INTRODUCTION

The Danube River has a hydrographic basin of 817,028 km², covering about 11% of the European continent. About 36% of the Danube basin are mountains (Alpine and Carpathian chains) with heights varying between 1,000 m and 4,000 m, and 64% are areas with medium and low altitude (hills, plateaux and plains). The average altitude of the Danube basin is 475 m.

The climate in the Danube basin is of temperate-continental type. The annual rainfall average is about 400 - 600 mm, while in the mountainous areas the rainfall average is higher: for the Carpathian Mountains, 800 - 1200 mm, in the Alps, 1800 - 2500 mm.

The hydrographic network of the Danube River is quite dense: the tributaries are over 120, distributed unevenly within the river basin (ICPDR IC/084/2005).

The Lower Danube basin has a surface of 240,000 km², the main tributary rivers being Timok, Jiu, Olt, in the Alps, Vede, Argeș, Ialomîța, Siret, Prut. Natural lakes are also part of the Danube hydrographical basin. Two very large barrages have been built at Iron Gates I (km 943) in 1973 and at Iron Gates II (km 863) in 1984 for producing electricity and facilitating the navigation along the Iron Gates gorge that crosses the Carpathian Mountains. The barrage lakes are also very large and have a strong impact on the hydrological regime of the river and on the environmental state of the region.

The Danube River average multiannual water discharge is of about 6,550 m³.s⁻¹, with a maximum of 20,940 m³.s⁻¹ (July 2, 1897) and a minimum of 1,350 m³.s⁻¹ (October 31, 1921). The Danube water discharge into the Black Sea is of about 5,990 m³.s⁻¹. The difference of 560 m³.s⁻¹ is generally due to the water retention into the Danube Delta, loses by evaporation and discharges through secondary outlets to the sea (Table 1).
The Danube ends at the Black Sea in a large delta that is in a continuous developing process: there are changes in the water distribution among the main distributaries of the delta (Chilia, Tulcea, Sulina and Sf. Gheorghe), in the evolution of the delta coastal zone and lagoons, as well as in the sedimentary processes inside the interdistributary depressions. These changes will be described below in the paper.

The Danube River is one of the most important inland waterways in Europe and consequently the problems of environmental state and socio-economic development of the Danube region, including the improvement of the navigation, are of primary importance. This imposes a good knowledge of natural conditions and processes within the region, and special programmes of research-development-innovation should be dedicated to sustainable management of the Danube River system, especially on its lower section from Iron Gates to the mouth zone. A special attention has to be focused on the river flow and sedimentary flux regime for improving the navigation and correcting different environmental problems occurring along the Lower Danube.

From a total length of 471 km of the section from Timok river mouth (km 844) to km 375, on about 244.1 km the banks are eroded and only 120.4 km affected by depositional processes. From the total length of eroded banks, 95.9 km are on the left side of the river, 51.5 km on the right side and 96 km along islands. From areas dominated by sediment accumulation, 28.1 km were on the left side, 11.1 km on the right side and 32 km along the islands.

On the same section, the Danube width is greater than 1,000 m along 65 km of which: on 1.6 km the Danube is wider than 1,500 m, on 16.3 km the width range between 1,500 and 1,200 m, on other 30 km the width varies between 1,199 m and 1,100 m, and on 17 km the width is between 1,109 and 1,000 m. In the areas where the riverbed is wider (>1,000 m) the waterway channel has a reduced depth (sometimes under 2.0 m).

Between km 931 and km 375, the number of islands, formed and developed along the river, is continuously increasing: 93 islands in 1934, with a total length of 283 km and 135 in 1992, with a total length of 353 km.

In natural fluvial ecosystem, the pollutants (e.g. heavy metals, pesticides) in the fluvial depositional processes are strongly associated with the sedimentary deposits. These types of deposits are considered as the historical depository of pollutants, especially if those accumulations are located within reservoirs.

It is known the fact that the concentrations of different pollutants (e.g. heavy metals, pesticides) in the fluvial deposits represents a source of secondary contamination (Macklin et al., 1997), by their remobilization during the erosion and transport processes. In addition, these types of deposits are considered as the historical depository of pollutants, especially if those accumulations are located within reservoirs.

This paper is trying to emphasize the human impact on the Lower Danube as one of the determinants of the changes during the period 2009-2013. The pollution phenomena the role of sediment is related both to the particle size of sediment and to the amount of particulate organic carbon associated with the sediment. The very fine grained sediments (under 63 μm) play an active role in adsorption of pollutants. Phosphorus and metals tend to be highly attracted by clay particles. Toxic organic contaminants (e.g. pesticides), are strongly associated with the organic carbon that is transported as part of the sediment load in rivers. River sediments adsorb most of the heavy metal ions from the water (Zhou and Kot, 1995). Investigating their adsorption onto river sediments different authors (Lee and Moon, 2003; Korfali and Davies, 2005, Xiaoyuong, 1983) showed that the carbon is the main factor to determine the adsorption value of heavy metal onto sediment.

Finally, the pollutants associated with river sediments can enter into the food chain (fishes and benthic organisms) or the pesticides accumulate in the predators, including the man (FAO Report, 1996).

It is known the fact that the concentrations of different pollutants (e.g. heavy metals, pesticides) in the fluvial deposits represents a source of secondary contamination (Macklin et al., 1997), by their remobilization during the erosion and transport processes. In addition, these types of deposits are considered as the historical depository of pollutants, especially if those accumulations are located within reservoirs.

