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MINERALOGY, SOURCES OF PARTICLES, AND SEDIMENTATION IN THE KRKA RIVER ESTUARY (CROATIA)

Mladen **JURAČIĆ** [1] and Esad **PROHIĆ** [2]

Key words: the Krka River, karst estuary, estuarine sedimentation, mineral assemblage, sedimentation rate.

In the frame of multidisciplinary investigations in the Krka River estuary, the mineralogy of recent sediments and sedimentation pattern in the estuary were analyzed. The data on mineral assemblages of recent sediments and of suspended matter from the Krka River estuary, are discussed in relation to the main sources of recent sediments.

The results on the mineralogical and chemical analyses along with the granulometric distribution of suspended matter and recent sediment samples indicate the restricted zone of prevalent sedimentation of terrigenous matter in the enlarged Prokljan Basin. The main source of terrigenous matter has been indicated in the Gudučа Creek, a right-hand tributary to the estuary. Nevertheless, the sedimentation rate in the estuary was found to be very low (due to scarcity of input). The other source of particles that deposit in the estuary are the carbonate biogenic remnants.

Ključne riječi: Rijeka Krka, krški estuarij, sedimentacija u estuariju, mineralni sastav, brzina sedimentacije.

U okviru višedisciplinarnog istraživanja u estuariju rijeke Krke određen je mineralni sastav recentnih sedimenata i način taloženja materijala u estuariju. Uspoređeni su mineralni sastav sedimenata i suspendirane tvari u estuariju rijeke Krke, te razmatrani utjecaji različitih izvora materijala.

Rezultati mineraloških i kemijskih analiza uz raspodjelu veličina čestica u suspendiranom materijalu i recentnim (površinskim) sedimentima ukazuju na taloženje pretežnog dijela terigenog materijala u proširenom dijelu estuarija (u Prokljanskom bazenu). Glavni izvor terigenih čestica je bujični potok Gudučа. Međutim, izmjerene brzine taloženja u estuariju su vrlo male zbog neznatnih količina materijala koji pristiže u estuarij. Drugi izvor čestica koje se talože u estuariju su ostaci karbonatnog biogenog materijala.

1. INTRODUCTION

In the frame of multidisciplinary investigations in the Krka River estuary (Center for Marine Research, Ruđer Bošković Institute, 1981-1991), mineralogy of recent sediments and sedimentation pattern in the estuary were found to be of prime interest. The distinction between terrigenous and autigenous sources of material that deposits within the estuary, has a significant role in predicting the behavior of anthropogenic input (PROHIĆ & JURAČIĆ, 1989). In this paper the data on granulometric distribution, on mineralogy of recent sediments and of suspended matter from the Krka River estuary are presented, and the main sources of recent sediments are discussed. In addition, the data for estimation of the sedimentation rate are reported.

1.1. TOPOGRAPHY, GEOLOGICAL BACKGROUND, AND MORPHOGENESIS

The Krka River estuary (figure 1) is located in the Outer Dinaric karst region, in the North Dalmatian erosional plane (ROGLIĆ, 1957). The hydrogeologic drainage area is of approximately 2427 km (STEPINAC, 1976).

The main lithologic units in the drainage area are the Jurassic, Upper Cretaceous and Eocene limestones. Subordinate quantities of clastic rocks and evaporite (gypsum) deposits (Permo-Triassic) are present in the upper part of the drainage area (springs zone).

