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Analysis of Surface Water Quality and Sediments Content on Danube Basin in Djerdap-Iron Gate Protected Areas

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Abstract: As water is essential to life and is an indispensable resource for ecosystems and their services and for nearly all human activities, the goal of this research was to evaluate the surface water quality of the Danube as it passes through the Romania–Serbia border in the nature reservations Djerdap and Iron Gate. The study aimed to assess the oxygen regime, nutrients and heavy metals contamination of the surface waters of the Danube on a length of about 240 km, between Bazias and Iron Gate II. Reference sampling and analytical methods (UV-VIS and AAS) were deployed to reach this goal. In addition, sediments were analyzed through back scattered SEM-EDAX for the elemental analysis of the sediment surface. Results obtained show a low environmental impact of heavy metals, while the Danube's oxygen regime is under stress due to nutrients' (nitrites and orthophosphates) significant concentration in the Danube surface water in the analyzed sector. Our approach can be applied to other water bodies in the area, to increase available scientific data together with societal awareness of the Danube's environmental risks.

Keywords: Danube; surface water quality; sediment EDAX analysis; Iron Gate Natural Park; anthropogenic impact on water resources

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1. Introduction

Oxygen regime (DO, COD and BOD) and main nutrients concentrations (nitrates, nitrites, phosphates, etc.) are of significant importance for water bodies due to their direct impact on aquatic ecosystems. A significant impact is also induced by the presence of heavy metals, especially due to their long life span and bioaccumulation, with a significant potential of toxicity. Numerous studies show that exposure to heavy metals such as Ni, Hg, Zn, and Cd can lead to major health issues, from autoimmunity and organ failure to death [1].

The Danube River, the second longest river in Europe, along its flow makes a natural border and a remarkable area between Serbia and Romania—Iron Gate, the pearl of the Danube River. This area is proclaimed as a protected area on both the Serbian and Romanian sides. Hence, on Romania's side, there is the national park Parcul natural Portile de Fier which covers 115,655 ha, the second largest national park in Romania. The national park Djerdap is the largest one in Serbia and covers a total area of 63,786 ha. In this border area, at about 100 km from the point of entry in Romania, the Danube forms its Iron Gate gorge, the deepest (170 m) and most unique in Europe. This area is the habitat of 1100 plant species (some unique in the world, such as Tulipa hungarica), more than 150 bird species and remarkable mammal diversity, in mostly forest-covered area [2].

The area has suffered significant anthropogenic interventions in the past years, from the Iron Gate I hydropower dam opening in 1972, which raised the Danube level by 35 m and formed an accumulation lake that spread up to the Danube confluence with the Tisa

River, to visible climate change impact in the past years that led to the Danube's surface water temperature rise, higher air temperatures and lower precipitation rates [3]. The importance of water sources protection is highlighted by EU water policy, and pollutants discharge from urban, agricultural and industrial sites in water sources being strictly regulated, including in Romania and Serbia, as both states have harmonized their legislation EU Directive 2000/60/EC, since 2000. As a result, significant improvement in surface water quality was observed, especially in reducing the excess of nutrients in the Danube and its main tributaries [4]. The reduction in nitrates concentration, not only in the Iron Gate area but in all of the Danube's course, started in 1990–2000 with Directive 91/676/ECE and the rational use of fertilizers in Europe agriculture. In the past years, due to severe drought periods, scientists could link the increase in nitrates concentrations in river waters with waste waters because the influence of agriculture is minimal due to low infiltration in soil [5].

Another significant threat on Danube surface water quality in the Iron Gate Natural Park area is given by the changing hydrological temporal and spatial character within Europe. In past decades, it was recorded that precipitation increased in northern Europe and decreased in the southern part [6], bringing stress both on water availability and its quality.

A lack of major polluters' presence in the investigated 240 km Danube length is important in terms of environmental status but also disadvantageous from a scientific point of view. While surface waters of the upper/middle [7–9] and lower Danube basin area [10–12] including tributaries are monitored constantly, in the area of current study the data coverage and availability are not so good. This is probably caused by the facts that the area is mountainous, with small scale agriculture, small urban agglomerations, and no major industrial facilities (mainly mining) as they were closed in the post-communist era and there is a lack of an academic/scientific local community.

Access to surface water quality data obtained through continuous monitoring systems is of high importance [13–16] for actual and correct management plans for major river basins. Where data gaps exist, studies which are discontinued but focused on targeted pollutants are important. Nutrients were for many years the main scientific concern for Danube waters [17,18], leading to European regulation to control their discharge (including heavy metals contamination), and more recently emerging pollutants (pharmaceuticals, microplastics, etc.) became of significant importance for ecological assessment [19,20].

The natural occurrence of heavy metals in surface waters is normal, especially in mountainous areas such as the Iron Gate area. However heavy metals are easily quantifiable in tributaries unaffected by anthropogenic activities due to its seasonal (rainfall) variability. In our region, the heavy metal sources originate from municipal waste, waste waters discharge [21] and mining activities at Moldova-Noua and Majdanpek. This led to our need to evaluate the sediments chemical composition, along with surface waters, especially as Danube is the main water source for all cities on its course through Iron Gate Natural Park. The final goal of the research is to attempt to quantify the level of the Danube and its main tributaries' surface water quality and sediments composition, with a focus on oxygen regime, nutrients and heavy metals.