This paper is trying to emphasize the human impact on the Lower Danube related to the 2009-2013 period, starting with km 1072 (the beginning of the river on the Romanian territory) and ending with the river mouths at the Black Sea. We will refer mainly to the sediment and heavy metals pollutants within the Iron Gates I and II reservoirs and along the Lower Danube to the Black Sea. Also, some considerations regarding the impact of the Danube River on the NW Black Sea will be presented.

**STUDY AREA**

The study was conducted at designated points and transects along the Romanian section of the River Danube, within the Iron Gates I and II reservoirs and along the Danube Delta distributaries (Fig. 1).

---

**Table 1.** Distribution of the water discharge (average percentage) among the main Danube Delta distributaries.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Chilia</td>
<td>62.85</td>
<td>65.99</td>
<td>68.00</td>
<td>69.90</td>
<td>67.90</td>
<td>66.18</td>
<td>65.10</td>
<td>64.39</td>
<td>62.60</td>
<td>59.60</td>
<td>54.50</td>
<td>54.60</td>
<td>51.50</td>
</tr>
<tr>
<td>Sulina</td>
<td>6.91</td>
<td>7.92</td>
<td>7.95</td>
<td>7.26</td>
<td>8.48</td>
<td>15.52</td>
<td>16.45</td>
<td>17.83</td>
<td>17.43</td>
<td>19.22</td>
<td>17.83</td>
<td>20.10</td>
<td>19.30</td>
</tr>
</tbody>
</table>

---

The study was conducted at designated points and transects along the Romanian section of the River Danube, within the Iron Gates I and II reservoirs and along the Danube Delta distributaries (Fig. 1).
Special chapters in this paper are dedicated to the Iron Gates I and II reservoirs, but also to the Danube Delta. The Iron Gates I and II dams are located at km 943, respectively at km 863, on the Romanian – Serbian border. The reservoirs accumulate sediments and pollutants coming from the upper and middle sections of the river course.

The Iron Gates gorge, located upstream km 943, passes complex geological sequences, from igneous and metamorphic rocks to sedimentary rocks, which forms the western termination of the Southern Carpathians. The Alpine geological units are flanked to the East and to the West by Miocene, Pliocene and Quaternary sedimentary deposits (Pop et al., 1997). It is necessary to take into consideration the geological basement of Iron Gates gorge and partially of the Iron Gates II reservoir, because the rocks of this basement are mineralized, which makes the regional geochemical background higher than Romanian or European standards related to the sediment and soil quality.

For the river section located downstream Iron Gates II dam (Fig. 1; 2, B, C) the main environmental impact comes from the tributaries coming from Romanian, Bulgarian and partially from Moldavian territories, as well as from the anthropogenic pollution, from spot or diffuse sources. The Danube Delta is the largest delta in the European Union covering about 5 640 km² (including the outer lagoons areas) of which 4 400 km² on the Romanian territory, and about 1 240 km² on the Ukrainian territory. 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. Nevertheless, important amounts of pollutants, carried by the water and sediments, are discharged in the NW Black Sea, having a negative impact on the marine ecosystem (Mee, 1992).

**SAMPLING STRATEGY**

Samples of water and sediment from the Danube River were collected as follows (Fig. 1, Fig. 2.1 – 2.5): km 1072 – where the river enter the Romanian territory; km 1059 – km 947 – within the Iron Gates I reservoir, km 937 – km 866 – in the Iron Gates II reservoir, km 845 – Mile 44 + 500 – along the section from the Iron Gates II dam to Cetățuia Ismail (the Danube Delta apex) and the Danube Delta territory (km 115+500 – km 3 Chilia Branch; Mile 34 – Mile 0 – Sulina canal; km 108+500 – km 2 – Sf. Gheorghe Branch) and additional control stations at the confluences of the main Romanian tributaries (Cerna, Topolnita, Jiu, Olt, Vedea, Argeș, Ialomița, Siret, Prut) with the Danube River. The samples were collected each year (in the 2009 – 2013 period) between March and April.

The superficial sediment samples were collected using Van Veen grabs, for deeper samples, Kullenberg gravity cores were used. Each cross-section consisted in 1 to 3 sampling stations placed two of them close to the river banks and one in the waterway. In some cases, where the river width was smaller, one single sample was collected, in general in the area of the deepest water.

At the confluences with the Romanian tributaries, bottom sediment and water samples were collected. In general, a single sediment sample was collected from the upstream of the confluence with the Danube. Five subsamples for the different analyses (grain size, chemistry, mineralogy, biology and a witness sample) were collected from each grab (top 10 – 20 cm) and stored in polyethylene bags under suitable conditions and then transported to the laboratory.

**METHODS**

**Hydrological measurements** on the river cross-sections were made using an Acoustic Doppler Profiler SonTek River Surveyor. The equipment measures the water current direction and the velocity, depth distribution, solid suspension concentration and water discharge. The acquisition and the processing software (River Surveyor, version 4.6) allow to visualization of the measured data. On each section two crossings were made.

