# Sediment Distribution and Trace Metals Contamination in the Neretva Channel (Croatia)

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### Abstract

The Neretva is the largest river of the eastern part of the Adriatic basin. Its catchment area is very broad and includes territories belonging to Bosnia, Herzegovina and, at the lowest reaches, Croazia. The river crosses areas exploited for agricultural, industrial and urban activities. Because of this, can become particularly severe given the location in karst area where erosion has already reached the geological base. The Neretva is characterized by a large amount of sediment that flows to the Adriatic sea into a narrow semi-enclosed basin, named Neretva Channel, located along the southernmost part of the Croatian coast. In order to contributeto the elevation of the distribution and the preservation potential of sedimentary deposits, the present study aims to trace the distribution of the Neretva River particle input toward the Adriatic Sea, in particular those associated to metal aggregates, and to follow their spatial vs. time distribution, using a suite of biogeochemical proxies like total and organic carbon, radiochemical data of $\delta^{13}$C and distribution of some metals.

## 1 Introduction

Coastal areas are the places where the peculiarities of land-sea transition systems emerge more clearly, in terms of chemical, physical and biological changes, and where most human pressure occurs. Particles, which accumulate in marine sediments, originate from a combination of river discharge, runoff of agricultural soils, roads and urban settlements plus atmospheric dry and wet deposition. In these areas, the sediment composition is mainly controlled by local geology, but can also reflect anthropogenic discharge from industrial and urban activities, thus enhancing concentrations of both organic matter and metals. [1].

Eastern Adriatic coast, from Croatia to Albania, is a typical transgressional environment formed during the Late Pleistocene-Holocene sea level rise by flooding of the pre-existing karstfied surface [2], and it is characterized by several small rivers that form large estuaries. One of the biggest is that of the Neretva River (mean annual water flow 296 $m^3s^{-1}$), which is characterised by an estuary-type delta with a relatively large reclaimed alluvial plain.

At present, Neretva Delta is threatened by different planned activities such as road construction, urbanization, and hunting that may cause the release of contaminants into the water [3]. Over 90% of the soil of the area is exposed to water and wind erosion of varying intensity. The situation may be particularly severe in the karst area, where erosion has already reached the geological base.

In this context, biogeochemical proxies,

such as concentrations of bulk sedimentary organic carbon (Corg), total nitrogen (N), and their stable isotope compositions ($\delta^{13}$C), may provide information on sources and fate of sedimentary organic matter in aquatic sediments [4, 5, 6, 7]. The $\delta^{13}$C and the N/C$_{org}$ (atomic) ratio characterize the origin (marine vs. terrestrial [8, 6] and the source of the organic materials. Although the C/N ratio has been more commonly used, the N/C ratio is the preferred parameter, since it behaves linearly in a mixing model [9, 10] and more reliably estimates the fraction of sedimentary organic carbon [11].
The present study aim to trace the spatial vs time distribution of the particle inputs from Neretva River, to contribute in evaluating the distribution and the preservation potential of some metals associated with particles in the Neretva Channel.

## 2 Study area

The Neretva is one of the largest river of the eastern part of the Adriatic basin. It flows into the sea in the southern part of the Croatian coast close to Ploče, through a wide Delta (surface 12,000 ha). The river flow to narrow triangular-shaped semi-closed basin, called Neretva channel, bordered by the Croatian Coast on the North-East and by the Peljesac Peninsula on the South-West, while it is open toward the Adriatic Sea on the North-West (Figure 1). The Delta has undergone extensive land-reclamation works, and its previously twelve branches, became three in modern age. Marshes several lakes and lagoons have disappeared and now the delta area suffers for the reduction of 90% of its surface due to irrigation, intense meteorological phenomena and increasing saline ingression that affect the life of animal and vegetal species of the area.
The river, 225 Km long, emerges in Zelengora mountain in eastern Bosnia and Herzegovina, through canyons, cliffs and hollows in its upper and middle reaches it forces its way through the Dinaric Alps to spread downstream of the village of Pocitelj in Herzegovina over a vast wetland valley and then finally flows into the Adriatic Sea.
Its upper part, called Hutovo Blato, is in Bosnia-Herzegovina. Here the river cuts several canyon in Jurassic limestone and dolomites carbonate platform sequence. Then, the valley along the last thirty kilometers of the Neretva River spreads abruptly into an alluvial fan named ”Neretvanske blatije” 20,000 ha wide, while in its lower reaches situated in the Republic of Croatia, the River branches creating a large delta. The riverbed is located on a very porous karst structure covered with sediment of low permeability.
The annual sediment discharge of the river is rather high (i.e., 3.6 tons in 2000), and can be considered similar to the sediment input of Po river (i.e., about 15.6 tons). The surficial currents, always oriented from SE to NW, are generally quite low (less than 10 cm$\cdot$s$^{-1}$) and become lightly stronger during winter season.