2. Materials and Methods

During the research, an in situ analysis of surface water samples was performed for parameters such as pH, temperature, total hardness, chromate (CrO_4^{2-}) and dissolved oxygen (DO), while for laboratory analysis, samples were taken by kayak in large bodies of water such as the Danube and Nera Rivers. All surface water samples taken for laboratory analysis were prepared for preservation with acids: HNO_3 (nitric acid) for metal concentration analysis [22–25], H_3PO_4 (phosphoric acid) for total nitrogen analysis and H_2SO_4 (sulfuric acid) for chemical oxygen demand analysis on Velp Eco6 and ammonia, phosphor, nitrite, nitrate, phosphate, etc. Sediment samples were collected from river banks in muddy/sandy areas where long-term depositions most likely occur. The sediment samples were oven-dried at low temperatures to avoid material losses.

International references and recognized analytical methods were used for laboratory analysis, as described in Table 1.

Table 1. Methods and analytical equipment used for chemical analysis of sediments and surface water samples.

Parameters	Sample Preservation (pH < 2)	Measurement Methods and Equipment
pH Conductivity Dissolved oxygen (DO)	none	Electric potential difference, electrolytic probe and galvanic probe
Chemical oxygen demand (COD–CCO-Cr)	H_2SO_4	Thermo-reactor, Velp Eco6
Biochemical oxygen demand (BOD–CBO5) Ammonia (NH_4^-) Nitrates (NO_3^-) Nitrites (NO_2^-) Orto phosphate (P-PO_4^{3-}) Sulphates (SO_4^{2-}) Chloride (Cl^-)	H_2SO_4 (for NH_4^-)	UV-VIS photometric method: Analytik Jena Specord 250Plus, HANNA HI 83200
Total nitrogen (TN)	H_3PO_4	Corrosion-free focus-radiation NDIR detection and furnace technology of combustion, Analytik Jena Multi N/C 3100
Sodium (Na^+) Calcium (Ca_2^+) Iron (Fe–total) Arsenic (As_3^+) Lead (Pb) Zinc (Zn_2^+) Cadmium (Cd) Manganese (Mn-total) Mercury (Hg)	HNO_3	Atomic absorption spectrometry in tandem spectrometer equipped with flame, hydride and graphite furnace, Analytik Jena ZEEnit 700 P and inductively coupled plasma optical emission spectroscopy equipped with segmented-array charge-coupled device, ICP-OES Perkin Elmer Optima 8300 [26]
Sediment surface composition	none	Back scattered electron and energy dispersive spectroscopy and FEI Inspect S equipped with EDAX

Surface water samples were collected in 48 sampling locations, as marked in Figure 1, from the Danube and its 5 main tributary rivers in the analyzed area of the Romania–Serbia border, in the natural parks of Iron Gate (Romanian side) and Djerdap (Serbian side). All samples were collected in July–September 2020.

In the area, 17 sampling locations were selected for Danube, 12 for Nera, 1 for Pek and Porecka, 8 for Berzasca and 6 for Cerna Rivers.

The total length of the analyzed water body is about 240 km.

Figure 1. Sampling points for sediments and surface water quality analysis on Danube.

Applied sampling, samples preservations and analytical techniques applied are presented in Figure 2. For each sampling point (Figure 1), surface waters were collected from 3 to 5 spots, at a ~20 min time frame and mixed in one 2 L bottle. From this unique sample, 4 analytical samples were separated in 0.5 L HDPE bottles, one being used for the in situ measurements of pH, conductivity and DO while the remaining 3 were preserved with specific acids for laboratory analysis (see Figure 2) [27–29].

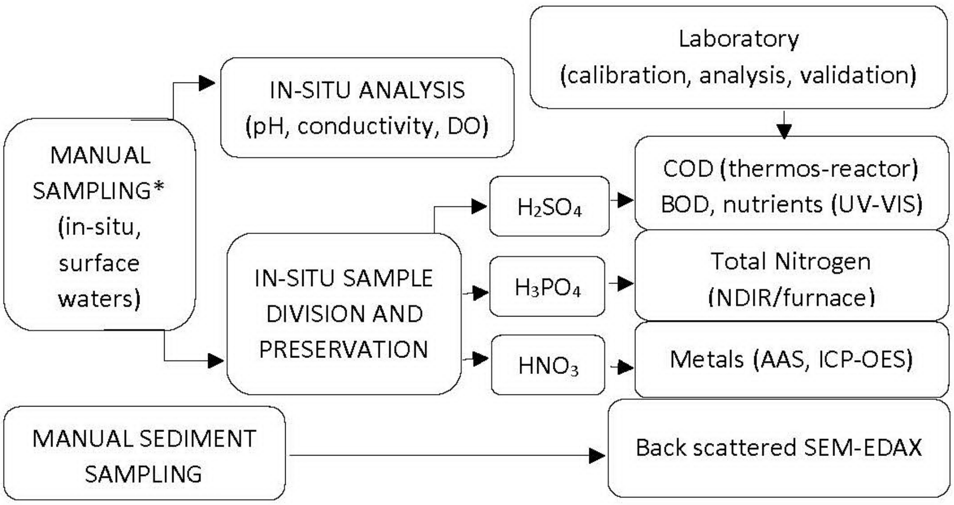


Figure 2. Applied methodology. Note: * in accordance with ISO 5667-6.