**Bathymetric measurements** were made using a single-beam (Ceeducer equipment) having an accuracy of 0.002%.

**Grain size analysis.** Grain size analysis of the fraction < 1 mm was done using the diffractometry method with the laser granulometer „Mastersizer 2000E Ver.5.20“, MALVERN UK. The accuracy of the measurements is 1%. The plant remains and the shell fragments bigger than 1 mm were removed from the sample. Lithic grains, bigger than 1 mm, were separated from the sample, weighted and sorted by sieving. The dimensional scale Udden-Wentworth (the sand/silt limit 0.063 mm, silt/clay 0.004mm), and the Shepard ternary diagram were used.

**Mineralogical analysis.** The mineralogical analysis has been carried out on the sandy fraction (1.0-0.063 mm) of each sediment sample. The light fraction content (carbonate and siliciclasts + oxides) was calculated using the weighing data, before and after removing the carbonate, by treating it with hydrochloric acid 11%. After the acid treatment, 20 g from each sample was gravitationally separated in separating funnels, using a heavy liquid, sodium politungstat (Na₂O₃(H₂W₁₂O₄₀)₉H₂O), with 2,82 g/cm³ density. The quantitative and qualitative analyses of the heavy minerals were done microscopically.

**Chemical analysis.** Sediment samples were first air dried and grounded until all the material passed through a 0.063 mm mesh sieve; afterwards they were subjected to a complex of analytical methods. Seventeen chemical components: CaCO₃, TOC, Fe₂O₃ (total), TiO₂, MnO, Rb, Co, Ni, Ba, Sr, Cu, Pb, Zn, Cd, Cr, V and Zr were analysed by different methods.

Titration methods were used for analysing CaCO₃ (Black, 1965) and total organic carbon (Gaudette et al., 1974). Zn, Ni, Co, Cu, and Pb were analysed by flame atomic absorption spectrometry and Cd by electro-thermal atomic absorption spectrometry on a Pye Unicam SOLAR3 939E double beam absorption spectrophotometer with deuterium lamp background correction. A wet digestion technique consisting
Fig. 1. Positioning of the monitoring cross-sections along the Romanian sector of the Danube River.
Fig. 2.1. Location of the geo-ecological monitoring cross-sections (details related the positioning): km 1072 – km 866 – Iron Gates I and II lakes sector

Fig. 2.2. Location of the geo-ecological monitoring cross-sections (details related the positioning): km 866 – km 595 sector

Fig. 2.3. Location of the geo-ecological monitoring cross-sections (details related the positioning): km 595 – km 375 sector
**Fig. 2.4.** Location of the geo-ecological monitoring cross – sections (details related the positioning): km 375 – km 167 sector

**Fig. 2.5.** Location of the geo-ecological monitoring cross – sections (details related the positioning): km 167 – Black Sea (Danube Delta) sector
of boiling with concentrated nitric acid (Jickells and Knapp, 1984) was used to solve the trace elements. After drying, the residue was heated to dryness with concentrated hydrochloric acid, solved in diluted hydrochloric acid and brought to 50 ml. Factory recommended parameters and optimizing procedures were used for setting up the analytical system. The system was calibrated with a series of standard solutions prepared from spectral pure metals. The analytical results represent the means of three consecutive readings; residual standard deviations were usually less than 2% for FAAS and less than 5% for ETAAS determinations.

Fe₂O₃ (total), TiO₂, MnO, Rb, Ba, Sr, Cr, Zr and V were analysed by X-ray fluorescence spectroscopy on a VRA - 30 XRF sequential spectrometer, fitted with a X-ray tube with wolfram anode, directly on compacted powders. An analyser crystal LiF 200 was used to select the characteristic wavelengths, measurements being done with a Na(Tl)J scintillation detector. Calibration was carried out with the help of a series of international standards kindly provided by US Geological Survey, The National Institute of Standards and Technology – USA and The National Research Council – Canada, using the relationship between concentration and the difference between the numbers of impulses recorded at the analytical line and the number of impulses at the background line.

Quality control was ensured by simultaneous analysis of SRMs.

RESULTS

Bathymetric and ADCP measurements

Yearly hydrological measurements campaigns (from 2009 to 2013) carried out in March-April every year, along the Romanian sector of the Danube River (km 1074 – Black Sea), allowed to follow the evolution of the flow parameters (current velocity, water and sediment discharges) and to monitor the riverbed morphology, and the sedimentary processes (Fig. 3).

During the considered period of time there were two years (2009 and 2013) with high stages, and one year (2012) with low water discharges. The measurements showed as well the evolution of the water discharge distribution among the Danube Delta distributaries.

The average water discharge for the 2009-2013 period at Mile 44 – Ceata Ismail cross-section (the apex of the Danube Delta where the splitting of the river in Chilia and Tulcea distributaries occur) was of 8 010 m³.s⁻¹, being considerably higher than the multiannual average discharge of the Danube River (6 500 m³.s⁻¹). This difference is due to the fact that the measurements were carried out during spring high stages of the river.

