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GEOCHEMICAL CHARACTERISTICS OF RIVERBED SEDIMENTS IN THE DANUBE DELTA, ROMANIA

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Abstract

Major ($CaCO_3$, TOC, and Fe_2O_3), minor (MnO and TiO_2) and trace (Zr, Cr, V, Zn, Cu, Ni, As, Pb, and Hg) elements from surface riverbed sediments were determined at 66 locations in deltaic environment, along St. George distributary and in the interdistributary depressions of the Danube Delta. The studied area is characterized by terrigeneous, either non-carbonated or low calcareous sediments, quite poor in organic matter. Most of the studied heavy metals showed high spatial variability, generally with higher concentrations in interdistributary depressions and adjacent canals, as well as on the meander Mahmudia (M1). Ni, Cu, and Cr showed concentrations frequently exceeding the quality criteria set in the Romanian legislation. Contamination Factor (CF) and Pollution Load Index (PLI) were used to assess the level of heavy metal pollution in the studied area.

***Key words**: major elements, trace elements, Danube Delta, hydrological processes, anthropogenic pressure.*

INTRODUCTION

Geochemical analyses are widely used by the scientists for the determination of the sediment provenance, weathering, diagenesis, heavy-mineral composition, anthropogenic impact and environmental risk assessment (Wu et al., 2013; Babek et al., 2015; Najamuddin et al., 2015; Campodonico et al., 2016; Zhang et al., 2017; Zakir Hossain et al., 2017; Li et al., 2017, Natali & Bianchini, 2017; Mureşan et al., 2019; Bucşe et al., 2020; Ispas et al., 2020; Teaca et al., 2020; Vasiliu et al, 2020). In the fluvial environment, the pollutants are transported by rivers, both as pollutants in solution and adsorbed to suspended solids suspended sediments, under specific flow conditions. The concentration of different pollutants (e.g. heavy metals, pesticides) in the fluvial deposits can be higher due to the remobilization of the older sedimentary deposits of pollutants during the erosion and accumulation processes (Oaie et al., 2005; 2015).

Antropogenic activities, such as construction of dams, hydrotechnical work on the channel planform (e.g. groins, embankments, jetties, meander cut-off) represent important factors in the sedimentary processes by segmentation or even interruption of the sedimentary flow downstream the reservoirs (Tiron Duţu et al., 2019). Two large dams were built at Km 943 (Iron Gates I) and Km 863 (Iron Gates II), in 1973 and 1984, respectively, in the Danube lower segment, having a significant impact on the water and sediment fluxes and, consequently, on the environmental state (Vadineanu, 2001; Panin, 2003; Romanescu, 2013; Romanescu & Stoleriu, 2014; Habersack et al., 2016). Combined with the hydro-technical regulation works along the Danube tributaries, abovementioned dams have dramatically decreased the sediment discharges measured at the Danube's mouths (within 25-30%) (Panin & Jipa, 2002; Panin, 2003; Panin et al., 2016).

Located in the south-eastern part of Romania, the Danube Delta is the largest delta in the European Union covering about 5640 km^2 with a very complex network of canals and lakes (Panin, 2003; Driga, 2004). The Danube input of freshwater supplies the natural lakes and channels through its main distributaries (Kilia, Sulina and St. George). The Danube Delta acts as a natural filter for about 7 to 10% of the total water, sediments and pollutants discharges of the river into the sea (Oaie et al., 2015).

In the Danube Delta, the present hydro-morphological and sedimentological processes are the result of a multiple series of anthropic works located in the Danube Basin but also

inside the delta. In the last 200 years, the cut-offs programme of the Sulina and St. George branches brought a redistribution of water and sediment discharges among the delta distributaries (Panin, 1999; Panin & Jipa, 2002; Driga, 2004; Romanescu, 2013). The artificial canals along the St. George branch produced aggradation on the former meanders and erosion of the artificial canals (Popa, 1997; Jugaru Tiron et al., 2009; Tiron Duţu et al., 2014) (Figure 1).