Surface sediment samples were taken from river banks, in a column of maximum 2 cm, with a manual sampler and stored in 50 mL recipients. During transportation and storage for laboratory analysis, all samples were maintained at ~4 °C. The recommendations of ISO 5667-1(3) were followed during sampling, manipulation and sample preservation.

3. Results and Discussion

3.1. Chemical Analysis of Surface Waters

In Table 2, a selection of the results obtained for samples from the Danube River are presented, grouped by oxygen content, nutrients and heavy metals.

Table 2. Results obtained for parameter analysis in samples of Danube, July–September 2020.

Parameter	Unit	D1	D2	D5	D6	D10	D11	D14	D15	D17	Eco State
pH	-	6.9	7.1	7.1	7.2	7.4	7.2	7.5	7.0	6.7	-
Conductivity	µS/cm	399	402	411	405	402	403	389	394	404	-
DO		7.5	7.2	7.2	7.2	7.2	6.9	7.4	7.0	6.4	IInd
BOD–CBO5	mgO_2/L	3.6	3.3	3.5	3.2	3.5	3.5	3.4	3.3	3.2	IInd
COD–CCO-Cr		26	22	25	22	26	27	20	20	18	IInd
Sodium		2.1	3.4	2.5	3.4	2.8	2.2	3.3	4.1	2.9	Ist
Calcium		4.5	5.8	6.5	6.8	5.8	4.7	4.9	5.8	3.9	Ist
Ammonia		0.11	0.21	0.18	0.28	0.16	0.14	0.18	0.28	0.33	Ist
Nitrates		0.77	0.84	0.99	0.92	0.79	0.72	0.72	0.72	0.66	Ist
Nitrites	mg/L	0.022	0.029	0.018	0.022	0.024	0.028	0.020	0.019	0.016	IInd
Orthophosphate		0.31	0.28	0.31	0.18	0.27	0.32	0.22	0.25	0.22	IIIrd
Sulphates		8.3	9.7	12.1	8.7	10.2	8.1	10.2	8.1	7.1	Ist
Chloride		3.5	8.1	5.7	8.1	5.1	3.6	5.2	7.6	11.1	Ist
Total Nitrogen		1.21	1.32	1.12	1.18	1.16	1.15	1.11	1.15	0.98	Ist
Mercury		0.011	0.017	0.012	0.014	0.011	0.009	0.010	0.009	0.015	Ist
Arsenic		0.09	0.12	0.12	0.14	0.10	0.11	0.09	0.11	0.14	Ist
Lead		0.21	0.24	0.28	0.21	0.21	0.22	0.22	0.22	0.31	Ist
Zinc	µg/L	21.1	18.5	20.1	18.5	17.9	19.1	19.7	19.4	18.1	Ist
Cadmium		0.004	0.009	0.008	0.012	0.014	0.008	0.011	0.042	0.088	Ist
Manganese		0.011	0.021	0.014	0.016	0.011	0.011	0.016	0.011	0.012	Ist
Iron		0.766	0.821	0.685	0.801	0.804	0.792	0.803	0.911	2.193	IIIrd

From the 17 sampling points, nine were selected from representability, equally distributed by Danube flow direction, from its point of entry in Romania at Bazias down to the area exit point (Iron Gate II) of the Romanian–Serbian border.

Sediments and surface water samples were collected during the summer of 2020, starting in July and ending in September, a period with relatively constant temperature, precipitation and Danube flow variations, avoiding the seasonal variability of pollutants concentration during sampling [30–32].

From a management point of view, the Danube River is divided into 15 water management regions and four main sectors, the Upper, Middle, Lower and Delta [33,34]. The results obtained and presented in Tables 2 and 3 are specific and limited to the lower part of the Middle Danube section. Today, this section is characterized by minimal local anthropogenic chemical discharge influence with only two exceptions: Majdanpek/Bor mining activities with waste waters discharge through the Pek and Porecka Rivers [35–38] and Drobeta Turnu Severin/Kladovo relevant urban agglomeration. The results are interpreted in the tables in terms of ecochemical status [39], or "eco state", classifying the surface water quality into five classes (color coded), from excellent to very poor, as described in Table 3.

Table 3. AAS analytical errors.

Element	R^2 (Calibration Curve)	SD (max.)	RSD (max.) %
Hg	0.9995	0.21	0.7
As	0.9995	0.16	0.4
Pb	0.9997	0.22	0.5
Zn	0.9999	0.09	0.2
Cd	0.9998	0.18	0.8
Mn	0.9997	0.11	0.4
Fe	0.9998	0.21	0.8

Reference-certified materials (Certipur/Merck) were used for sample preparation for analysis on Zeenit 700P Atomic Absorbtion Spectrometer. ICP multi-element standard solution IV, traceable to NIST SRM, were used for instrument calibration. The instrument is controlled by AspectLS software, with automated sample analysis and results validation and control. The calibration curve parameter R^2 and the measurement results' standard deviation and residuals are presented in Table 3.

