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The Zrmanja River Estuary (Adriatic Coast, Croatia) – the Need for Interdisciplinary Approach to Protection of Coastal Areas

Abstract

The Zrmanja River estuary is a semi-enclosed bay immersed in a karstic landscape of the eastern Adriatic coast. It represents a highly indented system which includes part of the Zrmanja River, downstream from the Jankovića Buk, the Novigrad and the Karin Seas, and the strait connecting the Novigrad Sea with the Velebit Channel. The very fact that the estuary of the Zrmanja River is located in the karst area makes this system highly vulnerable and susceptible to possible anthropogenic pressures. Preservation of such and similar water systems relies on the knowledge of the main factors that govern its physical, chemical, biological and geochemical features. Due to the lack of geochemical data for the Zrmanja River estuary, a comprehensive study was carried out to explain sedimentation processes and the origin of the material within this estuary and provide additional knowledge necessary for its sustainable use and preservation. This paper, therefore, attempts to summarize the obtained data, focusing on the main natural and anthropogenic factors that define the geochemistry of the Zrmanja River estuary.

Keywords: Zrmanja River estuary, Adriatic coast, geochemistry, sediments, water

1. Introduction

Estuaries represent unique water systems, a vital link between the land and the sea. They are among the most productive areas on earth as habitats and breeding locations for a great number of aquatic species. Their sheltered waters present protected spawning places for which they are often called the "nurseries of the sea". Not only that they represent critically important ecosystems, they have important commercial value as their resources provide economic benefits for tourism, fisheries and recreational activities. The coastal waters of estuaries also support important public infrastructure, serving as harbors and ports vital for shipping and transportation.

Following the latter, estuaries are nowadays under an increasing variety of pressures, including physical and chemical transformation, habitat destruction, changes in biodiversity, and recent climatic warming [33, 54]. According to UNEP-MAP RAC/SPA [69], estuaries and river inlets, as well as karst areas of the Mediterranean region are specificaly identified as critical by all or by the majority of countries, whereas the Adriatic area is considered one among Mediterranean areas with biodiversity most sensitive to climate changes, if not the most sensitive one. According to this document, the Zrmanja River, one of the karstic rivers discharging along the eastern Adriatic coast (Croatia), is also included in the areas identified as critical for impacts on marine and coastal biodiversity in two categories, as an estuary and as habitat of endemic fish species.

Peculiarity of karstic rivers, in general, lies in their intricate relationship between the underground and surface parts of their flow, but their uniqueness at the same time makes them extremely vulnerable to all forms of pollution. Namely, natural processes in combination with anthropogenic influence in karst areas can cause strong, sudden, unpredictable and generally immeasurable and dangerous consequences for both the environment and the society as a whole [55].

Although not as impressive as some other world rivers, given the length, the size of the drainage area and the discharge rate, the Zrmanja River and its estuary has attracted researchers studying its many features for decades. However, the largest number of studies focused on biological [5-9, 60, 61, 71] and hydrological [29, 47] characteristics of this karstic river, while very few described its geochemical features [49, 62]. Scarcity of such data prompted a comprehensive study in 2008, which aimed at explaining the sedimentation process and origin of materials within the Zrmanja River and its estuary, as well as the geochemistry of the estuarine water, the associated sediments and the surrounding soils.

This review, therefore, attempts to summarize the findings related to geological and geochemical features of the Zrmanja River estuary, and provide the basis for the recommendations that will ensure the sustainable management of this part of the Adriatic coast.

2. Karstic highly stratified estuaries

Out of the Earth's entire landmass (excluding the Antarctic, Greenland and Iceland), 13.2% is covered by karst regions, while the Dinaric karst, which includes the Zrmanja River drainage area, is one of the biggest in Europe, extending from Slovenia to Albania [74]. Despite the fact that many maritime countries have large karst regions, such as Bosnia and Herzegovina, Croatia, China, France, Greece, Iran, Italy, Montenegro, Russia, Serbia, Slovenia, Spain, Turkey, the United States etc., karstic estuaries remain a poorly described phenomenon. This applies even more so where highly stratified type of karstic estuaries are considered.

In general, the highly stratified type of estuary is common in low tidal amplitude seas (e.g. the Mediterranean), such as the Ebro Estuary [34, 59] and those from the eastern Adriatic coast, e.g. the Zrmanja River estuary [5] and the Krka River estuary [10]. While tidal range and flow rate define the intensity of mixing within the certain estuary, its geochemical features are primarily determined by the surrounding geological and lithological background.

The latter two rivers, the Zrmanja River and the Krka River, belong to the area of Dinarides, i.e. karstic landscape of the eastern Adriatic coast, characterized by low tidal regime [37]. While the Krka River estuary has provoked curiosity of many geochemists for decades [11-13, 15-17, 66], the estuary of the Zrmanja River has remained, until recently, only sporadically explored. Located relatively close to each other, and connected by underground flows, these two karst rivers are somewhat different from other rivers of the eastern Adriatic coast. The prevailing carbonate background, the formation of tuffa barriers and low quantities of suspended material have conditioned the minimal deposition at the river mouth of these rivers. This is oposite to other rivers from the eastern side of the Adriatic, such as Mirna, Raša, Rječina, Cetina and Neretva, whose cathment basins are characterized by occurences of flysch and other non-carbonate deposits, inducing higher amounts of suspended matter, and higher sedimentation rates at their river mouths, and consequently having different geochemistry.

3. Features of the wider area of the Zrmanja River estuary

3.1. Geographical characteristics

The Zrmanja River and its estuary are situated in the central part of the eastern Adriatic coast, Croatia (Figure 1), at the foot of the Velebit Mountain and about 20 km from the city of Zadar.

Geographically, the wider area of the Zrmanja River estuary is a very clearly differentiated space, composed of several units. The morphological elements are distributed in the NW-SE direction [2], with the Velebit mountain as the largest landform with elevations of up to 1800 m (Vaganski vrh, 1757 m). Towards the lower relief forms follow the Bukovica with elevations of up to 700 m (Jurišinka, 674 m), the Velebit slope (500-600 m), and the Ravni kotari as the lowest landform in this area, with altitudes not exceeding 300 m. The submarine relief units include the Novigrad Sea and the Karin Sea.