In the catchment area of the small torrent-type Gudučа Creek (a right-hand tributary in the estuary) Upper

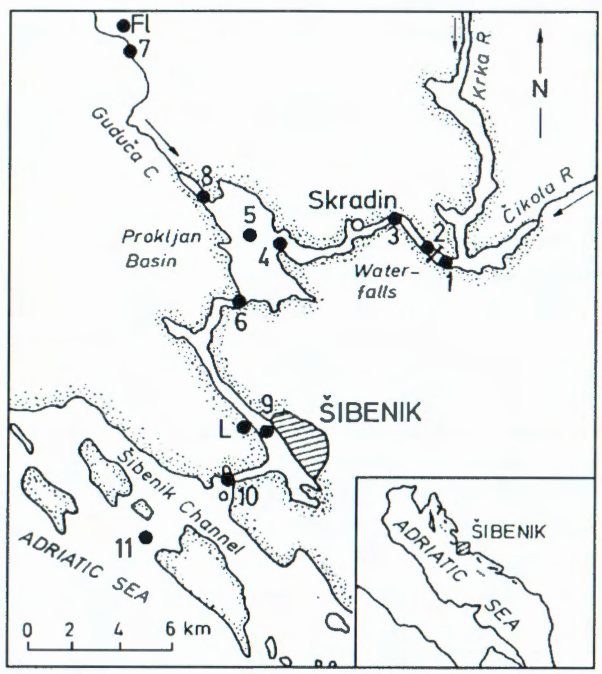

Fig. 1: The study area : the Krka River estuary with sampling stations.

Slika 1: Područje istraživanja: Estuarij rijeke Krke s lokacijama uzorkovanja.

Eocene-Oligocene “Promina Formation” flysch and flysch-like deposits dominate. These consist mainly of marls and silts, together with some carbonate rocks (PROHIĆ, 1984).

During glacial times (Upper Pleistocen - Würm 3, 40,000 to 17,000 years BP) the Krka River and its tributaries (Čikola, Gudučа) cut their canyons (down-

[1] Department of Geology, Faculty of Science, University of Zagreb, Kralja Zvonimira 8, 41000 ZAGREB, Croatia
[2] Institute of Geology, Sachsova 2, 41000 ZAGREB, Croatia

stream of the town of Knin) into the erosional plane (JURAČIĆ, 1987).

Recent morphology and the formation of the estuary had been the consequence of climatic changes since Upper Pleistocene, which caused substantial sealevel changes. The fast erosion during Würm glaciation has been assumed, due to humid climate with large quantities of snow and short summer periods when most of this snow went as a run-off. At the maximum glaciation (25,000 yBP) the sea level is assumed to be 96,4 m below the present level. The canyon morphology of the paleo-Krka can be traced down to the 100 m isobate between Zlarin Island and mainland.

In the postglacial period erosional power of the Krka River was lowered and at 8,500 - 8,000 yBP climates became favorable for calc-tufa formation (ŠEGOTA, 1968). In this period ten calc-tufa barriers have been formed in the Krka River valley. Moreover, the morphology of four dead calc-tufa barriers are visible in the drowned part of the river valley between Skradinski Buk waterfalls and the Prokljan Basin (ROGLIĆ, 1967).

The Krka River has a composite valley. In the main part downstream of the town of Knin, the Krka River cuts the geologic structures, probably through predisponed faults. In the parts where rocks liable to mechanical weatherig are exposed, enlargements parallel to the geological structures are formed. In the estuary these are the Prokljan Basin and the Šibenik Port.

.2. EXPERIMENTAL

2.1. SAMPLING

Sediment samples from the bottom surface were collected at 11 stations in the Krka River estuary (figure 1) along transects Visovac - Prokljan and Gudača Creek - open sea (Zlarin). Sample 7 from Gudača Creek was sampled from the bank, whereas other samples were collected by Scuba-diving. At station 5- Prokljan a 24 cm core was taken, using a plastic corer of 7.8 cm diameter, whereas on other locations only the uppermost part of the sediment (0 - 4 cm) was sampled.

Large quantities of water (100 L) from the surface water layer (0.5 m) at stations 1-Visovac and 5-Prokljan were filtered in order to collect enough material for mineralogic analysis. All samples were frozen within 12 hours.

The samples of two different source rocks were collected in the drainage area; one of Upper Eocene flysch marl (F1), and the other of Lower Eocene limestone (L).