In Table 4, a selection of the results obtained for samples from the Danube's main tributaries in the area are presented (the Nera, Pek, Berzasca, Porecka and Cerna Rivers), also grouped on oxygen content, nutrients and heavy metals.

Table 4. Results obtained for parameter analysis in samples of Danube's tributaries: Nera, Porecka, Berzasca, Pek and Cerna Rivers, July–September 2020.

Parameter	Unit	Nera			Pek	Berzasca		Porecka	Cerna		
		N11	N6	N1	SS10	B7	B1	SS12	C6	C3	C1
pH	-	7.81	7.76	7.94	7.79	8.07	8.11	8.17	7.31	7.38	7.34
Conductivity	µS/cm	297	301	293	698	290	288	613	377	388	372
DO	mgO_2/L	11.1	10.8	10.4	5.1	14.5	14.5	4.6	10.2	9.9	5.7
BOD–CBO5	mgO_2/L	2.7	2.9	2.9	1.9	1.4	1.5	1.3	2.2	3.1	7.4
COD–CCO-Cr	mgO_2/L	9.4	9.6	9.7	2.95 **	5.8	5.3	2.78 **	6.9	8.4	18.1
Sodium	mg/L	3.0	3.1	3.6	-	2.1	1.8	-	3.4	3.2	3.6
Calcium	mg/L	49.5	42.2	38.5	-	2.7	2.8	-	27.9	39.1	41.2
Ammonia	mg/L	0.38	0.33	0.38	0.42	0.07	0.06	0.07	0.09	0.11	0.74
Nitrates	mg/L	0.42	0.48	0.53	1.6	0.22	0.08	1.97	0.12	0.22	0.34
Nitrites	mg/L	0.030	0.032	0.041	0.09	0.011	0.005	0.03	0.014	0.017	0.028
Orthophosphate	mg/L	0.12	0.12	0.16	0.09	0.06	0.02	0.12	0.05	0.06	0.09
Sulphates	mg/L	11.7	12.4	15.6	150	8.4	3.9	90	4.8	34.1	37.2
Chloride	mg/L	0.3	0.4	0.4	-	0.2	0.2	-	0.2	0.3	0.6
Total nitrogen	mg/L	0.89	1.01	1.12	-	0.78	0.38	-	0.51	0.54	0.89
Mercury	µg/L	0.014	0.016	0.021	-	0.008	0.006	-	0.011	0.015	0.030
Arsenic	µg/L	0.18	0.21	0.33	<DL ***	0.074	0.060	<DL ***	0.079	0.087	0.088
Lead	µg/L	0.082	0.081	0.088	<DL ***	0.014	0.012	<DL***	0.017	0.018	0.054
Zinc	µg/L	13.2	13.1	12.7	32.78	1.14	0.77	31.81	7.5	10.1	12.1
Cadmium	µg/L	0.010	0.008	0.007	<DL ***	0.003	0.003	<DL ***	0.006	0.006	0.007
Manganese	µg/L	0.020	0.021	0.022	<DL ***	0.018	0.014	<DL ***	0.032	0.055	0.057
Iron	µg/L	0.849	0.815	0.893	2.309	0.087	0.065	0.482	0.394	0.499	0.462

Notes: Legend: Eco state classification by Directive 2000/60/EC, blue—high quality; green—good quality; yellow—moderate quality; orange—poor quality and red—bad quality; or water quality classes from Ist to Vth. **—method used for chemical oxygen demand is CCO-Mn. ***—DL—detection limit for ICP-OES Perkin Elmer Optima 8300.

In the case of COD—chemical oxygen demand—in two sampling sites, the Pek and Porecka Rivers, the COD-Mn method was used, as the analysis was conducted in Serbia, where the method of determining COD by the titration of sodium oxalate with potassium permanganate is widely used due to its advantage of not using pentavalent chromium and mercury sulphate, hazardous chemicals.

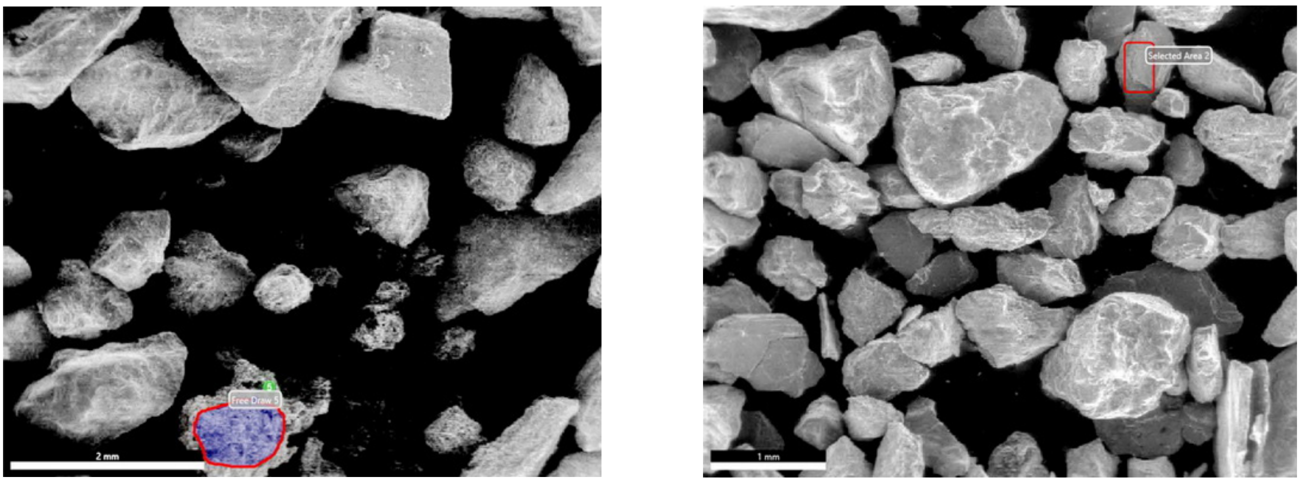
3.2. Chemical Composition Analysis of Surface Sediments