## 3 Materials and methods

Study area, sampling locations and batimetry are shown in Figure 1.
12 light box cores (subscript “BC”, Figure 1) and 9 grab samples (subscript “G”, Figure 1) were collected in May 2006 in order to sample both surficial and subsurficial sediments along tree SE-NW oriented transects. The BC short cores were radio-

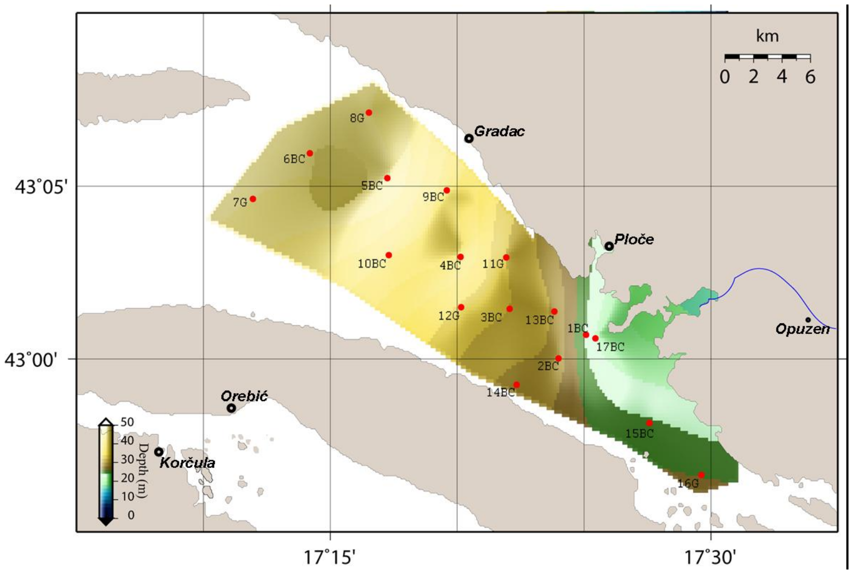

Figure 1: Study area and sampling location.

graphed and scanned for magnetic susceptibility. Then, the sediment was described for visual characteristics. Once the cores were opened, one half was stored as the historical archive and the other half was sub-sampled with a frequency of 2 centimeters for chemical and radiochemical analyses.

Before the analysis, sediments were dried at 60 °C in order to calculate their porosity according to Berner (1971), assuming a particle density of 2.5 $\mathrm{g{\cdot}cm^{-3}}$. $C_{org}$ and total carbon contents were determined using Fisons Elemental Analyser NA2000. In order to obtain organic carbon contents, the carbonate fraction was eliminated by pretreatment with 1.5 M HCl. Stable isotopic analyses of $C_{org}$ were carried out on the same samples by using a FINNIGAN Delta Plus mass spectrometer, that was directly coupled to the FISONS NA2000 EA (see details in [7]).

Grain size analysis were carried out by wet sieving after a pre-treatment with $H_2O_2$, to separate sand from the finer fraction. Silt and Clay fractions were determined with X-ray Sedigraph.

$^{137}$Cs was measured by non-destructive gamma spectrometry [12, 13] using coaxial intrinsic germanium detectors (Ortec HPGe GMX-20195P and GEM-20200). $^{210}$Pb was determined, by alpha counting its daughter $^{210}$Po, assuming secular equilibrium between the two isotopes [13, 14]. For metals analysis an aliquot of wet sediment was leached with $HNO_3$ and $H_2O_2$ (10:3) under reflux [15]. This procedure allows to determine a fraction of metal associated to the surface of sediment particles or dissolved in the interstitial water. Cr, Ni and Pb concentrations were determined by Furnace Atomic Absorption Spectrophotometers, and the results reported on a dry weight of sediment.