On the river section between Iron Gates II dam and Mile 44 – Ceata Ismail, the current velocity varied between 0.63 m.s⁻¹ and 1.24 m.s⁻¹. In the Danube Delta section (Mile 44 – Black Sea) the water velocity is more influenced by the free water surface slope, the morphology of the distributaries rive-
1990 and 452 kg.s\(^{-1}\) for the years 2000 - 2009 (Bondar et al., 1992);
- 304 kg.s\(^{-1}\) on the Chilia distributary, from Ceatal Ismail (Mile 43+500) to the mouth zone (km 3, on the Musura distributary);
- 146 kg.s\(^{-1}\) on the Tulcea distributary, where the river eroded its banks, increasing the sediment discharge (during the period 1981-1989);
- on the Sulina Canal (until 1980), the sediment discharge was evaluated at 51 kg.s\(^{-1}\). After the construction of the Crisan-Caraorman canal the sediment discharge of the Sulina distributary has diminished (1981-1989 period);
- For the Sf. Gheorghe distributary the sediment discharge for the 1981-1989 period was evaluated at 95 kg.s\(^{-1}\).

In the spring of 2013, the suspension load was for Sulina distributary at Hm 72 – 60 mg.l\(^{-1}\), for Chilia (km 20) – 77 mg.l\(^{-1}\), and for Sf. Gheorghe branch at km 8 – 72 mg.l\(^{-1}\).

**The Danube River sediments mineralogical constitution**

The Danube River sediments are formed of a light fraction (representing about 95% of a bulk sediment sample and some 82% of the sandy fraction for the considered sample) and a heavy fraction, formed of heavy minerals, being of about 3% from the bulk sediment sample (rarely the content of heavy fraction is lower, going to around 0.5%).

In the heavy fraction the most frequent are the garnets (almandine, pyrop) and the opacites (ilmenite – FeTiO\(_3\), magnetite - Fe\(_3\)O\(_4\), hematite - Fe\(_2\)O\(_3\), chromite - FeCr\(_2\)O\(_4\), leucoxene - TiO\(_2\) +/- muscovite. They represent about 25.14% of the heavy fraction (in the most of the samples the share of opacite exceeds 20%). The grains morphology is angular and sub-angular, but also rounded and sub-rounded mostly for the samples collected in the Danube Delta area.

Garnets are represented by almandine, pyrop and rarely grossular, spessartine or uvarovite. Quantitatively, the average is about 16% from the heavy minerals fraction. The sub-rounded morphology is most common. An exception is represented by the samples collected from Olt, Topolnița and Cerna rivers. Here the garnet forms associations with epidote and opacites (magnetite, chromite or hematite).

The assemblages opacite - epidote - zircon are frequent in some places as e.g. the confluences of the Danube with Cerna and Argeș rivers. Here the minerals show angular habitus. The epidote, the variety pistacite, together with zoisite and sometimes clinzoisite represent an average of 14.7% per sample. They form assemblages with garnet + opacite + zircon.

Zircon is present in a higher percentage in the confluence of tributaries with the Danube. It has mostly an angular, prismatic morphology, rarely sub-rounded.

Amphiboles are represented by green and brown hornblende. Tremolite and actinolite occur sporadically. Together with zircon and, sometimes, tourmaline form minor associations. Tourmaline has an average participation of 1.7%, missing in some samples.

Rutile is specific for the igneous source areas. Quantitatively, it is not important. Sometimes we noticed the presence of perfect crystals.

Sediment samples collected from the Danube River tributaries were also analysed. The heavy minerals contents in these sediments are higher than 0.21%. There is some differentiation in the heavy mineral content depending on the source area of each tributary. The Jiu and Olt rivers show a similar mineralogical diversity. The Jiu River sediments have constantly considerable amount of coal fragments. In the Topolnița river occur opaque minerals with the appearance of slag, supposedly of anthropogenic origin. Heavy mineral associations from Olt, Argeș and Ialomița rivers are garnet-dominated, while the opaque minerals dominate in Topolnița, Vedea, Siret and Prut rivers.

**The Danube River sediments chemical constitution**

In order to determine the quality of the Danube bottom sediments, samples were taken from key locations, such as:
- Danube entrance on Romanian territory (km 1072 – Baziaș) (Fig. 2.1);
- Upstream Iron Gates I (km 943) and II (km 866) dams in the respective reservoir lakes. They are known as decanters of the suspended sediments and of the associated pollutants (Fig. 2.1);
- Downstream the confluences with the main Romanian tributary rivers (Cerna, Topolnița, Jiu, Olt, Vedea, Argeș, Ialomița, Siret, Prut), in order to evaluate their impact on the Danube River (Fig. 2.2 – 2.4);
- Downstream Romanian harbours (Fig. 2), some of them associated with mining exploitations or large industrial sites (ex. Moldova Nouă, Drobeta – Tr. Severin, Tr. Măgurele, Giurgiu, Brăila, Galați, Tulcea);
- The Danube Delta apex (Mile 43+500 – Ceatal Ismail), for determining the impact the Danube water and sediments on the Delta area (Fig. 2.5);
- At the mouth zones of the Danube distributaries into the Black Sea, in order to evaluate the river impact on the NW part of the sea.

The geochemical analysis performed in the laboratory revealed very high Cu, Pb and Ba concentrations associated with Zn and Sr. The heavy metal association is typical for poly-metal mineralization with barite and celestine as secondary minerals (Fulga C. in Oae et al., 2005).

Mining has obviously contributed to the geochemical configuration in certain sites along the river (such as Moldova Nouă, the Timok basin on the Serbian-Bulgarian border).

Occasionally, increased heavy metal concentrations were found in the sediment samples collected from different sites where particular Romanian rivers empty into the Danube. Thus, the Cu, Pb and Zn content levels exceeded the guide-
line value in the Vedea, Ialomița and Argeș rivers (Fig. 4, 5). Here the pollution is generated by a wide range of anthropogenic factors, related mostly to farms and industrial plants, located in the catchment basins.