In addition to analyzing the chemical composition of surface water, we tried to analyze the composition of sediments by back scattered electron and energy dispersive spectroscopy (SEM-EDAX). The samples were taken from river banks (bays) where water had lower flows and sedimentation occurred constantly [40,41], and the results obtained are shown in Table 5.

Table 5. EDAX APEX results on sediment samples.

Element	Danube	Nera	Berzasca	Cerna
(Error %)		Weight %		
Na (±10.72)		9.92	3.75	
Mg (±11.16)	3.91	1.82	4.18	3.91
Al (±6.65)	19.06	18.93	18.31	8.42
Si (±5.58)	47.7	53.5	46.35	13.59
K (±6.31)	5.58	3.81	5.08	1.39
Ca (±3.01)	6.26	6.43	5.21	2.14
Ti (±7.75)	2.13	-	-	1.12
Fe (±11.08)	15.36	14.41	17.11	14.74
Co (±7.14)	-	1.17	-	-

Figure 3 shows the sample under an electronic microscope equipped with EDAX, for two samples from Danube and Cerna sediments, while Figure 4 presents the results obtained through EDAX elemental spectroscopy analysis.



(a) (b)

Figure 3. Sediment samples under electronic microscope: (**a**) example of Danube sample; (**b**) example of Cerna sample.

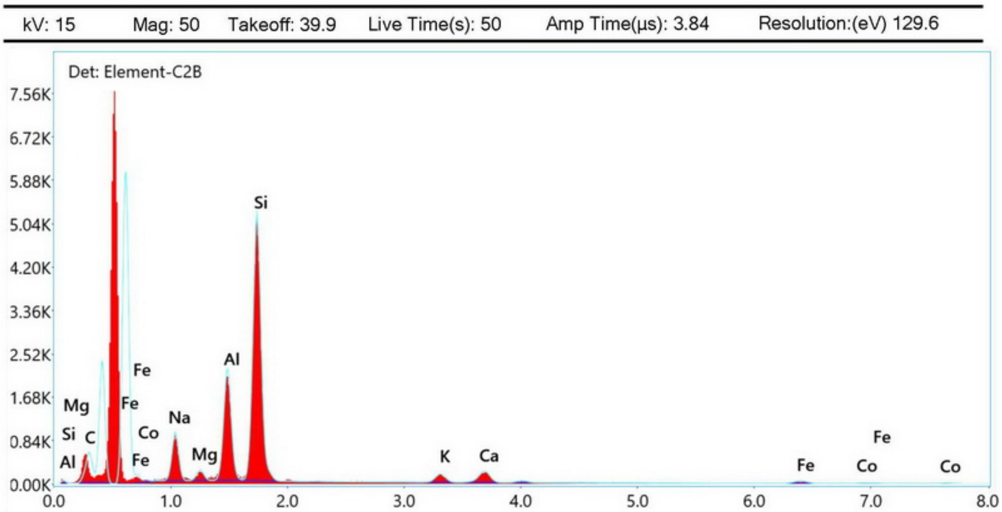


Figure 4. EDAX elemental spectroscopy analysis of Nera sediment sample.

Oxygen was removed from the EDAX results due to the risk of being present in the FEI microscope vacuum chamber due to sample manipulation.

This technique has the advantage that is applied directly to a dried sediment sample and can give a fast view on trace concentrations of heavy metals deposited on the surface of the sediment micro-pebble. The data obtained could be used to test and validate sediment deposition and transportation behavior through mathematical (CFD) models [42,43].

The goal of analyzing sediments surface composition instead of the standard mineralization method followed by atomic absorption spectrometry (or inductively coupled plasma-optical emission spectrometry) was to see if this much faster method could provide an overview of metals' presence on sediment grains, for more targeted AAS/ICP-OES analysis.

In this frame and after analyzing the results obtained by the AEPS project team experts after sampling and analysis surface water on the Danube, one can observe that Ecological Status Classification varies from high (quality) to good on the Danube, with oxygen concentration parameters (DO, COD and BOD5) all IInd class, good; most of the nutrients (Na^+, Ca^{2+}, NH^{4-}, NO^{3-}, $SO_4{}^{2-}$, TN) fall into Ist class, high quality, while orthophosphates $P\text{-}PO_4{}^{3-}$ concentrations classify Danube water quality in the IIIrd class, moderate.