2.2. ANALYSIS

Semiquantitative mineralogic composition of bulk samples was performed using an X-ray diffractometer (Philips P.W. 1050/25) equipped with a proportional counter, using CuK - α radiation.

^{14}C activity of the biogenic carbonate fraction in the 5-Prokljan core was measured and gas proportional counter was used at Radiocarbon Laboratory, The Research School of Pacific Studies, The Australian National Univ. Canberra (Dr. John Head).

Corollary granulometric measurements of the investigated sed iments (originally reported by JURAČIĆ, 1987 and PROHIĆ & JURAČIĆ, 1989) were performed by the combination of standard sieves and Coulter Counter TA II measurements.

Carbonate content (Ca and Mg) on the bulk samples was determined by complexometric titration with EDTA.

The total organic matter was determined as a weight loss after the samples had been treated with 15% H_2O_2 and heated at 450°C for 6 h (BIŠĆAN et al. 1991).

3. RESULTS

3.1. GRANULOMETRY AND CARBONATE CONTENT OF INVESTIGATED SEDIMENTS

In table 1 the mean size, the share of fraction smaller than 32 µm, the carbonate and organic matter share in investigated samples, are reported.

Size distribution of suspended matter (measured by

Table-Tablica 1

Granulometry, carbonate and organic matter share in the Krka River estuarine sediments.
Granulometrija, udjel karbonata i organske tvari u sedimentima estuarija rijeke Krke.

Sample	Mean size µm	%<32µ %	carbonate %	org.matter %
Suspended matter (surface layer)				
1 Visovac	11	98,5	high*	moderate*
5 Prokljan	23	63,4	low*	high*
11 Zlarin	31	47,2	-	-
Surface sediments				
1 Visovac	39	60,6	75,7	5,0
2 Gospa od zdravlja	54	32,4	85,7	4,5
3 Skradin	29	59,6	79,8	7,0
4 Oštrica	7,7	92,4	59,6	-
5 Prokljan				
0 - 4 cm	7,0	93,2	56,7	4,8
4 - 8 cm	5,5	94,7	-	-
8-12 cm	6,6	93,9	-	-
12-16 cm	6,8	94,0	-	-
16-20 cm	6,9	93,4	-	-
20-24 cm	7,0	92,1	-	-
6 Vukinac	4,8	93,5	55,1	5,5
7 Gudača mud	15	72,9	64,1	5,3
8 Gudača Mouth	13	70,4	64,2	8,7
9 Martinska	140	29,1	70,8	4,0
10 Čapaljena	36	32,0	66,7	3,8
11 Zlarin	412	4,4	91,7	2,9

* Estimation from X-ray analysis data

Coulter Counter in original water samples) varies significantly. The coarsening of particles toward the sea, might be due to flocculation of fine-grained riverine suspended matter in brackish and sea water and/or due to higher share of coarse grained living organisms found in estuary and the open sea (phyto and zooplankton).

Granulometric distribution of sediments ranges substantially. The mean size ranges from 4.8 to 412 µm and sediment type from fine grained silt to coarse sand. All samples are poorly sorted as a consequence of prevalently bimodal distribution, one mode between 5 and 10 µm and the other over 100 µm. A bimodal granulometric distribution indicates different sources of deposited material. The large part of coarse fraction is of biogenic origin. The inspection of this fraction indicated the dominance of shell fragments and foraminiferal tests. In the fine-grained fraction (silt/clay) the noncarbonate fraction (quartz and aluminosilicates) becomes important. The share of the fine-grained fraction (<32 µm) varies from only 4.4% in the sand sample from the station 11-Zlarin to 94% in Prokljan Basin (4-Oštrica, 5-Prokljan, 6-Vukinac.

Granulometric distribution in the Prokljan core is very uniform.

The total carbonate content (EDTA) in analyzed recent sediments varies from 55.1% (in the Prokljan Basin) to 91,7 % (near Zlarin, off the estuary). Along the transect from the Visovac Lake to the Prokljan Basin the carbonate share diminishes, while from Prokljan towards the open sea one can observe the increase.