Geochemical studies carried out on the Danube River (Secrieru & Secrieru, 1996; Oaie et al., 2000, 2005; 2015; Catianis et al., 2018) showed many pollution sources resulting from human activities (such as mining exploitations, the hydroelectric power stations, the waste and the sewage, the agriculture farms), and local natural impacts (e.g. geology of the basement; fossil littoral beaches).

A study on the distribution of the geochemical compounds on a rectified meander system of the Danube Delta (three rectified meanders of the St. George branch, Mahmudia, Dunavat de Sus and Dunavat de Jos meanders), realised by Tiron Dutu et al. (2019), concluded that the chemical composition correspond to terrigenous, non-carbonated and low-calcareous, with the occasional presence of calcareous sediments. According to the Order 161/2006, authors have found the quality of the sediments generally as good, with some isolate exceptions for Cr, Cu and Ni.

MATERIALS AND METHODS

This study present geochemical data acquired along the St. George branch in September 2020. The sediments were sampled in high flow period, at a daily discharge of 2,169 $m^3 \cdot s^{-1}$ (measured at Ceatal St. George knot) (Figure 1).

Surface sediment samples were collected with a grab sampler from 66 locations distributed along the branch, on the main channel and former meanders (Mahmudia, Dunavăţ de Sus, Dunavăţ de Jos, Perivolovca, Dranov de Sus, Dranov de Jos, Ivancea meanders, noted here as M1, M2, M3, M5, M5, M6 and M7, respectively); few samples have been collected in the interdistributary depressions (Uzlina and Gorgostel Lakes) and adjacent canals (Dunavat, Uzlina, Mahmudia, Perivolovca and Garla Tuceasca canals) (Figure 1).

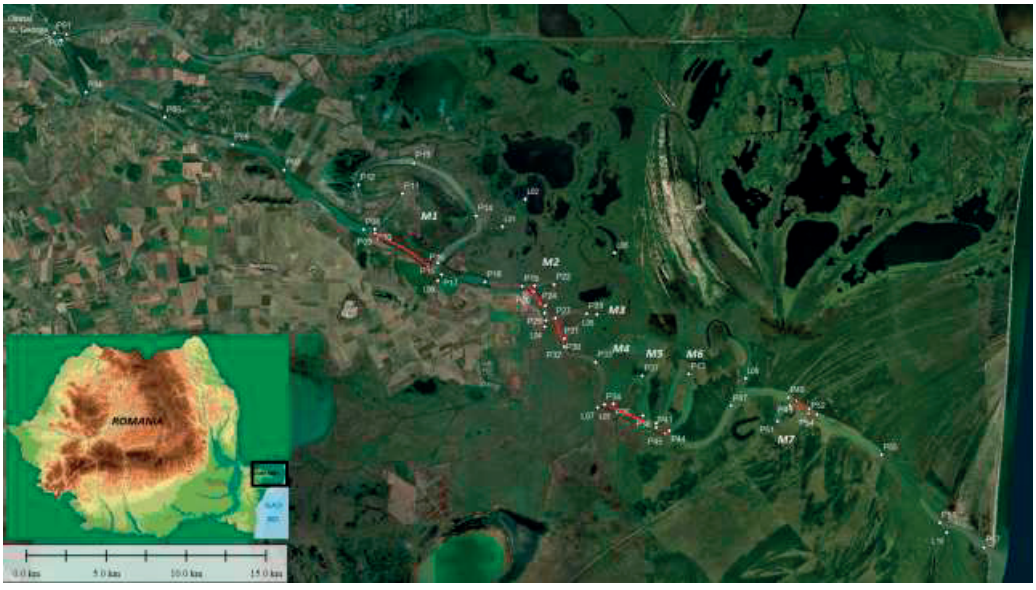

Figure 1. Location of the sediment samples along the St. George branch, in the Danube Delta. The lines in red represent the artificial canals of the rectified meanders