The surficial samples data were analyzed for a correlation check through the Pearson correlation coefficient [16]. The analyses were performed to evaluate the proportionality between variables. STATISTICA software packages were used for the statistical analysis.

The spatial distribution of parameter were built by the gridding interpolation, method usually utilized by geoscientists to produces maps (The Generic Mapping Tools-free software, [17, 18]). A mask grid with no data was matched on a map grid to limit the computing only at the study area. A Mercator projection was applied on the grid map with isotropy grid spacing of 0.1 minutes.

# 4 Results and discussion

The cores radiography showed no evident inner sedimentary structures, but many of the samples seem to be mixed by bioturbation. The sediment is composed principally by silty-clay and seems to be quite similar all over the study area (Figure 1), coarser grain size increase with the radial distance from the river mouth. A sandy fraction was recognized only at the NW sites (station 7G). The C/N, $\delta^{13}$C and Apparent Sediment Accumulation Rate (Figure 2a, 2b, 2d) showed similar areal distributions, very useful tools to trace the sediment sources and deposition patterns. Marine currents move particulate materials northward from the river mouth and, as expected, the sites close to the river inlet show a strong terrestrial input characterised by very low $\delta$13C values. On the contrary, at the farthest site, the marine input is strongly prevalent. The other stations show an increasing marine input moving northward, and the limit between marine and terrestrial sedimentation can be located around station 10BC. Hence, can assume that the particles are moved quickly by surficial currents but are released not so far from the river mouth and, in particular, in the area close to the coast.

However, its important to point out that our surficial sediment could represent a particular seasonal condition, and could be very different in other period. Moreover, the areal distribution of porosity (Figure 2c) shows a strange pattern with lower values close to the fluvial inlet, as expected, but also at the NW and NE of the coast in correspondence of the stations 9BC and 10BC. Together with the areal distribution of physical-chemical parameter, we tryed to investigate the spatial and temporal distribution in the area of some inorganic contaminant (Cr, Ni and Pb) associates to the particles. We choose Cr, Ni and Pb, because these metals may represent both anthropogenic and natural source. The metal concentration-depth profiles are related both to the characteristics of the inputs and to sedimentation mechanisms, and could be occasionally affected by bioturbation. These latter determine sediment accumulation as the net result of deposition and resuspension. Usually, anthropogenic metal peak values are found in correspondence of periods of maximum inputs of these contaminants. However, biological mixing may disturb the record and redistribute the settled particles, leading to more uniform concentration profiles.

Figure 3 shows concentration-years profiles of box cores sampled along the direction of main sediment deposition, where, date were calculated according to Apparent Sediment Accumulation Rate (as shown in Figure 2d). Actually, these profiles do not account for any clear variation of concentration with depth and present similar

| | Cr (µg/g d.w.) | Ni (µg/g d.w.) | Pb (µg/g d.w.) |
|---|---|---|---|
| Average surficial concentration | 56.3 | 58.2 | 25.0 |
| Minimum | 26.9 | 28.7 | 4.5 |
| Maximum | 84.0 | 86.8 | 67.9 |
| BG | 45.0 | 51.8 | 24.0 |
| WA | 100 | 40.0 | 10.0 |
| LCB * | 100 | 70.0 | 40.0 |
| LCL* | 360 | 75.0 | 70.0 |
| ERL** | 81.0 | 20.9 | 46.7 |
| ERM** | 370 | 51.6 | 218 |
| ISQGs** | 52.3 | 15.9 | 30.2 |
| PEL** | 160.0 | 42.8 | 112.2 |

Mean metal concentrations pre-seventies (BG); World Average (WA): Forstner and Wittman (1984); * Italian Sediment Quality benchmark: APAT & ICRAM 2007; ** International Sediment Quality Guidelines: Long et al., 1995; Long et al., 1998;Grimwood & Dixon., 1997.

Table 1: Averaged metal concentration in surficial sediments; minimum and maximum values in cores and international benchmarks.

trends for the three metals. Core chronologies, based on $^{137}$Cs and $^{210}$Pb data, show that box cores represent approximately the last 50 years, and identify along the direction of main particles deposition a light peak in the end of 90s in 4BC and 13BC. On the contrary, 1BC, 9BC and 5BC do not show any clear variation downcore could suggest an input of material not related to the river, but it is also possible that there was a disturb of the signal intensity in the others samples.

