Present work was based on data derived from an intensive monitoring program and provides an overview of the quality ecosystem between Calarasi (km 375) and Braila (km 175). The study shows that despite the large regional and local pressures from the point of view of natural and anthropogenic influences, the lower Danube ecosystem is not strongly affected by the presence of potentially toxic elements due to hydro-constructions. The presence of a slightly higher level for certain indicators, such as Zn, Cu and Ni, indicates a historical pollution probably caused by a combination of natural phenomena and anthropogenic sources, historical deposits that can be re-suspended and transported to the upper layers of sediment or diffused in water. Overall, the assessed ecosystem is not severely affected by the presence of potentially toxic elements in sediments, resulting also from the heterogeneous distribution of the elements represented in histograms. The presented results can be used as a database for specialists and environmental authorities to identify and reduce Danube environmental pollution.

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