Prior to geochemical analysis the sediment samples were oven dried (24-48 h/105°C), ground, and homogenized using a mortar grinder RM 200 (Retsch, Germany) and sieved with a 250 μm stainless steel sieve. The total organic carbon (TOC) and $CaCO_3$ concentrations were determined in accordance with WakleyBlack titration method modified by Gaudette et al. (1974) and Black (1965), respectively. The concentrations of Fe_2O_3, TiO_2, MnO, Zr, Cr, V, Zn, Cu, Ni, As, and Pb were measured by X-ray fluorescence spectrometry using an EDXRF Spectro Xepos spectrometer with a Pd/Co tube and XRF AnalyzerPro software (v. 3.3.2). Total Hg content was determined using an automatic mercury analyzer DMA 80 Milestone (Italy), by solid sample thermal decomposition, identification, and quantification of total Hg by atomic absorption spectrophotometry.

To validate the analytical methodology, a certified reference material (NCS DC 73022) was used. The measured and certified values of element/compound concentrations were compared (Table 1). All of the results obtained for this reference material were statistically similar to the certified values ($p<0.05$), demonstrating the reliability of the methodology and the estimated concentrations. The relative standard deviations of the measured replicates were all within ± 5%.

Table 1. Measured and certified values of standard material NCS DC 73022

Element	Measured value (mg/kg) ± s.d	Certified value (mg/kg) ± s.d	Recovery %
Fe_2O_3	7.13±0.31	7.05±0.11	101.1
MnO	0.11±0.03	0.103±0.03	106.7
Ti	0.50±0.06	0.45±0.02	111.1
Zr	253±3	241±30	104.5
As	289±2	304±20	95
Ni	31.8±0.15	29±1	110
Cu	513±4.8	483±20	106
Cr	75.5±1.8	72±3	104.9
V	97.7±1.9	101±3	96.7
Zn	900±10.9	874±19	103
Hg	0.122±0.005	0.115±0.023	106
Pb	134.0±0.9	126±5	106.3

RESULTS AND DISCUSSIONS

$CaCO_3$ showed relatively low concentrations, ranging within 5.11-16.25% (Table 2). 43% of those values were lower than 10%, while 57% were between 10 and 30%, thus suggesting terrigenous sediments (either non-carbonated or carbonated) according to (Emelyanov & Shimkus, 1986). The highest $CaCO_3$ concentrations were measured in the sampling sites located in the Ceatal St. George area (stations P01 and P02). Concentrations quite close to the maxima were also registered at the entrance of M5 (station P34) and in Gorgoştel Lake (L06).

Total Organic Carbon (TOC) showed very high spatial variability (coefficient of variation >130%), with concentrations varying between 0.002% and 2.60% (Table 2). This high variability is due to the biogenic origin of TOC, in addition to its chemical instability and the dependence of its conservation in sediments both on grain size (fine particles preserve much better the organic matter) and local physical-chemical conditions (Tiron Duțu et al., 2019). Most of the TOC concentrations were lower than 1%, especially on the main channel and meanders, thus suggesting coarse, sandy sediments that are well aerated and allow post-depositional remineralization of organic matter in those sites. TOC concentrations higher than 1% are more frequent in the lakes (Gorgoştel Lake, Uzlina Lake, and Erenciuc Lake) suggesting fine sediments, which allows the conservation of organic matter in sediments, but also a higher primary productivity of the water column.

Another major component of sediments, Fe_2O_3, showed values between 1.17 and 6.26% (Table 2) measured at stations P01 and P44, respectively. The spatial variability of Fe_2O_3 was rather moderate (CV = 43%), higher concentrations being found on meanders (especially on M1 and M6), while the minima were measured along the main channel.