Organic mater share is relatively high in the investigated sediments compared with open Adriatic sediments, indicating relatively high productivity in the area and/or low oxidation rate of deposited organics.

3.2. MINERAL COMPOSITION

In table 2, semiquantitative mineral share in suspended matter, surface sediments, and two typical source rocks are presented.

One can observe a large mineralogic composition difference between suspended matter samples from the Visovac Lake/Krka River (prevalence of calcite, minor share of quartz, no detectable feldspar and illite and from the Prokljan Basin (prevalence of "terrigenous" minerals).

Only calcite was detected in the Eocene limestone (L), whereas in the flysch sample (F1) in the carbonate fraction also dolomite was detected. The noncarbonate fraction is dominated by quartz and montmorillonite.

In estuarine sediments, one can distinguish four characteristic groups of minerals:

1) carbonate minerals,
2) clay minerals,
3) other "terrigenous" minerals, and
4) others.

The mineralogic composition of the core (5-Prokljan) was rather uniform.

Table - Tablica 2

Mineral composition of estuarine suspended matter, surface sediments and source rocks [a].
Mineralni sastav suspendiranog materijala, površinskih sedimenata i izvorišnih stijena u estuariju.

sample	Calc.	Dol.	Arag.	Mg-cal.	Quartz	Felds.	Ill.	Klao.	Montm.	Pyrite	Hemat.
Suspended matter (surface layer)											
1 Visovac	+++	+	-	-	++	-	-	-	(+)	-	-
2 Prokljan	+	-	-	-	+++	++	+	(+)	(+)	-	-
Surface sediments											
1 Visovac	+++	(+)	-	-	++	+	+	(+)	(+)	-	-
2 Gospa od zdravlja	+++	(+)	-	-	++	+	+	(+)	-	(+)	-
3 Skradin	+++	-	(+)	-	+	-	-	-	-	-	-
4 Oštrica	+++	(+)	-	-	++	+	+	+	+	(+)	-
5 Prokljan	+++	(+)	-	-	++	+	+	+	-	(+)	(+)
6 Vukinac	+++	+	(+)	-	++	+	+	+	-	(+)	-
7 Guduča mud	+++	(+)	-	-	+++	++	+	+	+	-	(+)
8 Guduča Mouth	+++	(+)	-	-	++	+	+	+	+	-	(+)
9 Martinska	+++	+	+	(+)	++	(+)	(+)	(+)	(+)	-	+
10 Čapaljena	+++	+	+	+	+	-	(+)	(+)	-	(+)	(+)
11 Zlarin	+++	+	+	+	+	-	(+)	(+)	-	-	-
source rocks											
Flysch marl	+++	(+)	-	-	+++	++	++	+	++	-	-
Limestone E_{1-2}	+++	-	-	-	-	-	-	-	-	-	-

[a] Estimations from X-ray analysis data: +++ very abundant (>30%); ++ abundant (10-30%); + fairly abundant (5-10%); (+) detected (>2%); - not detected.

1) Carbonate minerals

Four carbonate minerals can be distinguished by means of X-ray diffraction analysis: calcite, dolomite, aragonite, and high-magnesian calcite.

Calcite is the major mineral in both sediments from the estuary and in the drainage area. According to chemical data its share varies from 50 to 90 % in estuarine sediments. Depth profile shows no change in calcite share. With respect to different granulometric fractions, calcite is present both in the finer and coarser frraction, but in the letter it is followed by other carbonate minerals. The mean size of estuarine sediments in the Prokljan Basin is between 5 and 30 µm, and only few percents of granulometric fraction pertain to the fraction above 32 µm. High share of calcite in flysch marl and Guduča Creek sediment indicate that large part of the calcite in the fine grained estuarine sediments is of detritial origin deriving from weathering of marl and carbonate rocks in the drainage area and/or from abrasion of steep estuarine banks. The other important sources of carbonate grains are shell and foraminifera fragments and remnants. The microscopic inspection of the coarse fraction (> 63 µm) in samples 9-Martinska and 11-Zlarin indicated dominance of foraminiferal tests (*Miliolidae, Planorbulinidae, Asterigerinidae, Taralidae*) together with fragments of crustacea, brachiopoda, gastropoda, briozoa, with spiculae and fragments of echinoidea (Miknić, personal communication).