In any case, the similar trends showed by Cr, Ni and Pb in the cores may suggest that the variations are linked to the change of physical proprieties (i.e. porosity, grain size…) downcore. This might be related to the changes in river transport occurred in the last 10 years during the post-war reconstruction of the area. Moreover, the low range of variation in concentration with time may also highlight, on a shorter time scale, the influence of seasonal currents on a shallow basin that could reprocess, move and mix a large amount of sediment (N. Pinardi personal communication).

The Pearson correlation analysis (product-moment correlation r, [16]), applied on all data show a highly significant positive correlation ($p < 0.001$) between Cr and Ni,whereas highly significant negative correlations were observed between Cr and Ni with respect to both the total carbon and inorganic Carbon in turn, Pb did not show any significant correlation. On the other hand, sediment accumulation rates are significantly correlated with both $\delta^{13}$C and C/N ratio.

This analysis could point out that Pb is affected by different mechanisms of transport and deposition than Cr and Ni. In particular, the source of Cr and Ni has not to be ascribed to the river but it might be linked to the coastal runoff in South Dalmatia coast. In fact, Cr and Ni levels are in the ranges of concentration reported for the soil of South Dalmatia [19]. Moreover, the comparison of the Pearson correlation coefficient with the same parameter reported by other author [19] for the soil of the area at the Nord of the Neretva, shows a similar value (r = 0.73). Table 1 shows some preliminary result for metals concentrations in surficial sediment, with minimum and maximum values in cores. Some indications of potential contamination in present sediments may be obtained by comparing their concentration with preindustrial levels and with some internationally recognised concentration benchmarks. In particular, the surficial concentrations were compared with Sediment Quality Guidelines: Threshold Effect Level (TEL), Effect Range Low (ERL), Probable Effect Level (PEL), Effect Range Median (ERM) [20]. Moreover other benchmarks (Base Chemical Level, LCB and Limit Chemical Level, LCL) derived for Italian coastal areas with similar geochemical characteristic, were used [21]. All these guidelines are screening tools to predict potential sediment toxicity, linking sediment concentrations of contaminants to any adverse biological effect resulting from exposure to various chemicals. Pb and Cr levels in surficial samples usually do not reach either PEL or ERM thresholds as well as the Italian benchmarks, with some exceptions. However the effect incidence for these samples can be considered low (8-30% for Pb and 2.9-21.1% for Cr [20]). The Ni surficial concentration at all stations exceeded both PEL and ERM guidelines but not the Italian benchmark. This means that these elements could cause adverse biological effect, although their levels are similar to natural soil concentrations (mean 84 $\cdot g^{-1}$) in the area [19], and lower than the Italian benchmarks. In addition, the incidence of effect for exceeding ERM it is only 16.9 % [20] for Ni.

From a screening point of view, these results allow us to consider the Neretva Channel not contaminated by these three metals at time of sampling. On the other hand, a more reliable scenario is possible when the bottom sediment is reworked during winter season by storm or flood events and moved northward offshore along the Adriatic basin. Therefore, it will be necessary to repeat the sampling in other seasons in order to better evaluate the sedimentary conditions and the dynamic of the area.