The minor components of surface sediments, MnO and TiO_2, showed moderate to high spatial variability (CVs of 46% and 52%, respectively), with concentrations ranging within 0.02-0.18% and 0.15-2.24%, respectively. MnO showed maxima on meanders M1 (0.11-0.13%) and M6 (stations P40 - 0.13% and P42 - 0.18%), while TiO_2 registered maximum at station P42. Generally, the MnO concentrations were relatively low (0.07 ± 0.03%), suggesting weakly reducing

conditions in the sediments (including the sediments from the studied lakes).

Trace elements concentrations showed high spatial variability (coefficients of variation >45%), with maxima for Hg (154%), Cu (104%), and Zr (87%) (Table 2).

The spatial variability of Zr is determined by its presence exclusively in the form of zircon, whose sedimentation depends on the hydro-dynamic environmental factors, which determine the concentration of the mineral in accumulations of heavy minerals, characteristic of coarse sediments. The statistically significant positive correlation between Zr and Ti (Table 3) suggests the association of representative minerals in heavy mineral concentrations.

Table 2. Descriptive statistics for the concentrations of the studied variables

	TOC %	$CaCO_3$ %	$F2O_3$ %	MnO %	TiO_2 %	Cr mg/kg	Zr mg/kg	Ni mg/kg	Cu mg/kg	Zn mg/kg	As mg/kg	V mg/kg	Pb mg/kg	Hg mg/kg
Min.	0.002	5.11	1.17	0.02	0.16	21.59	36.76	13.47	0.15	15.46	1.92	10.64	8.81	0.007
Max	2.60	16.25	6.26	0.18	2.24	356.0	1055	73.5	73.4	141.0	15.79	105	36.93	0.64
Mean	0.34	10.49	3.23	0.07	0.53	95.36	189.0	35.27	18.54	55.3	6.01	48.47	16.87	0.06
St. Dev.	0.46	2.46	1.45	0.03	0.28	62.6	164.0	17.67	19.24	35.81	3.46	28.33	7.65	0.09
CV	135.7	23.4	43.5	46.2	52.9	65.6	86.7	50.1	103.7	64.7	57.7	58.5	45.3	154.2

Table 3. Correlation matrix (Pearson) for the major constituents, minor constituents and heavy metals

Variables	TOC, %	$CaCO_3$, %	MnO, %	Fe_2O_3, %	TiO_2, %	V, mg/kg	Cr, mg/kg	Ni, mg/kg	Cu, mg/kg	Zn, mg/kg	As, mg/kg	Pb, mg/kg	Hg, mg/kg	Zr, mg/kg
TOC, %														
$CaCO_3$, %	**0.45**													
MnO, %	**0.36**	**0.41**												
Fe_2O_3, %	**0.54**	**0.51**	**0.95**											
TiO_2, %	0.14	**0.33**	**0.80**	**0.67**										
V, mg/kg	**0.66**	**0.51**	**0.76**	**0.91**	**0.36**									
Cr,mg/kg	0.06	0.17	**0.60**	**0.49**	**0.65**	0.22								
Ni,mg/kg	**0.66**	**0.49**	**0.73**	**0.89**	**0.33**	**0.98**	0.18							
Cu,mg/kg	**0.81**	**0.40**	**0.63**	**0.79**	**0.25**	**0.90**	0.13	**0.89**						
Zn, mg/kg	**0.74**	**0.41**	**0.74**	**0.87**	**0.36**	**0.94**	0.22	**0.93**	**0.98**					
As, mg/kg	**0.63**	**0.41**	**0.69**	**0.83**	**0.28**	**0.92**	0.16	**0.91**	**0.87**	**0.90**				
Pb, mg/kg	**0.76**	**0.28**	**0.64**	**0.77**	0.24	**0.87**	0.13	**0.87**	**0.97**	**0.97**	**0.89**			
Hg, mg/kg	**0.61**	**0.26**	**0.40**	**0.48**	0.15	**0.54**	0.09	**0.52**	**0.75**	**0.71**	**0.64**	**0.76**		
Zr, mg/kg	-0.01	**0.28**	**0.62**	**0.47**	**0.88**	0.19	**0.48**	0.14	0.08	0.18	0.11	0.05	0.09	