The river itself emerges from the strong spring beneath the Poštak mountain in the southern part of Lika, at an altitude of 335 m, and flows into the Adriatic Sea (Velebit

Channel), 12 kilometers from the city of Obrovac. The total length of the Zrmanja River open watercourse running from the spring to the mouth of the river in the Novigrad Sea is about 69 km, while its drainage basin covers an area of about 1460 km^2 [63, 76, 77]. Its main tributary is river Krupa with Krnjeza and Dobarnica streams. Its distinctive upstream canyon character ends below the Ogari Buk waterfall, downstream from the confluence of the Krupa and the Zrmanja Rivers, and its flow becomes slower in the wide field area, including the artificial lake of the hydropower plant Velebit. However, downstream of the last travertine barriers at the Jankovića Buk waterfall (Figure 2a, b), the river valley becomes a canyon (Figure 1c, Figure 2c, d) stretching all the way to the Novigrad Sea.

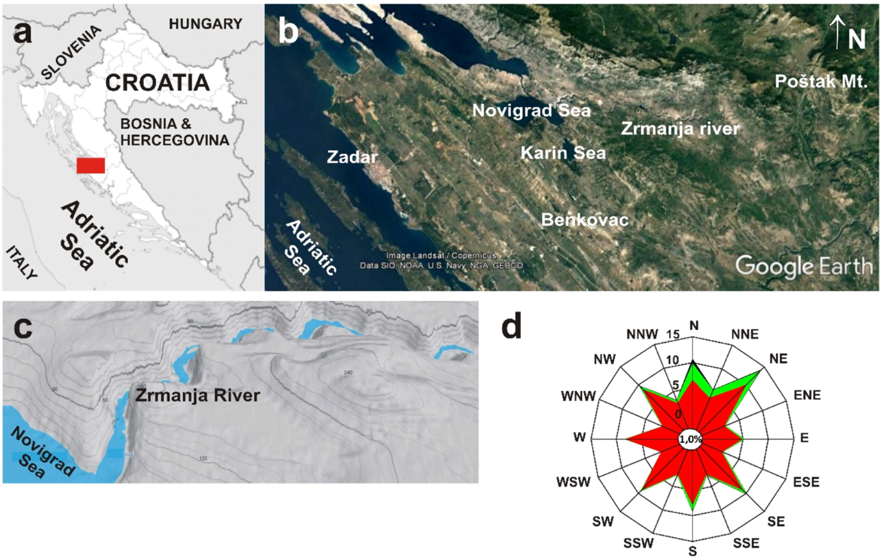

Figure 1 - a) Location of the Zrmanja River estuary; b) Detailed view of the Zrmanja River estuary; c) Canyon of the Zrmanja River (VantagePoint software, Adriatopo topographic map); d) Wind rose for Benkovac in 1981-2010 (courtesy of the Croatian Meteorological and Hydrological Service).

According to Köppen's climate classification, the research area climate is of the Cfa type, moderately hot humid climate with hot summers [58]. The average annual precipitation rate in the Zrmanja River drainage basin is about 1400 mm, while in the area of southern Velebit the precipitation rate ranges from 1493 mm to 3419 mm [50, 58, 77]. The average air temperature in the Novigrad town (by the Novigrad Sea) ranges from 6.0°C in January to 24.3°C in July. Summertime is warm and hot with a mean air temperature of 35°C, while in the winter temperature drops to -9°C. The wind dominating this area is the bora, i.e. a northern to north-eastern katabatic wind

(Figure 1d), followed by east and west winds [48]. Northeast and east winds are the result of lowering of aerial masses from Velebit, while west winds are a result of the channeling effect from the sea along the Zrmanja River valley. All the other directions are much less frequent there.

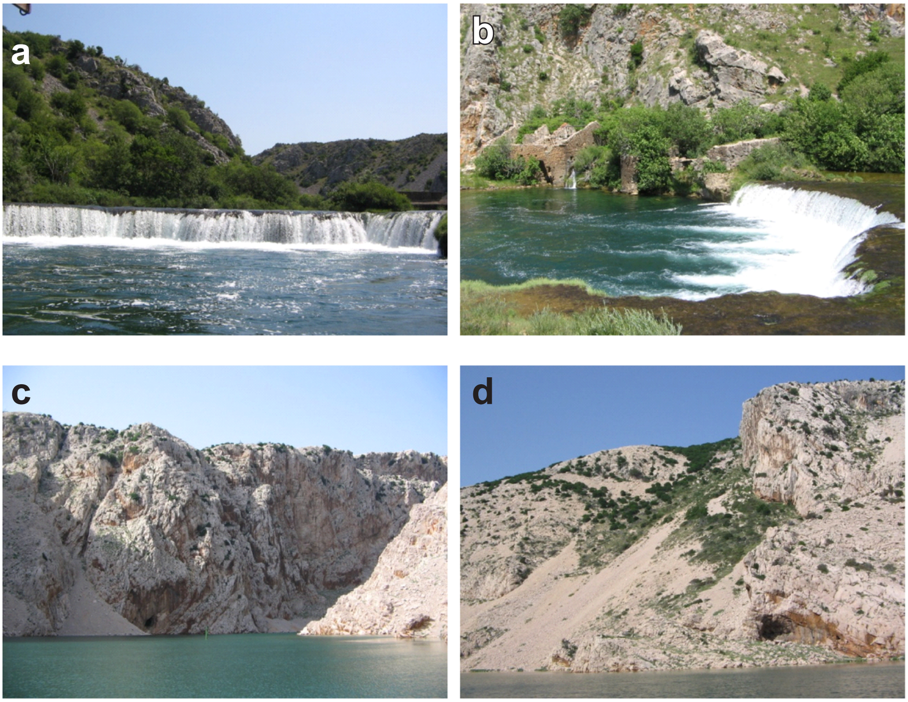

Figure 2 - The Zrmanja River at the Jankovića Buk waterfall (a, b) and further downstream (c, d).

2.2. Geological characteristics

The studied area belongs to the External (Outer) Dinarides and is mainly built of the Mesozoic carbonates (Jurassic and Cretaceous limestones, dolomites and carbonate breccias), transgressively covered with Paleogene carbonates and clastites (Eocene limestones, dolomites and clastites, Oligocene conglomerates and limestones), while Triassic schists, limestones, and clastites occur only sporadically [30, 31, 35, 36, 43, 44].