Similar circumstances and results were evidenced at km 375 and at km 4.5 on the Măcin branch (Fig. 2.4). At km 375, the pollution is considered to be generated by the significant amounts of sewage carried off from Silistra (Bulgaria) and Călărași (Romania) towns and harbours, while at km 4.5 Măcin branch the pollution might be generated by shipwrecks.

In the Danube Delta (Fig. 2.5) the heavy metal concentration levels are found to be within the river quality standard, except for Hm 72 Sulina Canal and km 3 on the Stambulul Vechi branch (Chilia Delta). At Hm 72 the higher concentration levels in Cu, Pb, Zn and Cd are presumed to come from sewage carried off to the river. Yet, the Zn, Cu, Pb and Cd levels assessed for the profile situated at the mouth of the Stambulul Vechi branch were high during 2005 only; therefore, the drilling of the nearby Bystroe Canal might have triggered increased concentrations.

Significantly increased levels of TiO$_2$, Cr, V and Zr were found, mostly, in areas with heavy mineral accumulations (for ex, Danube Delta).

Lack of a significant link between CaCO$_3$ and Sr indicates the presence of carbonate in the form of Sr-poor calcite. The relatively low Sr levels/contents of the samples are mostly of terrigenous origin, indicative of a wide compositional variability, with a coefficient of variation exceeding 50%.

**Fig. 3.** Hydrologic and bathymetric transects on the Romanian sector of the River Danube – Profile km 1072 Bazias – The beginning of the river on the Romanian territory
The highest coefficients of variability pertain to the technophile metals which indicate a strong human intervention on those particular metal concentrations. All the technophile metals (Zn, Cu, Pb, Cd) are closely linked proving a common origin. Also, their association with Fe, Rb and/or TOC indicate that the metals are associated/concentrated in the finer silt and clay fractions.

A peculiar correlation is the one between Ba and Sr due to the genetic association of the barite with the strontianite. Both are secondary minerals in the sulphur ores. The fact that there are high concentrations in the samples collected both from the Moldova Nouă area and downstream of the mouth where the Timok river empties into the Danube (the samples were collected on the km 840 profile) play an important part in this correlation.
Most of the analysed samples (about 61%) are sands; even coarser or finer samples, gravels respectively silts, contain a substantial proportion of sand. This explains the relatively low content of pollutants (heavy metals) and some of the higher concentrations of TiO₂, Zr, Cr and V, usually related to the heavy minerals accumulations concentrating in coarser sediments.

The concentrations of some major (Fe₂O₃), minor (MnO) and trace (Rb) non-technogenic components and partially the content of pollutant heavy metals (Cr, Zn, Ni, Cu, Pb, Cd) from the predominant sandy samples, depend on many factors. The most important is the percentage of femic minerals in sand, which depends on the geological composition of the source area. The samples collected from Argeş, Olt and Jiu rivers, have the lowest Fe, Mn and other heavy metals concentrations, originate from the high purity quartz sands.

Another important factor, which can significantly affect these concentrations, is the deposition of hydrated iron and manganese oxides coatings on the sand grains surface, phenomenon well highlighted in some samples from the Danube. These oxides display remarkable absorbent properties, which may cause samples enrichment in trace elements, mostly Ni and Co. The enrichment degree is determined by the availability of those minerals in the environment, which depends on natural factors (abundance of source areas, chemical alteration), but also human activities. In these circumstances, some heavy metals high concentrations, unusual for sands, can reflect anthropic pollution processes.

The quality limits for sediments (MMGA Order Nr. 161/16. 02. 2006 establishing the ecological status of water bodies) are systematically exceeded, sometimes significantly, by Ni (approx. 45% of samples) and Cr (approx. 33% of samples) concentrations. This does not mean, necessarily, that their origin areas are contaminated with both metals. The maximum Cr concentrations are clearly due to the Cr minerals from heavy minerals accumulations, and maximum Ni concentrations are due to Ni adsorption by hydrated manganese oxides. At the same time both metals are highly spread in the Earth's crust, with average concentrations of Ni – 84 ppm and Cr – 102 ppm; in the analysed samples their concentrations are significantly reduced (Ni – approx. 50%). It should be emphasized that magic and ultramafic rocks that contributes to the natural enrichment of the natural background with Ni and Cr, are present in the geological basement in the river sector between km 1040 and km 957. In these conditions, the high concentrations of the two metals might be due to the natural background (geological substrate rich in mineralization) and pollution processes due to well-developed mining industry in the area.

For other polluting heavy metals (Cu, Zn, Cd), the limits from the Order 161/2006 (Cu – 40 ppm, Zn – 150 ppm and Cd – 0.8 ppm) are being exceeded occasionally in clayey samples. Pb does not exceed the established limit within the current standards (85 ppm).

**DISCUSSION AND INTERPRETATION**

**The impact of the Iron Gate I and II Dams on sediment accumulation and pollutants storage**

The average water volume of the Iron Gates I reservoir is 2,2 x 10⁶ m³, the lake is 140 km long and has a surface of 330 km². The Iron Gate II reservoir is 0.8 x 10⁹ m³, 80 km long and a surface of 79 km². For both dams the average annual water discharge is 5,550 m³ s⁻¹.