Values in bold are different from 0 with a significance level alpha = 0.05

The very high heterogeneity of Hg is mainly due to an abnormal peak (0.64 mg/kg) observed at station P03, where also Cr (132 mg/kg) and Cu (60.3 mg/kg) showed high concentrations, suggesting a local pollution. Hg concentrations exceeding the quality criteria in effect in Romania (Order 161/2006) were observed mostly in the interdistributary depressions and adjacent canals (0.10-0.24 mg/kg), but also on M1 (0.11-0.15 mg/kg). Cu and As, which showed maximum in the sediments of Gorgostel Lake (L06) and Uzlina Canal (L01), respectively, while the other analysed heavy metals presented the highest concentrations on meanders, specifically M1 (V, Zn, and Pb) and M6 (Ni). The lowest values of heavy metal concentrations were generally measured on the main channel (Cr at station P01, Cu and Pb at station P19, As at station P23 and V, Ni, Zn, and Hg at station P31).

Cu, Ni, Pb, V, As, Zn, and Hg showed significant positive correlations either each other or with TOC and Fe_2O_3 (Table 3), thus suggesting their association in the terrigenous material (sediments). Cr showed significant positive correlations with MnO, Ti, Sr, and Zr

(Table 3), indicating its predominantly natural origin.

Depending on their concentrations in sediments, some chemical compounds can adversely affect benthic organisms, which live on the surface of sediments or in their mass. For such compounds, including some of the heavy metals determined in this study, the Romanian competent authority issued the Order 161/2006, which provides a number of quality criteria (Table 4).

Table 4. Quality criteria for heavy metals in sediments (Order 161/2006) and number of samples exceeding the criteria

Metal	UM	Ord. 161/ 2006	Concentrations exceeding Ord. 161 criteria
Total chromium (Cr^{3+}+Cr^{6+})	mg/kg	100	15
Copper	mg/kg	40	12
Lead	mg/kg	85	0
Zinc	mg/kg	150	0
Nickel	mg/kg	35	30
Arsenic	mg/kg	29	0
Total mercury	mg/kg	0.300	1

Among the analysed metals, Ni, Cu, and Cr showed frequent exceeding of the quality criteria (Table 4). Similar situation was found by Tiron Duțu et al. (2019), who showed the relatively high number of concentrations of Cr, Cu and Ni exceeding the quality criteria is mainly due to their geogenic origin. Hg exceeds the quality criterion only at station P03, while V, As, Pb, and Zn presented all concentrations below the allowed limits.

However, besides the national quality criteria, a pollution index, namely the Contamination Factor (CF) was used for assessing the level of sediment pollution in the studied area. CF is the ratio obtained by dividing the concentration of each metal in the sediment by the background value (concentration in uncontaminated sediment), according to the following formula 1:

$$CF = CF_i = \frac{c_{i,s}}{c_{i,b}} \text{.....(1)}$$

where:

$C_{i,s}$ is the concentration of metal i in the sample;

$c_{i,b}$ is the background concentration of metal i. Since no background data for metals in uncontaminated sediments in the study area are available, the concentration of metal i, $C_{i,b}$ (mg/kg), in the surface sediments of upper continental crust reported by Rudnick and Gao (2003) was used as a background value (*i.e.*, $c_{As,b}$ = 4.8 mg/kg, $c_{Pb,b}$ = 17 mg/kg, $c_{Cu,b}$ = 28 mg/kg, $c_{Hg,b}$ = 0.05 mg/kg, $c_{Ni,b}$ = 47 mg/kg, $c_{Cr,b}$ = 92 mg/kg, $c_{V,b}$ = 97 mg/kg and $c_{Zn,b}$ = 67 mg/kg).