A detailed geological map and description of litostratigraphic units are found on the Basic geographic map (OGK) SFRJ M: 100 000, leave Obrovac [35], Zadar [43] and Knin [30] and Interpreter for the listed sheets [31, 36, 44]. A simplified schematic geological map of this area by Fiket et al. [26] is shown in Figure 3.

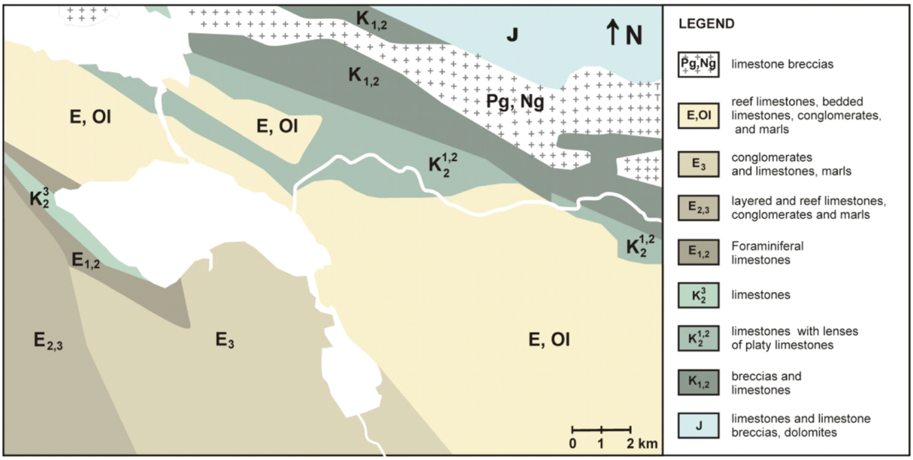

Figure 3 - Simplified geological map of the study area [26].

The Zrmanja River valley started to develop once the orogenic movements of the Pyrenean and Savian phases had been accomplished, during the periods of the Upper Eocene and the transition from the Oligocene to the Miocene. The regional fault, developed during this period, was the main feature of the Zrmanja River flow direction [27]. The old course of Zrmanja once led to the river Krka, while today's river valley developed more than 100 m below the level of the old watercourse [4].

The area is characterized by a number of bauxite deposits of different geological age found at the base of the upper Triassic clastic sediments, Palaeocene and Eocene deposits. The most common soils are *terra rossa*, residual red soil formed over limestone substrate in the Mediterranean climate conditions [1], sandy soils and soils with high content of limestone debris.

2.3. Hydrological characteristics

The hydrogeological and hydrological characteristics of the study area are the result of extremely complex lithology, tectonic structures, climate and geomorphological evolution [2].

Namely, the catchement area of the Zrmanja River is mostly composed of fractured and karstified carbonate rocks [4]. Because of intensive tectonic dynamics in this area, these rocks are karstified to a high extent. It is assumed that the depth of karstification reaches up to 1000 m. Thus, in the Zrmanja River catchment, there are practically no real barriers for the karst groundwater.

The canyon of the Zrmanja River was cut toward the former erosional base during periods of lower sea level, partly passing through the former karstic *polje, i.e.* today´s Novigrad Sea. By the onset of the rapid late Pleistocene-Holocene transgression, both karstic forms, i.e. the river canyon and the *poljes* (including the present Karin Sea) were submerged, but still recognizable as typical drowned karstic landscapes [52].

Today, surface watercourses created between Velebit Mt. and Bukovica Mt. fill the Zrmanja River basin, including its short, but rich tributaries, Krupa with Krnjeza and Dobarnica. At the spring, the mean discharge of the Zrmanja is 5.20 m^3 s^{-1}, while in the lower part, near Jankovića Buk (upstream from Obrovac), it can reach 40.0 m^3 s^{-1}, which is conditioned by tributary Krupa and numerous springs [29].

In general, the Zrmanja's catchment basin is characterized by a complex water circulation pattern [3], a typical feature of karstic watershed areas. In addition to the mentioned watercourses, there are numerous permanent and temporary springs connected with sinkholes ('ponors') in the hinterland, as well as the underwater springs discharging water directly into the estuary, especially during rainy periods [3].

3. The Zrmanja River and its estuary

3.1. Hydrogeological setting

Downstream from the Jankovića Buk, i.e. the last 14 km, the Zrmanja River has properties of an estuary. The estuary is formed by the inflow of the Zrmanja River into the Novigrad Sea (28.7 km^2), an enclosed basin connected in the north-western part to the Velebit Channel and in its south-eastern part to an even smaller basin, the Karin Sea (5.7 km^2) (Figure 4). Seawater flows in from the Velebit Channel near the bottom [40] progressing upstream along the Zrmanja River and to the Karin Sea, with the simultaneous out-flow of fresh surface water carried by the Zrmanja River and to a lesser extent by Karišnica River [23, 71, 72] into the Velebit Channel. The estuary of the Zrmanja River is a highly stratified system with a sharp halocline separating the brackish and the marine layers [40, 71].

In general, the estuary can be divided into three parts: the upper part (downstream from the Jankovića Buk waterfall to the Novigrad Sea), the middle part (the Novigrad and Karin Seas) and the lower part (the strait connecting the Novigrad Sea and the Velebit Channel) [72].

Figure 4 - The Zrmanja River estuary with indicated locations of the Obrovac and the Jankovića Buk waterfall.

As a result of its location in the semi-enclosed Novigrad Sea, the Zrmanja River estuary is under minor influence of waves and currents [37] and can be defined as a microtidal estuary.

The average depth in the central part of the Novigrad Sea and the Karin Sea is about 28 m and 12 m, respectively, while depths greater than 30 m occur just in front the strait connecting the Novigrad Sea and the Velebit Channel (Figure 5).

In relation to the total volume of the Novigrad Sea (511.5 x 106 m^3), the Zrmanja River brings annually, on the average, 2 to 3 times more water (1167 x 106 m^3) [29] strongly influencing physico-chemical and biological [6] as well as hydrogeological properties [29] of the estuary. Due to high river inflow, stratification is maintained in the estuary for most of the year [6]. In winter, at a discharge of 30 m^3, flushing period of the brackish layer in the upper estuary is estimated to 1–2 days [47]. In summer, the reduced riverine flow leads to higher salinity and a longer water residence time of 8.6 days [47]. For comparison, under typical winter conditions, the residence times of the brackish and marine layers in the Krka River estuary are 6–12 and 15–45 days, respectively [41].