One can not exclude the possibility that at least a part of the calcite, preferentially in the fine fraction, could be authigenic, meaning that it is of chemical origin deposited from highly saturated and warm marine water in the estuary (LEGOVIĆ et al., 1991a).

Dolomite share increases towards the open sea. It is not abundant in the fraction larger than 63 µm (more biogenic fraction). Dolomite is entirely of a detrital origin, because the authigenic origin can be hardly assumed in this environment.

Aragonite share increases with the larger sea influence, and it is almost completely present in the large granulometric fraction, indicating its biogenic origin. Aragonite forming organisms were already reported in the Adriatic Sea (PAUL,1970; OGORELEC et al., 1981).

High-magnesian calcite (9 and 12 molar % $MgCO_3$ in calcite), similar to aragonite, was only found in the lower (seaward) part of the estuary and in the diffraction pattern of the granulometric fraction larger than 63 µm. This fraction is preferentially of biogenic origin in the investigated area. Although the high-magnesian calcite could be anorganically precipitated in situ, the biogenic origin of high-magnesian calcite is more probable. High-magnesian calcite remnants were already reported in samples from the Northern Adriatic (OGORELEC et al., 1981; RANKE, 1976).

2) Clay minerals

In the X-ray diffractograms of investigated samples illite, montmorillonite, kaolinite and mixed-layer clays could be distinguished. A distribution of illite is rather uniform over all observed transects and profiles, while distribution of kaolinite shows seaward decreasing share. It could show the terrestrial origin of kaolinite, and fast sedimentation assuming differential flocculation (GIBBS, 1986; KRANCK, 1981).

A distribution of montmorillonite shows a similar pattern as kaolinite. Its most probable sources are the flysch-like sediments in the drainage area of the Guduča Creek. This assumption is suported with a high montmorillonite peak in the source flysch-marl sample. Mixed-layer clays were present in such small quantities that no conclusion could have been drawn.

3) Other"terrigenous"minerals

Quartz and feldspar belong to this group although some of the already described minerals are also partly or entirely of terrigenous origin.

A quartz share increases from Visovac Lake to Prokljan and decreases from Guduča Creek towards the sea.

A feldspar distribution follows the distribution of quartz indicating the same origin of these minerals in sediments.

4) Other minerals

Among other minerals, iron minerals (pyrite and hematite) and zeolite were detected.