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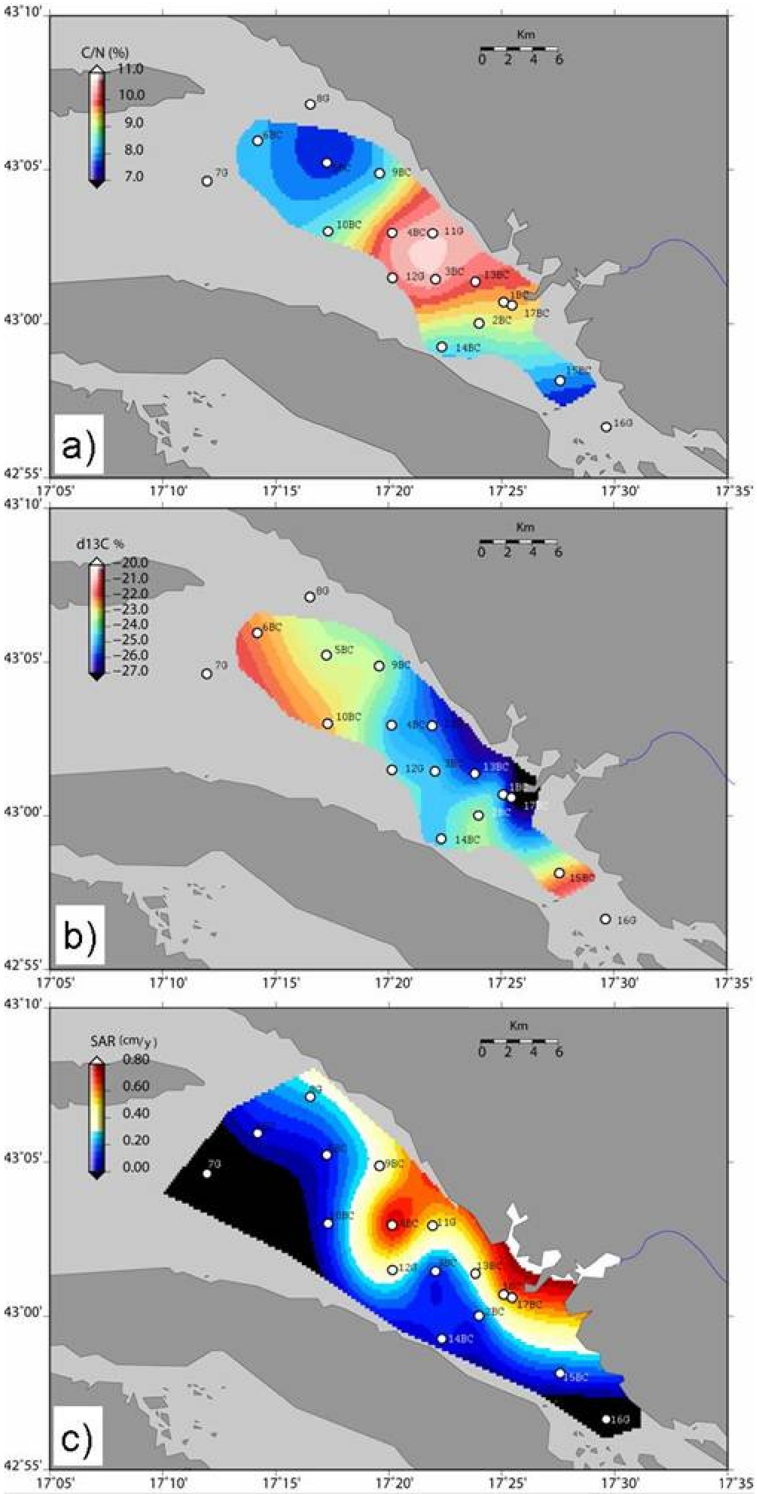

Figure 2: Areal distributions of a) C/N ratio, b) $\delta^{13}$C, and Apparent Sediment Accumulation Rate in the study area.

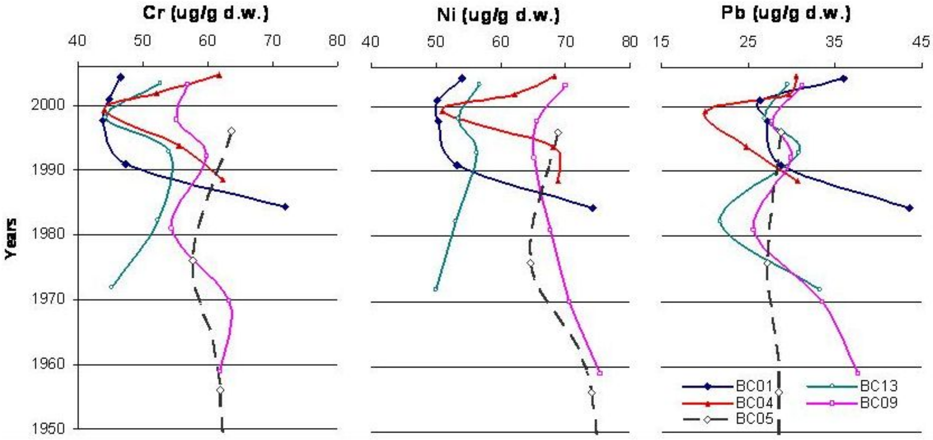

Figure 3: Metals concentration profiles in selected cores as function of time.

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