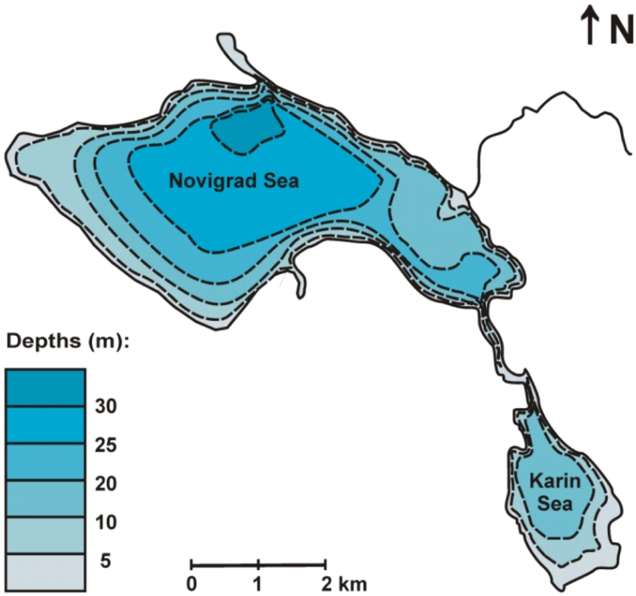

Figure 5 - Bathymetric map of the study area (from Fiket et al. [26], according to map section MK 12 Novigrad sea - Zadar Channel, scale 1: 100000, the Hydrographic Institute, Croatia).

The Karin Sea is influenced by several watercourses, of which the largest are rivers Karišnica and Bijela. These rivers are characterized by their overall short length (8.0 km and 6.7 km, respectively) and occasional strong torrential flows. The inflow of fresh water into the Karin Sea results in the formation of brackish lagoon whose salinity varies throughout the year, depending on the rainfall.

3.2. Physico-chemical properties

Table 1 summarizes the physico-chemical properties of the water of the Zrmanja River and its estuary. The water of the Zrmanja River is characterized by high transparency (6.7 m on average) and oxygen saturation (98.8% on average) [6], while according to its chemical composition, it belongs to typical calcium-bicarbonate karstic water [62].

Table 1. Physico-chemical parameters for the Zrmanja River estuary [6, 23].

Parameter	Zrmanja River estuary		
Temperature (°C) [6]	15.9		
Oxygen (%)[6]	98.8		
Transparency (m) [6]	6.7		
	Upper estuary	**Middle estuary**	**Lower estuary**
Salinity (surface water) [23]	2 – 3	2 – 14	17
Salinity (benthic water) [23]	25 - 36	34 - 38	38

Given that the Zrmanja River estuary is a highly stratified estuary, vertical distribution of salinity corresponds to the position of two water masses, with freshwater on the top and seawater in the bottom. This is reflected in low salinity values in the upper, surface layer, ranging from 2 in the river part to 17 in the Novigrad Sea, and high salinity values in the bottom layer, ranging from 20 to 38 [23]. The distribution of salinity between the surface and the bottom layers mirrors the surface discharge of fresh water from the Zrmanja River into the Novigrad Sea and further to the Velebit Channel, and inflow of seawater from the Velebit Channel into the Zrmanja River and the Novigrad Sea in deeper parts. The location of the salt wedge varies with the season and flow conditions, reaching the Jankovića Buk in the summer months [73]. In winter, under conditions of higher water level and flows greater than 50 $m^3 s^{-1}$, the head of the estuary moves for about two kilometres downstream of the Jankovića Buk and the upper part of the estuary functions as a river [72].

The strong influence of the Zrmanja River on the whole area of the Novigrad Sea, including the southern part of the Velebit Channel is evident. However, in addition to the freshwater inflow by Zrmanja, the Novigrad Sea-Karin Sea system receives freshwater through the inflow of Karišnica, in the sourthern part of the Karin Sea, and through the influence of small, temporary creeks depending on the rainfall regime.

3.3. Biological charateristics

The Balkan Peninsula is recognized as one of the most important biodiversity hotspots worldwide and the area of the Zrmanja River does not make an exception. It is a nursery ground and habitat of various fish populations [57, 60, 61]. Distribution of phytoplankton, extensively studied by several groups of authors [5-8, 72], was found to be mainly composed of marine diatoms, dino-flagellates, cryptophytes, green flagellates, and cocco-lithophorids. Stable conditions, in terms of salinity fluctuation in the middle and lower estuary, have provided a suitable setting for development of micro-phytoplanktonic diatoms, whereas unstable conditions (i.e. frequent salinity variations) at the head of the estuary have favored nanophytoplankton. According to Burić et al. [6], salinity, temperature, and river inflow are the main factors that govern the phytoplankton development and distribution, while nutrients, on the other hand, strongly limit phytoplankton growth to the summer period when the river discharge is at its minimum.

Also, Burić et al. [7] reported the occurences of the centric diatom *Cyclotella choctawhatcheeana*, found for the first time in the Adriatic Sea. This diatom was found to generally develop dense populations in this highly stratified, oligotrophic, karstic estuary.

In addition to abovementioned species, the Zrmanja River estuary is a habitat of several endemic species. Žganec et al. [75] studied the distribution, habitats and conservation status of two endemic amphipods, *Echinogammarus acarinatus* and *Fontogammarus dalmatinus* in the Dinaric karst rivers, including the Zrmanja River. The occurence of two subspecies of F. Dalmatinus (*F. dalmatinus dalmatinus* and *F. dalmatinus krkensis*) in both the Zrmanja River and the Krka River is yet another confirmation of the connection between these rivers.

Based on the prevailing marine phytoplankton species, the Novigrad Sea was classified in the highest category of natural eutrofic areas of the eastern Adriatic [9, 57], under slight anthropogenic influence [70, 72]. Within the Strategy and Action Plan for protection of biological and landscape diversity of the Republic of Croatia [68], the Zrmanja River estuary was proclaimed as protected area, under the category of a nature park.