Pyrite was detected in samples from the central

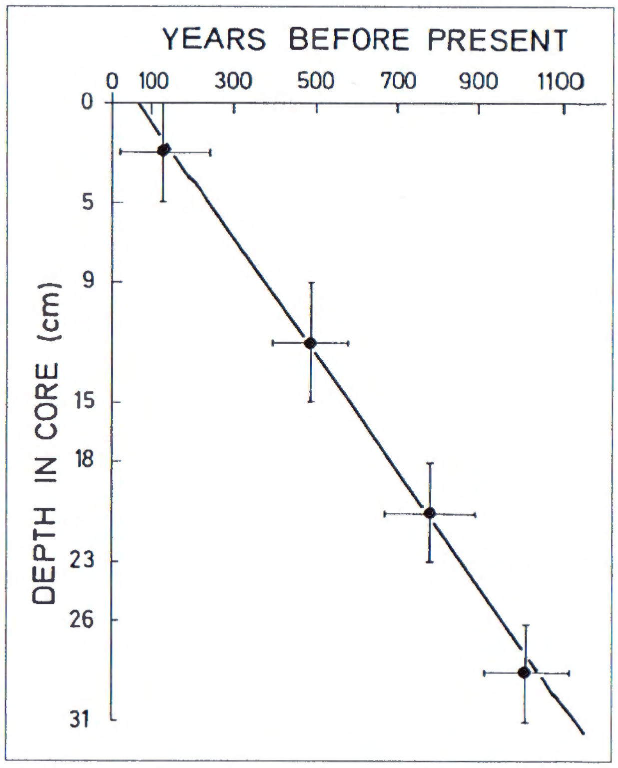

Fig. 2 : Age of biogenic carbonate material (> 63 µm) extracted from core 5 - Prokljan
vertical bar = measured core interval
horizontal bar = 1 s standard deviation
correlation coefficient, r = 0.99

Slika 2: Starost biogenog karbonatnog materijala (> 63µm) iz jezgre 5 - Prokljan
uspravna crta = debljina mjerenog uzorka
vodoravna crta = 1 s standardna devijacija
koeficijent korelacije, r = 0.99

part of the estuary (the Prokljan Basin) and not in the Gudučа Creek. This might indicate its authigenic origin within estuarine sediments (at least a part of it). In some locations (5, 10) both pyrite and hematite were found in the same sample (surface layer 0-4 cm) indicating either redox boundary within the sample, or the metastability of the one of iron minerals. The hematite share is generally low, but increases towards the sea. It is supposed to be of detritial origin, as insoluble remnant of carbonates weathering, or is derived directly from a terra rossa soil.

Traces of zeolite were also detected . They were most probably replacing some of calcite in shell fragments.

3.3. SEDIMENTATION RATE

^{14}C measurements of the biogenic fraction (larger than 63 μm) in the core 5-Prokljan indicate a sedimentation rate in the central part of the estuary of only 0.27 mm/year (figure 2). The good correlation $r = 0.99$ and the slope indicate no bioturbation in sediments.

4. DISCUSSION

The mineralogic composition, along with differences in the granulometric distribution, indicates two major sources of material that deposits in the Krka River estuary. One is weathering of carbonate and noncarbonate rocks in the drainage area, and abrasion of carbonate shores within the estuary, and the other is autigenous biogenic formation of carbonate particles and its subsequent sedimentation.

4.1. TERRIGENOUS SEDIMENTATION

Specific geology of the drainage area (prevalence of carbonate rocks), and the morphogenesis of the Krka River (ten natural calc-tufa barriers with lakes behind them), cause that the main river entering the estuary, the Krka River, brings small quantities of suspended terrigenous matter to the estuary. Also, the mineralogic difference of suspended matter samples between Visovac Lake/Krka River and Prokljan Basin, indicates different sources of particles in the Prokljan basin than the Krka River. Granulometric distribution pattern (mean size diminishment from Guduča Creek toward Prokljan) and the distribution of "terrigenous" minerals in recent sediments, along with the type of exposed rocks in the Guduča Creek catchment area (flysch sediments), and the absence of calc-tufa barriers along the water course, strongly indicate the Guduča Creek as the main supplier of the suspended terrigenous matter to the estuary. The Rivina Jaruga torrent (near Skradin) could also bring some of the terrigenous particles to the estuary. Nevertheless, these are relatively small quantities that prevalently deposit in the central enlarged part of the estuary, the Prokljan Basin, evidenced by quartz, kaolinite and montmorillonite distribution pattern. The reasons why terrigenous sedimetation is restricted to the Prokljan Basin are the following:

a) sheltered position with relative low energy of the environment due to low tidal range (up to 50 cm), and slow bottom currents due to the basin enlargment;
b) estuarine type circulation in highly stratified estuary (seawater bottom countercurrent bringing back particles that sink form the surface brackish layer);
c) physico-chemically and biologically induced flocculation of fine grained matter in the brackish waters in the surface layer in the Prokljan Basin (JURAČIĆ, 1987).