The values of individual parameters for oxygen regime and nutrients concentration are similar with those observed during other scientific studies (for the summer season). For the middle Danube sector, the BOD ranged from 2.5 to 3.5 mg/L, ammonia from 0.1 to 0.2 mg/L, total nitrogen from 0.5 to 1.3 mg/L, nitrites from 0.06 to 0.12 mg/L, nitrates from 0.7 to 1.7 mg/L and orthophosphates from 0.04 to 0.07 mg/L on the Danube River in the region between Novi-Sad and Smederevo, Serbia [44–46]. A statistical analysis study [47] showed that in terms of nutrients Danube River surface water quality in Serbia has been slowly but constantly improving since 2013. Other studies focused on the Budapest region and found similar nutrient pollution values [48]. In the lower Danube basin, surface water quality shows improvement in the Galati area (main polluting source). In 2008, the water quality was classified in the fifth quality class for iron and copper, and in 2018 it was classified in the second quality class [49]. In the Lower Danube basin, the "hot spot" is given by the Galati area but significant improvements are observed. In 2010, in the Galati area the nitrites ranged between 0.2 and 0.6 mg/L and nitrates between 1.2 and 4.8 mg/L, mainly due to municipal and industrial waste waters discharge [50]. In the next years, mainly due to Romania accessing the EU structural funds, the situation improved, with nitrites values ranging between 0.04 and 0.1 mg/L and nitrates between 0.8 and 1.5 mg/L in 2015, lower than in pre-accession era [51]. Extensive studies on water quality in the Lower Danube basin, conducted on approximately 1500 samples analyzed between 2011 and 2017, showed that water quality can be characterized as moderately polluted (class III), indicating that the EU Water Framework Directives are not met [52]. A recent study conducted in the Galati-Tulcea area and analyzing 150 samples collected from 15 sampling points, in 2019, showed an improvement, with nitrites concentrations ranging from 0.02 to 0.036 mg/L [53].

The heavy metals concentration in Danube surface waters in the analyzed area were all (Hg, As, Pb, Zn, Cd and Mn) very low, well into I^{st} class, high quality. The only exception was found for Iron (Fe), whose values were constantly, at all lengths of the analyzed area, into IIIrd class, moderate water quality. With the exception of the Berzasca River, all other investigated rivers (Cerna, Nera, Pek and Porecka) showed a similar pattern for heavy metals. While all (Hg, As, Pb, Zn, Cd and Mn) showed concentration well under Ist class, iron (Fe) was constantly in the IInd or IIIrd quality class. This would bring to our minds that this pattern may suggest that high iron (Fe) concentration in the surface waters of the Danube, Nera, Cerna, Pek and Porecka may be caused by the regional geomorphic characteristics of the surrounding mountains and that iron concentrations are given by the washout of naturally occurring iron deposits.

Based on other studies focused on the heavy metal pollution of Danube surface waters, significant differences were recorded for the Middle and Lower Danube basins. In the Hungarian Pannonian area [54], the values of lead were 0.7–1.5 μg/L, of mercury were 0.02 μg/L, of arsenic were 0.9–2.6 μg/L and of zinc were <10 μg/L, while in Galati area [55], the values of lead were 2.49–3.88 μg/L and of zinc were 10–45 μg/L.

Another issue observed was on nutrients concentrations (orthophosphates, ammonia, nitrates, nitrites and sulphates). The issue was found on Nera, as the river flows through numerous villages, probably collecting washouts (or direct dump) from villages, households and farms' septic tanks. As both summer and autumn of 2020 were in extreme drought, it is unlikely that nutrients reaching the Nera River came from agricultural land washout. A similar or worse situation was found on the Pek and Porecka Rivers. Danube, on the other hand, was in the first class of water quality (high quality) in terms on nutrients, due to its volume and capacity of self-purification, with one exception, orthophosphates.

One significant cause for the high content of nutrients in Serbian river bodies can be deducted from Figure 5, which shows the technological status of urban waste treatment plants in Europe, in correlation with a population that benefits from centralized urban waste water collection systems. The most performant waste water treatment plants are so called "tertiary", meaning that they provide phosphorus and nitrogen reduction before dumping.