The dams have changed the Danube sediment flux rate. The average annual sediment discharge, before the building of the Iron Gates dams, was about 67,500,000 t.y⁻¹ (Panin and Jipa, 1998). Today, the sediment flux, along the Lower Danube River is estimated at ca. 30,000,000 t.y⁻¹. The difference between the mentioned quantities is trapped in the Iron Gates reservoirs. The construction of the Iron Gates II induced the accentuation of the decrease of the sediment discharges downstream the dam showing values smaller by at least 50% compared to the value of pre-damming sediment flux regime (Panin, Jipa, 1998).

Upstream the Iron Gate I dam, in the reservoir lake, the sediments accumulate continuously. They are represented mainly by silts and fine sands. The pollutants are also trapped and accumulate in the sediments.

The present paper presents data on the concentrations of pollutants (nutrients and heavy metals) in the sediments of the Iron Gate reservoirs for the interval 2009 – 2013.

**Iron Gates II – Danube Delta section characterization**

Between Iron Gates II dam (km 863) and the Danube Delta apex (Mile 43+500) the Danube River flows on the so called Danube Plain. The river is wide up to 1 500 m, with minimum water depths of around 2.00 m. The current velocity, measured on cross-sections, ranged between 0.69 and 1.16 m.s⁻¹ (Strechie-Sliwinki et al, 2008), with few exceptions due to the cross-section position.

The anthropogenic intervention along this Danube section, even though is less important than for other sectors, has nevertheless impacted the river course causing physical degradation of the river bed by erosion, its widening by bank erosion, decreasing its depth under the action of depositional type processes, increasing number of islands and secondary branches, increased number of navigation bottle-necks (from 26, in 1967, at 62 in 1990) (Bondar, 2002).

The grain size of suspended load varies between 0.1 mm and 0.005 mm, the average diameter being around 0.020 mm. The grains size the bed-load, varies between 0.06 mm and 1 mm, the average diameter being around 0.185 mm.
The Danube Delta section

The Danube Delta starts (the apex of the delta) at the first bifurcation of the Danube River (Ceatal Izmail, Mile 44) into Chilia and Tulcea distributaries.

The Chilia Distributary is of 116 km long. Its configuration is complex, with meanders and many secondary branches, islands and islets. At its mouth zone there is a secondary delta, Chilia Delta with many distributaries and a surface of about 244 km² (Panin and Jipa, 1998).

Tulcea distributary extends from Ceatal Izmail (Mile 44) to Ceatal Sf. Gheorghe (Mile 34), on a unique course, with a total length of about 17 km. At Ceatal Sf. Gheorghe Tulcea distributary splits into Sulina and Sf. Gheorghe branches.

The Sulina distributary has a unique course, with a total length of 71.7 km. After the meander belts cut-off works carried out by the European Danube Commission between 1868 and 1902 the Sulina distributary was rectified and shortened by about 25% (83.8 km before the cut-offs and only 71.7 km nowadays). The Sulina mouth is flanked by two jetties initially intended to keep the velocity of the river flow high enough for pushing the location of the mouth bar as far as possible offshore and insuring thus the needed depth for navigation. The present-day length of these jetties is about 8 km.

The Sf. Gheorghe distributary is of 108 km long and partly meandering course. In the 1981 – 1992 period an important meander belts cut-off programme was carried out. By this programme the distributary was shortened by 32.58 km and consequently its hydrological characteristics were considerably changed.

Inside the Danube Delta territory there were other hydrotechnical works carried out (e.g. dredging canals between main distributaries or towards the interdistributary depressions) and that led to important hydrological, morphological and sedimentological changes.

The distribution of the water and sediment discharges of the delta distributaries have changed considerably, due to natural and anthropogenic factors, described above (Table 1) and this has a direct impact on the evolution of the Danube Delta coastal zone.

The Chilia distributary water discharge decreasing trend since 1895 is due to high sediments accumulation rate within the Chilia Delta and consequently increasing flow resistance at the mouth zone, as well as to the Sulina and Sf. Gheorghe cut-offs works that modified the hydrological characteristics of these two distributaries.

The river bed sediments erosion and active re-suspension of fine-grained sediments by the high flow during flooding (up to 2 - 9%, Vuković et al, 2014) and moving them downstream, towards the Danube Delta, and finally to the Black Sea, are processes that influence considerably the environmental state.

The Danube River impact on the North-Western Black Sea

The former studies estimated the sediment supply of the Danube River to the Black Sea at 51,700,000 t/y (Bondar et al., 1991) to 67,500,000 t/y (Panin, Jipa, 1998), of which the coarser sediments transported as bed-load varied between 2,180,000 t/y (Bondar, Panin, 2001) and 4,000,000 – 6,000,000 t/y (Panin and Jipa, 1998). Calculations made on multiannual data, from 1840 to 1990, have shown average annual values of minimum 224 kg/s (for 1871) and maximum 4,780 kg/s (for 1990) (Bondar, Panin, 2001).

The changes in water and sediment discharges as well in the distribution of these discharges among the main delta branches, affect significantly the hydrological, hydrochemical and sedimentary processes offshore the Danube Delta front zone. For example, the diminishing of the Danube sediment supply to the Black Sea coastal zone caused a strong deficit in the sedimentary balance of the beaches along the Romanian littoral (Dan et al., 2011; Dan, 2013) and, consequently, in same places the coastline is retreating by several meters per year.