4. Anthropogenic influence

In demographic sense, the natural characteristics of this area, including the relief, geological composition of the terrain, climate, hydrology, and the soil composition, are rather unfavorable. Where these are added to poor traffic connections, it is evident that the demographic and economic development is quite restricted. For centuries, the population there had been oriented to agriculture, mainly to stock breeding (goats and sheep), but during 1970's the agricultural production started slowly decreasing and the population was forced to emigrate and settle in more prosperous parts of the country.

According to the census taken in 1991, the Municipality of Obrovac had 11,557 inhabitants, while according to the first census taken in 1857 there had been 8,070 inhabitants there, which means a 43.2% increase in 134 years. On the other hand, comparing the situation before and after the war (i.e. 1991 and 2001), the 57.5% decrease reflects the impact of the war on demographic situation.

Nowadays, the majority of the population in this area (around 4,500 inhabitants) lives in the Obrovac region (Figure 4), the largest town by the Zrmanja River. The population is primarily employed in the tourism and travel industry, in services and manufacturing industry, while only 4% of the population are engaged in agriculture, forestry and fisheries [64]. Mariculture activities primarily include shellfish farming in the area of the Novigrad Sea, using the traditional farming technology of floating parks [45].

Although the wider area is poorly populated, the recognized anthropogenic pressures include the decommissioned alumina factory Jadral [24, 38, 58] and the reversible hydroelectric power plant Velebit [4, 24].

The ex-alumina factory Jadral is situated on the right bank of the river canyon, about 8 km upstream from the mouth of the Zrmanja River into the Novigrad Sea (Figure 6). Despite the fact that the plant was in operation from 1978 to 1981, due to its unprofitable production and lack of own resources it left behind large amounts of alkaline sludge (650,000 m^3) and red mud (850,000 m^3) enriched with metals [38]. The remediation of residues and removal of the factory had started in 2006 and during the field study in 2010 it was not yet completed. Due to the weather conditions in the study area, dominated by strong bora wind [21], the particles transpored from the vicinity of the former alumina plant over the surrounding area have created a vegetation barren landscape. The study by Fiket et al. [24] confirmed the transfer of particles from the immediate vicinity of the former alumina factory to the surrounding environment and their influence on the estuarine sediment geochemistry.

Figure 6 – A detailed view of the Zrmanja River with indicated locations of the ex-alumina factory Jadral and the hydroelectric power plant Velebit.

Further upstream the river, there is situated the reversible hydroelectric power plant Velebit (RHEPP Velebit) (Figure 6). It was under construction from 1978 to 1984, and since 1985 has been in regular service. The RHEPP Velebit instantaneously and drastically changed the complex natural dynamics of the Zrmanja River hydrology [3]. The hydrological regime of the Zrmanja River became highly variable, due to water losses along the open streamflow [3]. Bonacci and Roje-Bonacci [4] have studied the changes in the hydrological regime along the Zrmanja River caused by the RHEPP Velebit. According to data reported by these authors, the decrease in the mean annual discharges along the Zrmanja River can be mainly related to the operation of the RHEPP Velebit, while climatological changes have only a slight effect on observed trends. Namely, a small decrease in the mean annual discharges (in %) at the Jankovića Buk station was associated with a natural decrease in precipitation and an increase in the air temperature. Their data also show that the introduction of the RHEPP Velebit into the environment has not changed the maximum annual discharges [4].

Although the average water discharge rates do not indicate any significant differences, the operation of the RHEPP Velebit has changed the sedimenation pattern of the river/estuarine sediments [26]. Namely, changes in the water regime have caused the deposition of finer sediment fractions further downstream as compared to the periods preceding the construction of the plant.

Undisputably, both the former alumina plant Jadral and the Velebit hydroelectric power plant have affected the Zrmanja River estuary, the former having localy affected the sediment gechemistry, while the latter has influenced both the hydrogeological and sedimentological features of the estuary. In addition to these anthropogenic pressures, the Novigrad Sea is also the area of shellfish production [45]. Farming includes Mediterranean mussel (*Mytilus galoprovincialis*) and European flat oyster (*Ostrea edulis*), using traditional farming technology of floating parks. Other production areas on the Croatian coast include the ones on the western coast of Istria, at the Krka River mouth, and in the Bay of Mali Ston and Malo more. The production is based on the gathering of wild fry and by 2015 it reached about 750 tonnes of mussels and about 50 tonnes of oysters. Specific issues related to aquaculture in terms of environmental protection are regulated by different specific laws and regulations, and all these areas, including the Novigrad Sea, are under constant supervision in terms of water quality monitoring.

5. Geochemical and mineralogical features of the Zrmanja River estuary

5.1. Water geochemistry

Only until recently, the composition of the Zrmanja water was very scarcley investigated. As mentioned before, the calcium-bicarbonate water of the Zrmanja River [62] is a typical water of the karst area. Fiket et al. [23] studied the multielement composition of the surface and bottom waters of the Zrmanja River in its estuary section. According to their study, which encompassed 26 trace elements, the composition of water in the estuary of the Zrmanja River is primarily determined by natural factors. The levels of dissolved concentrations of trace elements in river water primarily reflect the geological and hydrogeological characteristics of the catchment area, while the distribution of concentrations of elements along the water column in this highly stratified estuary primarily reflects different water masses, the river on the surface and the seawater at the bottom. Concentrations of most elements in the water of the Zrmanja River are relatively low and they feature unpolluted water [23].

Table 2 shows the comparison of the mean element concentrations in the surface layer of the Zrmanja River with an average element concentrations reported for world's largest rivers [28] and some typical carbonate waters [18, 53, 67].

The levels of trace elements in the Zrmanja River reported by Fiket et al. [23] are 2 -25 times lower than the average values for world rivers, with manganese concentrations up to two orders of magnitude lower than those reported by Gaillard et al. [28]. There were only levels of Mo, U and V found to be comparable to the average concentration of these elements in world's rivers. The only element found in the Zrmanja River water in the concentrations higher than those reported for world's rivers was lithium, present in the Zrmanja River water in levels up to three times higher than the average global river concentration [28].

Table 2. Comparison of mean element concentrations in the surface layer of the Zrmanja River with literature values, expressed in µg L-1.