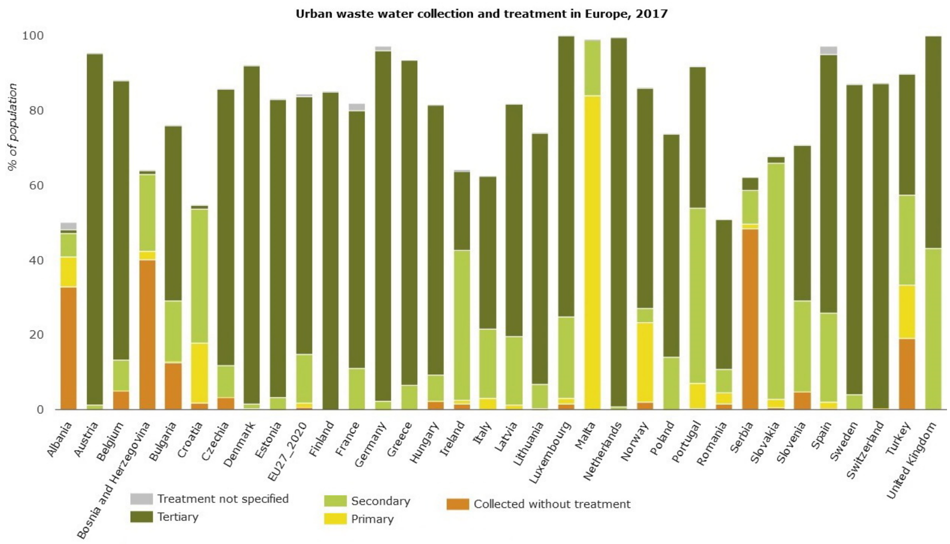


Figure 5. Urban waste water collection and treatment in Europe, 2017 [56].

The "secondary" waste water treatment plants provide only biological treatment, "primary" means that the system is only equipped with settling tanks and "collected without treatment" means that the urban waste water system only collects the waste waters from the population and dumps it without any treatment into natural water bodies.

Unfortunately, in the Serbian case, only a handful of urban waste water systems are in the "tertiary" zone, while more than 50% of the Serbian population that benefit from waste water systems are serviced by "collected without treatment", bringing a significant stress onto the ecological status of Serbia rivers.

Up to 2000, Romania was in a similar situation as Serbia, in terms of waste water systems. The situation improved significantly (as seen in Figures 5 and 6) with efforts to join the European Union Community and with 2007 as a target year to the enforcement of EU directives and with significant financial support through EU cohesion policy. However, even with significant progress in urban waste water treatment systems (such as in western Romania: Timisoara, Arad and Oradea), in other areas the progress was slow, as an example in Bucharest (with over 3 million inhabitants) the waste water system spills into the Dimbovita River (and subsequently into the Danube) about 50% of its waste waters without any treatment.

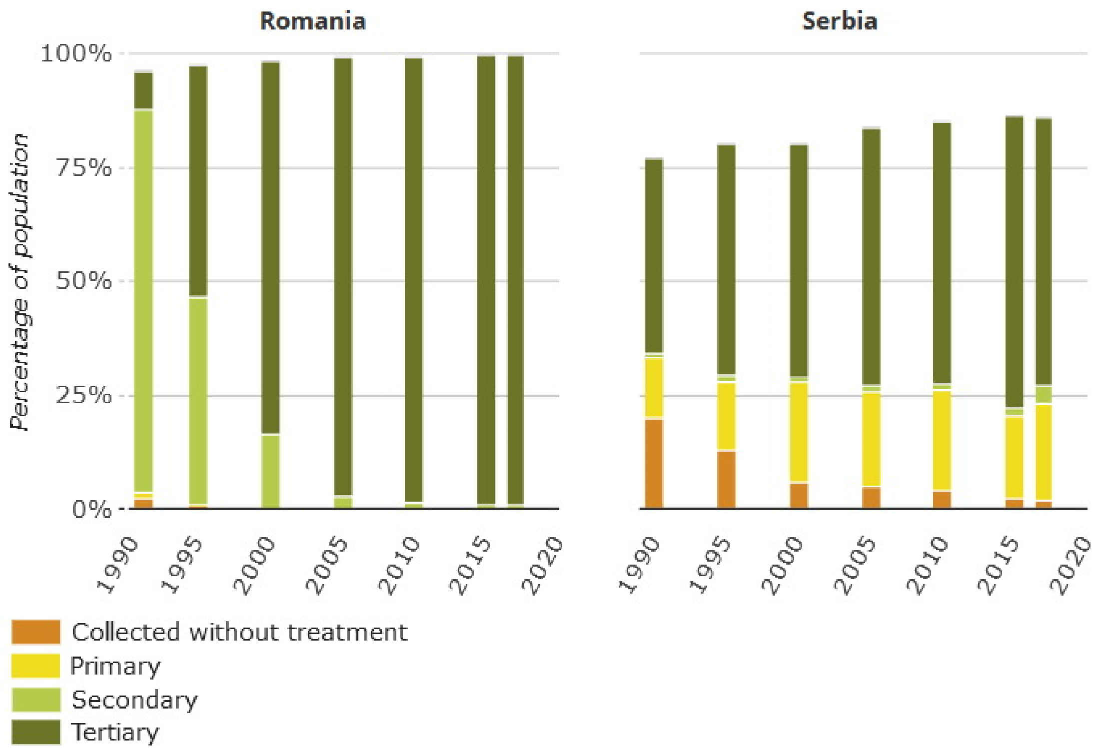


Figure 6. Urban waste water collection and treatment in Romania and Serbia, 2017 [57].

At the European level, the stress on surface waters quality has constantly decreased in the last 2 decades, with the main water quality parameters such as biological oxygen demand, ammonia, phosphates and nitrates following a significant decrease in concentration [58]. However, a new stress on the Danube basin is given nowadays by climate change in terms of water supply scarcity due to more frequent and for longer periods droughts in South-Eastern Europe, bringing into our attention that water is a resource that should be used in a sustainable way [59].