The hydrological and hydrochemical processes in the contact area of the river fresh waters with the marine salty waters are also perturbed (Mee, 1992).

Sediments and pollutants from the Romanian tributaries

The bottom sediments collected from the Romanian tributaries mouths, starting with the Cerna river and ending with Prut river (Fig. 2 A-D), show different grain-size characteristics. On the Jiu and Olt rivers the sediments are composed of coarser sand, followed by gravels. The sediments on the Jiu river contain frequent coal fragments. On the Cerna and Topolniţa rivers the sediments are composed, in general, of sands, followed by silts and clay. The sediments from Argeş contain higher percentage of sand, followed by silts and rarely gravel elements. The ones on the lalomita are silty, followed by clay and extremely reduced quantities of sand. The sediments from Siret river bed are mostly composed of sand and silty sand, being coloured in yellow, because of the particles coming from the erosion of loess formations. The sediments from Prut river are rich in silt, at the surface presenting clayey mud coatings and layers.

Due to the clear dominance of the coarser grain size fractions in the composition of the river sediments the heavy metal content are usually low, with slightly higher concentrations in sediments from the Siret and Prut rivers, where the percentage of fine fractions is greater.

The content temporal variations are also low for most of rivers, notably the Cerna, Jiu and Olt. However, the sediments from the rivers Argeş and lalomita are marked by significant increase of heavy metal concentrations, especially Cu and Zn, for 2012 to 2013 (Fig. 4, 5). Most of these variations are largely due to changes in the grain size composition of the sampled...
sediments, either as a result of slight changes in the location of the sampling site or different hydrological regimes at the sampling time.

Anthropic activity is probably also affecting the very high concentrations of Zn, Ni, Cu in the sediments from the Olt river.

**Significant pollution sources on the Lower Danube River**

Sedimentological and chemical analysis of the sediment samples reflected the current pollution state of the Lower Danube River with nutrients and heavy metals, marking trends of the region environmental state. The yearly survey conducted along the Romanian Danube River from 2009 to 2013 outlined several zones, which in terms of bottom sediment quality, can be ranked from “suspect of pollution” to “certainly polluted” (Fig. 6).

The identified main pollution sources resulting from human activities and natural causes as well are:

- the mining works (Moldova Nouă area and connected mining dumps close to the Iron Gate I lake banks);
- the hydroelectric power stations and related hydro-technical works at Iron Gates I and Iron Gates II. The sediment and pollutants coming from the Danube upstream sections and accumulated in the Iron Gates I and Iron Gates II lakes represent chemical “hot spots” and “time bomb”. The interruption by the dams of the river sedimentary flux strongly affects the downstream Danube section and the Black Sea coastal zone. At the same time, the Lower Danube, downstream the dams is less polluted as the most of the pollution load is stopped in the reservoir lakes. The high water discharge of the Danube River and its diluting capacity play an important role in maintaining the river water quality;
- the waste and the sewage (from home and industrial sites) discharged without treatment into the Danube River (e.g. Călărași – Silistra area; Brăila – Galați area);
- local natural impact (e.g. geology of the basement; fossil littoral beaches), as well as anthropogenic diffuse sources from agricultural farms located in the river floodplain or in the drainage basin;
- possible accidents in the region.

**CONCLUSIONS**

The anthropic interventions on Lower Danube basin lead to some important changes of the environment quality and sedimentary processes.

The hydro-technical works carried out for improving the river and maritime navigation had as effect changes in the water and sediments flow regime that influenced morpho-dynamic and sedimentary processes within the Danube riverbed, Danube Delta and coastal zone of the Black Sea.

The building and constant extension of the jetties on the Sulina branch mouth had modified the water and sediment circulation along the coastal zone in front of the Danube Delta, favouring the erosional processes.

The suppression of the wetlands along the Danube, has favoured the accentuation of flooding events effects and of riverbed processes.

![Fig. 6.1. Areas “suspicions of pollution”, located along the Romanian Danube River sector.](image)
Fig. 6.2. Areas “suspicious of pollution”, located along the Romanian Danube River sector. Cernavoda and Braila - Galati areas (km 174 – Mile 78)

Legend:
- Possible polluted area
- Geoecological cross-section

Fig. 6.3. Areas “suspicious of pollution”, located along the Romanian Danube River sector. Chilia (km 20 – km 3) and Sulina Distributaries (Mile 2.8 – Km 74)

Legend:
- Possible polluted area
- Geoecological cross-section
The use of chemicals in agriculture, industrialization and urbanization within the Danube drainage basin, contributed to the water and sediments pollution.