Element	Zrmanja River[23]	World rivers[28]	Baikal Lake[67]	Groundwater[53]	Plitvice Lakes[18]
Al	1.28	32	0.52	-	0.731
As	0.203	0.62	0.41	0.20	0.110
Ba	14.5	23	10.3	5.2	4.59
Co	0.011	0.148	0.034	0.11	0.006
Cr	0.217	0.7	0.048	-	0.115
Cs	0.010	0.011	-	0.003	-
Cu	0.063	1.48	0.87	0.19	0.107
Fe	8.23	66	-	-	0.988
Li	5.65	1.84	1.93	0.94	0.068
Mn	0.168	34	0.14	-	0.186
Mo	0.528	0.420	1.28	0.16	0.301
Ni	0.054	0.810	0.57	-	0.196
Rb	4.02	1.63	0.47	0.31	-
Sr	320	60	104	197	39.2
U	0.442	0.372	0.50	0.37	0.556
V	0.616	0.71	0.44	-	0.873

On the other hand, element concentrations reported for the Zrmanja River water are similar to those from other carbonate waters worldwide; the ultra-fresh, hydrocarbonate and calcium water with a low content of total dissolved solids (<100 mg L^{-1}) of the Baikal Lake [67], the pristine karstic freshwater from the Plitvice Lakes [18] and the groundwater draining carbonate bedrock [28] (Table 2). Only exceptions are tipical lithogenic elements, Al, Fe, Li, Rb and Sr, whose concentrations in the water of the Zrmanja River estuary are higher in comparison to values reported for abovementioned carbonate waters. The latter was attributed to the hydrogeological background of the drainage system characterized by numerous tributaries and underground streams along the whole river flow, as well as the occurrences of bauxite deposits in the downstream region and the predominance of red soil, both of which contain higher concentrations of these elements [23].

Nonetheless, the overall distribution of elements in the Zrmanja River estuary is comparable with the one reported for the neighboring Krka River Estuary [11], not only with respect to the stratification, but also to an overall low level of metal input by the river.

5.2. Sediment mineralogy and grain size distribution

The Zrmanja River estuary sediments consist mainly of carbonates and quartz with minor amounts of clay minerals and both Fe-Al-oxides and –hydroxides [26]. Calcite, dolomite and aragonite predominate in the upper estuary, whereas calcite and aragonite prevail in the middle estuary sediments. Despite its predominance, the carbonate content of the estuarine sediments is, on the average, lower compared to an average value reported for the eastern Adriatic Sea bottom sediments (61%; [51]). Namely, only in the upper part of the estuary, i.e. the river part, the carbonate content (ranging from 39% to 64%, [24]) is similar to values reported by Pikelj et al. [51] for the Adriatic Sea sediments. In the middle part of the estuary, on the other hand, carbonate share in the sediments is much lower, amounting to 20% and 32% in the Novigrad Sea and the Karin Sea sediments, respectively. The presence of relatively abundant carbonate minerals, calcite, Mg-rich calcite, dolomite and aragonite, points to combined influence of geological substrate and biological production on the estuarine sediment composition. Namely, the presence of both dolomite and calcite is related to the karst setting underlained by Mesozoic and Palaeogene carbonates, whereas the presence of Mg-rich calcite and aragonite in estuarine sediments is of biological origin, similar as in the rest of the Adriatic Sea [51].

A grain size distribution of sediments follows the changes in the mineral composition. Looking from the upper part towards the middle part of the estuary, the sediment granulometry shows changes from very fine sand and medium silt to fine silt and clay. Accordingly, sediments of both the Novigrad Sea and the Karin Sea contain rather high shares of clay fraction, with an average of 16%. Although the drainage area of the Zrmanja River is a typical karst landscape [55], the lower part of the Zrmanja River estuary is surrounded by Eocene deposits (Figure 3), including flysch [32]. The higher content of clay fraction in the middle estuary is, therefore, the result of an additional input of terrigenous material through Karišnica River and small streams [24].

The prevalence of easily soluble carbonate rocks in the drainage area [55] is generally responsible for very low sedimentation rates in karstic rivers [51, 65]. Specifically, in typical karstic rivers of the Dinaric region, only approximately 20% of the river-borne material is suspended and the rest is dissolved [47]. The river and the sea bottom of eastern part of the Adriatic thus remain only partly covered with sediment compared to its western part, which is characterised by intensive filling with suspended material carried by river Po and other Apennine rivers [39]. The same applies for the Zrmanja River estuary. The coarse sediment carried by the Zrmanja River is mostly deposited directly at the river mouth, and a lesser amount of materials in suspension is carried away further on to be deposited in deeper parts of the Novigrad Sea. Given an additional input of terrigenous material by the small Karišnica River and ephemeral creeks in the southern and western part of the drainage area, the Novigrad Sea as well as the Karin Sea contain higher shares of clay fraction [26] than expected, but still low enough to prevent intensive filling of these karstic forms.

Sedimentation rates for the middle and lower part of the Zrmanja River estuary, calculated based on the ^{137}Cs activities in sediments, amount to 8 mm a^{-1} and 4 mm a^{-1}, respectively [26]. Such a difference in sedimentation rates between the middle and the lower part of the estuary reflects not only the predominant deposition of fine-grained materials in this confined and hydrodynamically subdued sedimentary environment [40] but also the reduced possibility of its removal from the system due to the limited communication with the open sea [24, 40, 72].

5.3. Sediment geochemistry

Element levels in sediments of the Zrmanja River estuary correspond to element concentrations reported for sediments of the Adriatic Sea [14, 39, 46], the Plitvice Lakes [18], the nearby Krka River estuary [13] and the mean value of element concentrations in sediments of European rivers [56] (Table 3). Only a few geogenic elements (Al, Cr, Li, Ni and Rb) are present in the middle part of the estuary at slightly higher levels than the maximum values reported by abovementioned authors [13, 18, 20, 39, 46], as a direct consequence of higher shares of clay fractions there. When compared to sediments of the port of Rijeka (Istria, Croatia), which are reported to be moderately to heavily contaminated with Ag and moderately contaminated with Cu, Zn, Mo and Sn [14], the Zrmanja River sediments contain two to ten times lower levels of these metals (Table 3). Moreover, sediments of the Zrmanja River estuary contain element concentrations below the values of Effects range low (ERL) and Effects range medium (ERM) of the quality guidelines for marine and estuarine sediments reported (for Ag, As, Cd, Cr, Cu, Ni and Pb) by Long et al. [42] indicating a low level contamination of the Zrmanja River estuary.