Nitrates (nutrients, in general) can be naturally removed from surface waters through deposition in floodplains, such as the Pannonian basin and Danube Delta [60–62]. The area investigated in the present study, the Iron Gate accumulation lake formed on the Danube by the Iron Gate I dam, also functions to remove pollutants through deposition, as it holds over 2200 million m^3 of water, providing a buffer zone for the Lower Danube basin.

The decrease in BOD and ammonium concentrations is mainly because of a general improvement in waste water treatment throughout Europe. However, further improvement in waste water systems is needed on domestic, municipal and industrial sites [63–65]. The decrease in phosphorus concentration is likely related to improvements in waste water treatment and the reduction in phosphorus content in detergents. The decrease in nitrates is likely related to the effects of measures to reduce the agricultural inputs of nitrate and improvements in waste water treatment. In Central and Eastern European countries, the economic decline of the 1990s also contributed to a decrease in pollution from manufacturing industries [66].

In terms of the chemical status of surface waters in the Iron Gate Natural Park area, all surface waters investigated, the Danube, Nera, Pek, Cerna, Porecka and Berzasca Rivers, showed high quality or good quality chemical status. Chemical status is defined by concentrations of priority substances defined in the Environmental Quality Standards Directive 2008/105/EC amended by the Priority Substances Directive 2013/39/EU). Our findings are consistent with the Water Information System for Europe (WISE) in the frame of the Water Framework Directive map that contains information from the second River Basin Management Plans (RBMPs) reported by EU Member States, as seen in Figure 7.

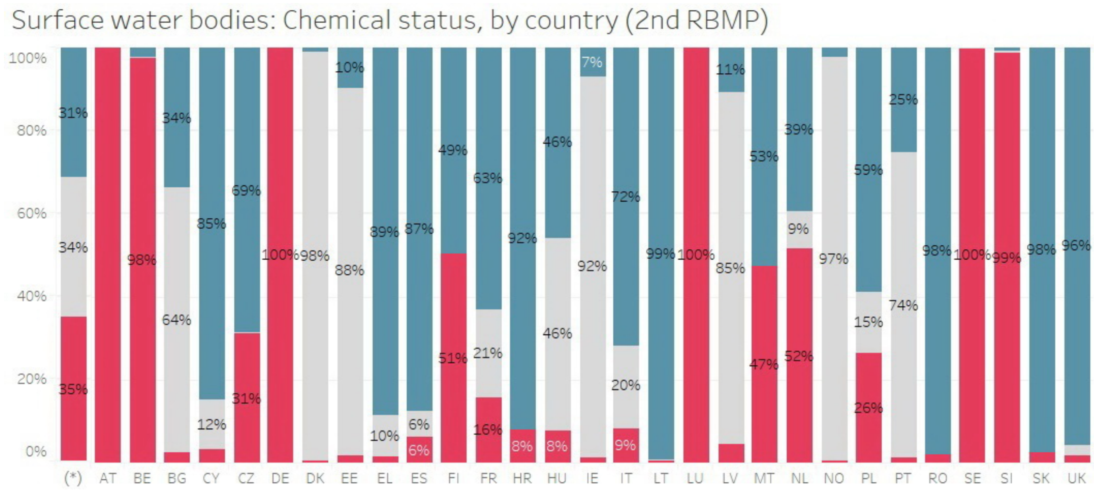


Figure 7. EU surface water bodies: chemical status by country (EU Water Framework Directive—Second River Basin Management Plan) [67]. Note: * column—all states.

4. Conclusions

In conclusion, in the area analyzed by us, the Djerdap and Iron Gate natural parks, the surface water quality of the Danube and its main tributaries in the area, the Nera, Porecka, Berzasca, Pek and Cerna Rivers, can be classified as high quality along its course and good or moderate quality on various segments of water bodies.

Results obtained are limited to a 240 km length of a part of the Middle Danube Basin defined by the Romanian–Serbian border. Another limitation of representativeness is given by the relatively low number of sampling locations, 17 on the Danube and 28 on the Danube tributaries in the studied area. However, the results presented fill in a lack of surface water quality data available for this specific area.

The main stresses identified in the analyzed area are from waste water treatment systems (or the lack of them), agricultural land washouts contributing to the pollution of surface waters with ammonia, phosphates and nitrites, and industrial activity with an emphasis on mining activity's impact in Majdanpek on the water quality of the Pek River and in Moldova-Noua on the Danube directly.

The study aimed to obtain relevant data for the oxygen consumption, nutrients levels and heavy metals contamination of targeted surface waters, with an additional potential application of the SEM-EDAX characterization of heavy metals deposition on sediments' micro-pebbles surface. Based on the fast SEM-EDAX result, one can analyze, for a specific heavy metal, if a time-consuming sediment sample mineralization followed by AAS detection is necessary.

In our Romania–Serbia cross-border area, especially as it is one of the most beautiful and wild parts of the entire Danube's course to the Black Sea, we must give more focused attention to prevent organic pollution from waste water as well as diffuse runoff from agriculture, as they negatively affect aquatic ecosystems, causing a loss of oxygen and changes in species composition, deteriorating the ecological status of the Danube and its surrounding areas.

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