The phases of anthropogenic impacts on the Danube River after 1850 can be summarised as follows:

- Starting with 1858 the European Danube Commission carried out a large programme of Sulina meander belts cut-offs for improving the navigation on the distributary. These rectifying works shortened the distributary by about 25% and induced a significant enlargement of its water discharge (from 7-9% to 15%);
- After 1905 specific digging hydro-technical works within the Danube Delta have been carried out in order to open the fresh water supply to different remote zones of the delta and to facilitate navigation towards these areas;
- The next phase of anthropic impact started after 1950, when a programme for complex exploitation of Danube Delta natural resources was approved. About 110,000 ha of marshes and wetlands have been dammed and drained for agricultural use and later abandoned as the crops were very difficult to obtain. Mining of sands from old beach ridges and opening of new canals for navigation were also carried out with negative effects on the environmental state of the delta;
- In 1970 started the building of the hydroelectric systems at Iron Gates I and II. The erection of dams lead to a decrease in the sediment discharge supplied by the river to the Black Sea and, consequently, to an increase of the delta coastal zone erosion. Downstream the dams the Danube riverbed suffers significant hydro-morphological degradation (the rate of enlargement and bank erosion was about 1 m.s\(^{-1}\), the depth is reducing by few cm.s\(^{-1}\), the number of bottle-neck points for navigation increased from 26 in 1967 to 62 in 1990) and the navigation become more difficult. Moreover, the fine-grained sediment accumulations in the hydroelectric power stations lakes lead to the occurrence of pollution "hot-spots" and "time bomb" difficult to manage;
- After 1980 the Sf. Gheorghe distributary was rectified through a meander belt cut-off programme. The length of the distributary shortened by 32.58 km and consequently the discharge increased by 5-10%;
- In the last years (after 2004) the hydro-technical works carried out for opening a new waterway for navigation along Bystroe distributary of the Chilia Delta (Ukraine) have a low impact on the Chilia Delta and its delta-front area.

The Lower Danube River hydrological regime can be characterised (based on field long series measurements) as follows:

- The average multiannual water discharge was of 5 699 m\(^3\).s\(^{-1}\) at Orșova, 6 150 m\(^3\).s\(^{-1}\) at Zimnicea, 6 216 m\(^3\).s\(^{-1}\) at Vadu Oii and 6 550 m\(^3\).s\(^{-1}\) at the Danube Delta apex;
- The average multiannual suspended load discharge was 816 kg.s\(^{-1}\) at Orșova, 1 102 kg.s\(^{-1}\) at Zimnicea and 1 356 kg.s\(^{-1}\) at Vadu Oii.
- The grain size of suspended sediments shows an average value of 0.0251 mm at Turnu Severin and 0.0212 mm at the Danube Delta apex.
- The multiannual bed-load discharge was of 2.55 kg.s\(^{-1}\) at Orșova, 4.90 kg.s\(^{-1}\) at Zimnicea, 4.32 kg.s\(^{-1}\) at Vadu Oii and 2.21 kg.s\(^{-1}\) at the Danube Delta apex. The average grain size of the bed-load was of 0.444 mm at Turnu Severin and 0.145 mm at the Danube Delta apex.

The geochemical study allowed defining several zones that could be considered as “suspicious of pollution” (Fig. 6.1-6.3), as follows:

- Iron Gates I lake, downstream Moldova Nouă mining area. Here the sediments have abnormal contents of Cu, Cd, Zn and Ni;
- km 957 – 947, close to the Iron Gates I dam, where the bottom sediments are predominantly fine grained (silts and muds) is characterised by high concentrations of heavy metals (especially Cu, Zn and Ni) and thus can be called pollution "hot-spot" or "time bomb";
- The area from the starting point of the Danube – Black Sea Canal (Cernavodă area) and the pumping station for cooling water for the Nuclear Electro-power Station Cernavodă has fine-grained sediments (muds, silts and very fine sands) that adsorb the heavy metals, among them Ni showing the highest concentration;
- The Brăila - Galati section, starting at km 174 until downstream the Galati port, is considered “suspicious of pollution”, because the concentrations of heavy metals in the sediments are significantly increased (e.g. Cr);
- The mouth areas of the Stambulul Vechi (Chilia branch) and Sf. Gheorghe distributaries are dominated by generally fine-grained bottom sediments. The laboratory analyses showed here abnormal concentrations of Cr in the sediments. The variation coefficients of Cu and Cd were generally very high (126%, 91.50%), indicating anthropic influences.

The Danube River's own regeneration capacity and the very high water discharge (the multiannual average value of 6 550 m\(^3\).s\(^{-1}\) at the Danube Delta apex) that produces high dilution of pollutants are the main natural factors contributing to preserving the quality of the environment. The adoption of adequate protection measures imposed by the Danube River Environmental Protection Convention led also to the abatement of negative effects generated by the anthropic activity.

Acknowledgements. The authors would like to acknowledge the Ministry of Education and Scientific Research for funding the monitoring programme of the Romanian section of the Danube River carried out by the Institute of Marine Geology and Geo-ecology – GeoEcoMar in the framework of its own Research Core Programme. We would also like to express our thanks to prof. Nicolae Panin, member of Romanian Academy, for their useful technical and scientific observations, and to all the colleagues involved in the project for their specific contribution.
REFERENCES


JICKEL S. T., KNAP A. H. 1984. The distribution and geochemistry of some trace metals in the Bermuda coastal environment. Estuarine, Coastal and Shelf Science, 18, 245-262


VUKOVIC D., VUKOVIC Z., STANKOVIC S. 2014. The impact of the Danube Iron Gate Dam on heavy metal storage and sediment flux within the reservoir. Catena, vol. 113, 18 - 23

XIAOYUANG W. 1983. Adsorption of heavy metals on Jinshajiang river sediment. Environ. Chem.11: 1, 628 - 634


FAO CORPORATE DOCUMENT REPOSITORY. 1996. Natural resources-Control of water pollution from agriculture. ManageNet and Environment Department

ICPDR DOCUMENT IC/084.2005. The Danube River Basin District