4.2. BIOGENIC SEDIMENTATION

In the lower part of the estuary and the open sea sedimentation of terrigenous particles is very low. There biogenic autigenous sedimentation becomes more important. The coarse carbonate fraction (encountered in the upper part of the estuary only in small fraction) dominates in the lower part of the estuary. It is prevalently of recent and subrecent biogenic origin (as indicated by presence of aragonite and Mg-calcite and by microscopic observations). The presence of dolomite and its seaward increase, indicates that a part of sediment could be of abrasive origin (limestone and dolomite grains) or that preholocene (Pleistocene) sediments are present on the bottom surface. These older sediments might be mixed by bioturbation with recent biogenic fragments.

4.3. REDOX CONDITIONS IN SEDIMENTS

The presence of pyrite in Prokljan Basin surface sediments, along with relative large share or organic matter in sediments, and indication of no bioturbation in ^{14}C profile of the Prokljan core suggests the presence of anoxic conditions in the surface sediment layer, and temporary in the bottom water layer in the Basin. Recent investigation revealed temporary anoxia in the water below 14 m in the Prokljan Basin (LEGOVIĆ et al., 1991b).

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MINERALNI SASTAV SEDIMENATA, IZVORI ČESTICA I SEDIMENTACIJA U ESTUARIJU RIJEKE KRKE

M. Juračić i E. Prohić

U okviru višedisciplinarnog istraživanja u estuariju rijeke Krke (Slika 1) određen je mineralni sastav recentnih sedimenata i način taloženja materijala u estuariju. Uspoređeni su mineralni sastav sedimenata i suspendirane tvari u estuariju rijeke Krke, te razmatrani utjecaji različitih izvora materijala. U tablici 1 navedeni su srednja veličina čestica, udjel frakcije manje od 32 μm, udjel karbonata i organske tvari u istraživanim uzorcima suspendiranog materijala i sedimentima, a u tablici 2 prikazan je semikvantitativni mineralni sastav uzoraka suspendiranog materijala, površinskih sedimenata i dvije tipične izvorišne stijene. U sedimentima estuarija određeni su kalcit, aragonit, visokomagnezijski kalcit i dolomit od karbonatnih minerala, ilit, montmorilonit, kaolinit i miješanoslojne gline od minerala glina, kremen i glinenci od ostalih terigenih minerala, te pirit, hematit i zeoliti od ostalih minerala. Na temelju određivanja apsolutne starosti biogenih ostataka u jezgri 5-Prokljan u središtu Prokljanskog bazena (slika 2) određena je brzina sedimentacije od svega 0,27 mm/godišnje.

Navedeni rezultati mineraloških i kemijskih analiza uz raspodjelu veličina čestica u suspendiranom materijalu i recentnim (površinskim) sedimentima ukazuju na taloženje pretežnog dijela terigenog materijala u proširenom dijelu estuarija (u Prokljanskom bazenu). To se može objasniti malom energijom okoline u Prokljanu zbog zaštićenosti i malih amplituda morskih mijena (do 50 cm), estuarijskim tipom cirkulacije vode (pridnena protustruja morske vode koja čestice nosi natrag prema rijeci), i fizikalno-kemijski i biološki uvjetovano mflokulacijom sitno-zrnatih terigenih čestica u boćatoj vodi u površinskom sloju u Prokljanu. Pretpostavljeni glavni izvor terigenih čestica je bujični potok Gudeča, a ne rijeka Krka. Međutim, izmjerene brzine taloženja u estuariju su vrlo male zbog neznatnih količina materijala koji pristiže u estuarij. Drugi značajni izvor čestica koje se talože u estuariju su ostaci karbonatnog biogenog materijala. Nalaz pirita i relativno veliki udjel organske tvari u površinskim sedimentima Prokljana, te nedostatak bioturbacije u sedimentima ukazuju na anoksične uvjete u površinskom sedimentu i povremeno u pridnenoj vodi u Prokljanu.