*Table 3. Comparison of element concentrations in sediments of the Zrmanja river estuary with literature values, expressed in mg kg^{-1} or *%.*

Element	Zrmanja River estuary[23]			Krka River [13]	European river [56]	Plitvice Lakes [18]	Adriatic Sea				
	Karin Sea	Novigrad Sea	Zrmanja River				Average [46]	Rovanjska [46]	Northern and central part [39]	Open sea [39]	Rijeka harbour [14]
***Al**	3.1	5.2	2.1	2.2-4.6	-	1.02	-	-	-	2.27-5.58	1.77
***Ca**	17.9	7.99	17.7	13.8-30.2	1.67	-	22.2	13.9	11.6	9.02-19.2	8.86
***Fe**	1.62	2.68	1.06	1.61-2.82	2.5	0.75	0.9	0.873	2.38	1.66-3.16	2.74
***K**	0.91	1.51	0.78	0.92-1.95	1.67	0.15	0.6	0.67	1.49	0.74-1.84	0.4
***Mg**	10.6	16.7	5.66	2.8-11.0	6	-	19.7	11	7.3	1.49-3.24	1.4
***Na**	0.67	1.6	0.77	-	-	-	-	-	-	-	1.03
Ag	0.288	0.349	0.18	-	-	-	-	-	-	0.5-1.3	1.07
As	10.6	16.7	5.66	2.8-11.0	6	3.14	19.7	11	7.3	1-32	21.4
Ba	97.5	185.8	98.7	-	-	41.5	-	-	-	117-231	86.3
Be	1.29	1.81	0.693	-	-	-	-	-	-	1-2.3	0.92
Bi	0.199	0.309	0.134	-	-	-	-	-	-	-	0.46
Cd	0.413	0.324	0.392	-	-	1.36	-	-	-	-	1.07
Co	6.36	9.86	4.55	7.6-10.2	-	3.6	-	-	-	10-23	12.9
Cr	66.9	98.2	34.4	44.1-70.7	63	19.6	57.3	< 60.3	85.8	39-165	71.6
Cs	4.47	7.32	2.84	-	-	-	-	-	-	-	1.77
Cu	13.4	18.4	6.11	-	-	8.99	-	-	-	9.8-32.7	145
Li	45.7	61.4	26.8	-	-	9.07	-	-	-	-	38.9
Mn	248	351	170	227-539	612	205	130	139	542	-	343
Mo	1.59	2.27	0.64	-	-	0.58	-	-	-	-	3.53
Ni	31.2	45.4	12.2	26.2-42.9	21	17.4	23.8	9.9	37.9	60-173	86.1
Pb	19.5	33.8	18	0.10-21.8	20.5	24.3	52.7	16.5	29.7	7-14	227
Rb	59.5	96.4	39.7	37.3-94.6	70	-	34.3	35.3		-	31.3
Sb	0.692	0.885	0.401	-	-	-	-	-	-	-	1.62
Sn	1.82	2.94	1.56	-	-	-	-	-	-	-	6.66
Sr	247	226	136	-	-	57.3	-	-	-	-	213
Ti	2054	3248	1540	1900-3100	3745	-	995	1746	2397	1100-2500	-
Tl	0.574	0.785	0.357	-	-	0.32	-	-	-	-	0.39
U	2.09	2.62	1.57	-	-	1.45	-	-	-	1.2-3.7	2.61
V	70.7	97	37.1	-	-	26.6	-	-	-	50-116	72.4
Zn	74.7	112	76.6	81.9-297	20.5	44.8	206	73.6	29.7	38-95	369
Y	9.86	13.1	10.2								11.3
****REE**	73.2	147	80.1								58.3

***REE – sum of concentrations of all rare earth elements (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu).*

Similarly as the water, the geochemistry of recent sediments of the Zrmanja River estuary reflects predominantly natural factors; the composition of bedrock, existing hydrodynamic conditions and the isolation of the studied basin. However, there is also a slight but indisputable imprint of anthropogenic activities in this area [24].

The spatial distribution of the majority of reported major and trace elements in the estuarine sediments [24] was linked to the grain size distribution in sediments, i.e. an increase in the share of fine-grained fraction in sediments going from the river part of the estuary towards the deeper parts of the basin (Figure 7). Even the variability in the element content of surface sediments in the upper estuary, i.e. the river part, was related to differences in granulometry between sampled locations [24]. Only for elements related to the input of carbonates of terrigenous and/or biogenic origin, i.e. Ca, Cd and Sr, Fiket et al. [24] reported somewhat different trends (Figure 7). Ranges of element concentrations found in sediments from different parts of the estuary are shown in Table 4 (summarized from Fiket et al. [24, 26]).

*Table 4. Ranges of element concentrations in sediments from different parts of the Zrmanja River estuary, expressed in mg kg^{-1} or *g kg^{-1} (from [24, 25].*

Element	Upper estuary	Middle estuary		Lower estuary
	Zrmanja River	Novigrad Sea	Karin Sea	Velebit Channel
Ag	0.023 - 0.305	0.103 - 0.519	0.088 - 0.464	0.462
***Al**	3.39 - 29.9	25.7 - 70.5	9.92 - 55.6	26.9
As	1.65 - 8.24	7.81 - 30.2	2.98 - 19.4	11.6
Be	0.062 - 1.21	1 - 2.77	0.149 - 2.26	0.777
***Ca**	86.8 - 319	51.8 - 82.1	120 - 380	190
Cd	0.274 - 0.461	0.212 - 0.345	0.351 - 0.411	0.208
Co	1.58 - 6.95	4.56 - 13.9	3.28 - 10	6.51
Cr	6.1 - 50.6	36.2 - 110	44 - 99.9	49.8
Cu	2.97 - 11.7	8.48 - 31.2	7.45 - 18.8	12.2
***Fe**	3.21 - 15	12.7 - 36.1	6.4 - 26.7	14.1
Li	4.04 - 39.1	32.6 - 87.3	12.1 - 75.1	35.2
Mn	111 - 405	155 - 1011	110 - 504	539
Ni	3.64 - 19.7	15.2 - 60.3	16.5 - 50.4	23.7
Sb	0.109 - 0.845	0.386 - 1.11	0.387 - 1.01	0.583
Sn	0.683 - 2.83	1.38 - 3.51	1.11 - 3.44	2.01
Sr	95.7 - 164	76.9 - 225	269 - 375	1119
Pb	2.5 - 33.6	17.6 - 42	10.9 - 28.2	20.8
Rb	6.07 - 56.7	48.4 - 138	17.2 - 104	48
Ti	232 - 2107	1638 - 4160	826 - 3308	1837
Y	5.68 - 13.2	6.9 - 19.1	5.41 - 18	11.4
***REE**	29.7 - 124	86.0 - 181	39.0 - 122	122