CF values were interpreted as suggested by Hakanson (1980), where CF < 1 indicates low contamination; 1 < CF < 3 is moderate contamination; 3 < CF< 6 is considerable contamination; and C > 6 is very high contamination.

The CF values were from 0.2-3.9 (Cr); 0.3-1.6 (Ni); 0.1-2.6 (Cu); 0.2-2.1 (Zn); 0.4-3.3 (As); 0.1-1.1 (V); 0.5-2.2 (Pb); and 0.1-12.8 (Hg). Arsenic and total chromium showed the highest mean CF (1.3 ± 0.7 and 1.1 ± 0.7), each of them with ca. 50% of values between 1 and 3, thus suggesting a moderate contamination. The abnormally high CF for mercury is associated with the peak registered at station P03. Although excluding this value, the number of CF_{Hg} > 1 were rather high (ca. 40%), thus suggesting a moderate contamination as well. Cu, Ni, Zn, and Pb showed low to moderate contamination; means < 1 and smaller percentages of the CF value between 1 and 3 (31%, 31%, 18%, and 37%, respectively).

In order to assess the spatial variability in pollution intensity, an empirical index, namely Pollution Load Index (PLI), was used. PLI is determined as the n^{th} root of the product of n CFs, according to the formula 2 below:

$$PLI = \sqrt[n]{(CF1xCF2xCF3x \ldots . xCFn} \text{.....(2)}$$

According to Tomlinson et al (1980), PLI values > 1 suggests that pollution exists, while PLI < 1 means that there is no metal pollution.

In the studied are, PLI ranged from 0.2 to 1.9, with 35% of the values >1, suggesting that heavy metal pollution exists some sampling sites. Most of these sites are located in the interdistributary depressions and adjacent canals, as well as on M1.

CONCLUSIONS

The studied area is characterized by terrigenous, non-carbonated and low-calcareous sediments ($CaCO_3$ within 5.11-16.25%), relatively poor in organic matter (TOC within 0.002-2.60%). Only few of TOC concentrations were > 1, mainly in the interdistributary depressions and adjacent canals.

The mean concentrations of heavy metals were 189.02 mg/kg (Zr), 95.36 mg/kg (Cr), 35.27 mg/kg (Ni), 18.55 mg/kg (Cu), 55.31 mg/kg (Zn), 6.01 mg/kg (As), 48.47 mg/kg (V), 16.87 mg/kg (Pb), and 0.06 mg/kg (Hg). Cr, Cu, and Ni frequently exceeded the quality criteria set in the national Order 161/2006, but it does not necessarily mean an intense pollution process.

The heavy metal pollution in the studied area was investigated based on the following indices: CF (contamination factor), and PLI (pollution index load). The highest CF was determined for As, followed by Cr and Hg (moderate contamination), while the lowest CF, suggesting no contamination was observed V. Ni, Cu and Zn showed low to moderate contamination. PLI values showed that the surface sediments are partially polluted (35% of PLI higher than 1), mainly in the interdistributary depressions and adjacent canals, but also on M1.

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REFERENCES

Bábek, O., Grygar.T. M., Faměra, M., Hron, K., Nováková., T., Sedláček., J. (2015). Geochemical background in polluted river sediments: How to separate the effects of sediment provenance and grain size with statistical rigour? *Catena*, 135, 240-253.

Black, C.A. (1965). *Methods of Soil Analysis. American Society of Agronomy*, Monograph 9, Madison, Wisconsin.

Bucse, A., Vasiliu, D., Balan, S., Parvulescu, O.C, Dobre T. (2020). Heavy Metalspatial Distribution and Pollution Assessment in the Surface Sediments of the North-Western Black Sea Shelf, *Revista de Chimie*, 71 (4), 155-170.

Campodonico, V.A., García, M.G., Pasquini, A.I. (2016). The geochemical signature of suspended sediments in the Parana River basin: Implications for provenance, weathering and sedimentary recycling. *Catena*, 143, 201–214.

Catianis, I., Secrieru, D., Pojar, I., Grosu, D., Scrieciu, A., Pavel, A.B., Vasiliu, D. (2018). Water Quality, Sediment Characteristics and Benthic Status of the Razim-Sinoie Lagoon System, Romania. Open Geosciences De Gruyter 10, 12-33.

Driga, B.V. (2004). *Delta Dunării - Sistemul circulaţiei apei.* Casa Cărţii de Stiinţă Cluj-Napoca. p. 256.

Gaudette, H.E., Flight, W.R., Toner, L., Folger, D.W. (1974). An inexpensive titration method for the determination of organic carbon in recent sediments. *Journal of Sedimentary Petrology*, 44, 249-253.

Habersack, H., Hein, T., Stanica, A., Liska, I., Mair, R., Jager, E., Hauer, C., Bradley, C. (2016). Challenges of river basin management: Current status of, and prospects for, the Riber Danube from a river engeneering perspective. *Science of the Total Environnement*, 543, 828-845.

Hakanson, L. (1980). Ecological risk index for aquatic pollution control. A sedimentological approach. *Water Research*, 14, 975–1001.

Ispas, B. A., Tiron Dutu, L, Grosu, D., Caraivan, G. (2020). Assessment of actual water quality and sedimentological conditions of the Corbu I Lake, Western Black Sea coast. *Carpathian Journal of earth and Environmental Sciences*, 15, 2, 481-490.

Jugaru Tiron, L., Le Coz, J., Provansal, M., Panin, N., Raccasi, G., Dramais, G., Dussouillez, P. (2009). Flow and sediment processes in a cutoff meander of the Danube Delta during episodic flooding. *Geomorphology,* 106 (3-4), 186-197.

Li, W., Hu, Z., Zhang, W., Ji, R., Nguyen, T.T.H. (2017). Influence of provenance and hydrodynamic sorting on the magnetic properties and geochemistry of sediments of the Oujiang River, China. *Marine Geology*, 387, 1-11.

Mureşan M., Teaca, A., Popa A., Begun T. (2019). Free-living marine nematodes community structural changes within a post-dredging site at the Romanian shelf. *Journal of Environmental Protection and Ecology,* 20, 2, 753-760.

Najamuddin, Tri Prartono, Harpasis S., Sanusi, I., Wayan Nurjaya. (2016). Seasonal distribution and geochemical fractionation of heavy metals from surface sediment in a tropical estuary of Jeneberang River, Indonesia. *Marine Pollution Bulletin*, 111, 1, 456-462.

Natali, C. & Bianchini, G. (2017). Geochemical proxies of sediment provenance in alluvial plains with interferinf fluvial systems: A study case from NE Italy. *Catena*, 157, 67-74.

Oaie, Gh., Szobotka, S., Secrieru, D., Stanica, A., Soare, R. (2000). Pollution state of sedimets dredged from the Sulina distributary and their influence to the Danube Delta front area. *GeoEcoMarina,* 4, 37-42.

Oaie, Gh., Secrieru, D., Szobotka, S, Fulga, C., Stanica, A. (2005). River Danube: sedimentological, mineralogical and geochemical characteristics of the bottom sediments. *Geo-Eco-Marina*, 11-12, 77-85

Oaie, Gh., Secrieru, D., Bondar, C., Szobotka, S., Duţu, L., Stănescu, I., Opreanu, G., Duţu, F., Pojar, I., Manta, T. (2015). Lower Danube River: characterization of sediments and pollutants. *Geo-Eco-Marina*, 21, 19-34.

Panin, N., (1999). *Danube Delta: Geology, Sedimentology, Evolution*. Association des Sédimentologistes Français, Maison de la Géologie, Paris, p. 66.

Panin N. & Jipa, D. (2002). Danube River Sediment Input and its Interaction with the North-western Black Sea. *Estuarine, Coastal and Shelf Science*, 54, 2, 551-562.