**REE – sum of concentrations of all rare earth elements (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu).*

However, when both the spatial and temporal distribution of major and trace elements in the sediments of the Zrmanja River estuary are taken into account, the anthropogenic influences on this system become noticeble [24]. The distribution of lithogenic elements clearly projects the changes in the downstream water regime of the Zrmanja River, caused by the construction of the RHEPP Velebit [24]. Distribution of other trace elements displays a strong similarity with lithogenic ones corroborating a relationship between the sources. However, a detailed analysis of trace element composition of estuary sediments along the sediment cores (20 – 50 cm length; [26]) revealed sporadic signatures of the ex-alumina factory Jadral. Namely, the impact of the Jadral factory was recognized at several locations in river sediments, based on the rare earth element (REE) signature. This was not surprising given that the red mud, i.e. waste generated by alumina production from bauxite through the Bayer process, contains about 900 ppm of rare earths on the average, i.e. up to ten times more than bauxites (<100 ppm to ~500 ppm ΣREE, [19]). Transfer of such particles from the former alumina factory to the Zrmanja River was recognized on the basis of the REE distribution in the Zrmanja River sediments [24, 25].

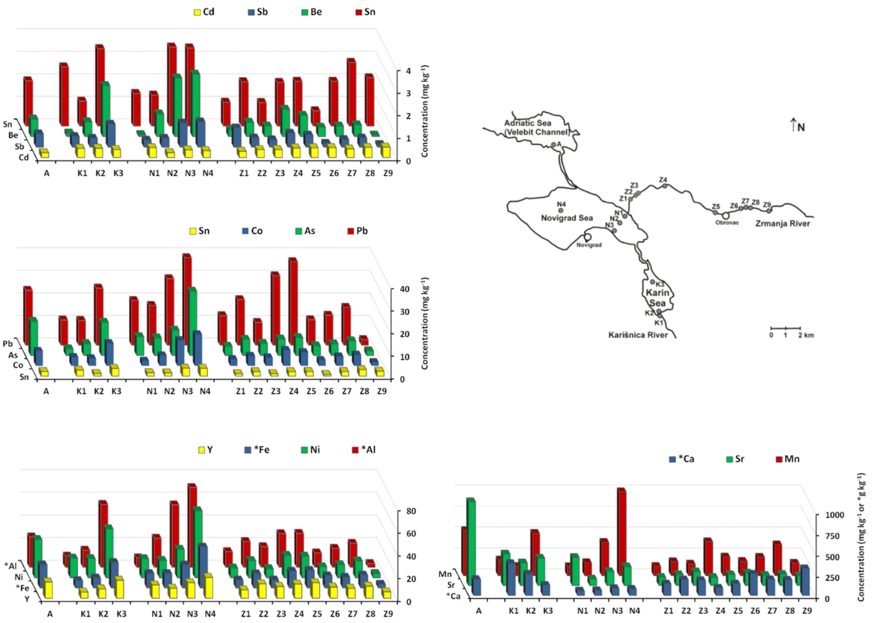

Figure 7 - Spatial distribution of major and trace elements in surface sediments of the Zrmanja River estuary*

5.4. Sediment porewater geochemistry

Based on the estimated fluxes, the Novigrad Sea and the Karin Sea sediments have different potentials as repositories of various trace elements [22]. Despite their small size, interconnection and the fact that they belong to the same estuary system, in one part sediments act as a source of certain elements, while in another they represent a permanent geochemical sink.

A higher content of organic matter along with greater isolation of the Karin Sea (Figure 7) and only periodical inflow of fresh water from the Karišnica River [26] are responsible for periodic occurences of oxygen deficiency at the sediment-water interface, thereby creating favourable conditions for element diffusion from the sediment back into the water column.

The observed differences in the sediment pore water geochemistry and the role of the sediments in terms of mass exchange at the sediment-water interface could not be solely attributed to the sediment characteristics and are considered to be influenced by the input of organic matter and local hydrogeological setting. Even in conditions of low terrigenous input and discharge of fresh water from the mainland, occurrences of oxygen deficiency at a local scale can create favourable conditions for element diffusion from the sediment back into the water column. Although the latter is designated as a local phenomenon [25], such events can have an impact on the entire system. Given that the Zrmanja River estuary falls into the category of indented coastline or estuary systems with limited circulation, it is necessary to consider the possibility of episodic occurrences of sediment anoxia when developing the strategy for the conservation of its water resources and maintenance of a healthy ecosystem.

6. Conclusion

The geochemical features of the Zrmanja River estuary are primarily governed by its geological setting (karstic catchment with flysch deposits in the lower part of the estuary), topography of the basin (general isolation of the basin, especially the Karin Sea), prevailing hydrogeological conditions (influence of the karstic Zrmanja River, the small Karišnica River, and ephemeral streams draining flysch deposits, combined with limited circulation of the basin with the open sea) and existing biological production.

Despite the predominance of natural influences on the estuary, the karstic background combined with the enclosed nature of the estuary and its limited water circulation makes this system an extremely sensitive one, whereas any increase in anthropogenic pressures (agricultural activities, tourism and associated intensive littoralisation) could induce and enhance various negative effects.

So far, conducted studies indicate only minor and locally restricted anthropogenic influence in the wider area of the Zrmanja River and its estuary [24]. However, the increasing number of highways and roads in the vicinity, the influence of nautical traffic, over-construction of the coast, influence of the waste water, etc., present realistic pressures that may affect the geo(bio)chemical balance of the Zrmanja River estuary in the future.

The comprehensive study conducted over the last ten years demonstrated the need for a multiparametric approach in determination of such pressures. Such an approach will provide timely recognition of potential threats to this vulnerable part of the Adriatic, as well as a proper response to avoid water devastation and, consequently, deterioration of the quality of living for people on its shores.

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