Panin, N. (2003). The Danube Delta. Geomorphology and Holocene evolution: a Synthesis. *Geomorphologie: relief, processus, environnement,* 4. pp. 247-262.

Panin, N., Tiron Duţu, L., Duţu, F. (2016). The Danube Delta - an overview of its Holocene evolution. *Mediterranee,* 126, 37-54.

Popa, A. (1997). Environment changes in the Danube Delta caused by the hydrotechnical works on the St. George branch. *Geo-Eco-Marina*, 2, 135-147.

Romanescu, Gh. (2013). Alluvial transport processes and the impact of Anthropogenic intervention on the Romanian littoral of the Danube Delta. *Ocean & Coastal Management*, 73, 31-43.

Romanescu, Gh. & Stoleriu, C.C. (2014). Anthropogenic interventions and hydrological-risk phenomena in the fluvial-maritime delta of the Danube (Romania). *Ocean & Coastal Management*, 123, 123-130.

Rudnick, R.L. & Gao, S. (2003). *Composition of the continental crust.* In: Holland, H.D., Turekian, K.K. (Eds.), The Crust (ed. R. L. Rudnick) Vol. 3 Treatise on Geochemistry. Elsevier-Pergamon, Oxford, 1–64

Secrieru, D. & Secrieru, A. (1996). Anthropic increases of trace element concentrations in sediments from the Black Sea Romanian shelf - Danube Delta-Black Sea System under Global Changes Impact. *Geo-Eco-Marina*, 1, 93-98.

Teaca A., Muresan M., Menabit S., Bucse A., Begun T. (2020). Assessment of romanian circalittoral soft bottom benthic habitats under Danube River influence. *Regional Studies in Marine Science*, 40, 1-15.

Tiron Duţu, L., Provansal, M., Le Coz, J., Duţu, F. (2014). Contrasted sediment processes and morphological adjustments in three successive cutoff meanders of the Danube Delta. Geomorphology, 204, 154-164.

Tiron Duţu, L., Duţu, F., Secrieru, D., Opreanu, G. (2019). Sediments grain size and geo-chemical interpretation of three successive cutoff meanders of the Danube Delta, Romania. *Geochemistry*, 79, 399-407.

Tomlinson, D.L., Wilson, J.G., Harris, C.R., Jeffrey, D.W. (1980). Problems in the assessment of heavy-metal levels in estuaries and the formation of a pollution index. *Helgoländer Meeresuntersuchungen*, 33, 566–575.

Vadineanu, A. (2001). Lower Danube Wetlands System (LDWS). *Observatorio Medioambiental*, 4, 373-402.

Vasiliu, D., Bucse A., Lupascu N., Ispas B., Gheablau C., Stanescu I. (2020). Assessment of the metal pollution in surface sedimentsof coastal Tasaul Lake (Romania). *Environ Monit Assess*., 192:749. https://doi.org/10.1007/s10661-020-08698-0.

Wu, W., Zheng, H., Xu, S., Yang, J., Liu, W. (2013). Trace element geochemistry of riverbed and suspended sediments in the upper Yangtze River. *Journal of geochemical Exploration*, 124, 67-78.

Zakir Hossain, H.M., Kawahatab, H., Roserc, B.P., Sampeic, Y., Manakad, T., Otani, S. (2017). Geochemical characteristics of modern river sediments in Myanmarand Thailand: Implications for provenance and weathering. *Chemie der Erde*, 77, 443-458.

Zhang, G., Bai, J., Xiao, R., Zhao, Q., Jia, J., Cui, B., Liu, X. (2017). Heavy metal fractions and ecological risk assessment in sediments from urban, rural and reclamation-affected rivers of the Pearl River estuary, China. *Chemosphere,* 184, 278-288.

Order 161/2006 of Ministry of Environment and Water Management – Ecological status of water bodies.