LOOKING FOR SEDIMENT DISTRIBUTION AND HEAVY METALS CONTAMINATION: THE CASE STUDY OF NERETVA CHANNEL (CROATIA)

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INTRODUCTION

Coastal areas, are places where the peculiarities of land-sea transition systems emerge more clearly in terms of chemical, physical and biological changes and where the human pressure assumes often dramatic aspects. occurs. Trace metals are common contaminants of coastal areas, and those accumulated in marine sediments derive from a combination of natural weathering and anthropogenic activities. Therefore, while sediment composition is mainly controlled by the local geology and geochemical processes, the content of trace metals can be enhanced by wastes from industrial and urban settlements (Kljaković-Gašpić et al., 2009).

This paper presents an approach to the study of an area characterized by very few information about sediment dynamics and presence, distribution and history of contamination.

STUDY AREA

The Neretva is the largest river of the eastern part of the Adriatic basin. It is characterized by the transport of a large amount of sediment that flows to the Adriatic sea into a narrow semi-enclosed basin, named Neretva channel and located along the southernmost part of the Croatian coast.

The upper part of the river, called Hutovo Blato, belongs to Bosnia-Herzegovina. Here it cuts several canyons in Jurassic limestone and dolomite carbonate platform sequences. Then, the valley along the last thirty kilometers of the Neretva River spreads abruptly into an alluvial fan named "Neretvanske blatije", whereas in its lower part, 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 area of the delta is especially threatened by different planned activities, such as road construction, urbanization, and hunting that cause the release of contaminants into the water (Calo and Parise 2009). Furthermore, over 90% of the soil of the delta area is exposed to water and wind erosion of varying intensity. The situation is particularly severe in the karst area, where erosion has already reached the geological base. Intensive and unregulated water uses is also slowly increasing the intrusion of salinity and contamination in the delta area, which has already posed a threat to both marine biodiversity and resident population.

From 1993 to 1995, this zone was also heavily affected by the war in Bosnia and Herzegovina, the symbol of this period being the Neretva Old Bridge in Mostar destroyed by Croatian artillery. The annual sediment discharge of the river is rather high (e.g, about 13.6 tons in 2000).

MATERIALS AND METHODS & WORKING STRATEGIES

With the aim to trace the distribution of the particle input of Neretva River, in particular linked to metals aggregates, in the Adriatic Shelf and follows their spatial vs. time distribution, a suite of biogeochemical proxies was used, such as total (TC) and organic (OC) carbon, $^{13}\delta C$, radiotracers and some heavy metals.

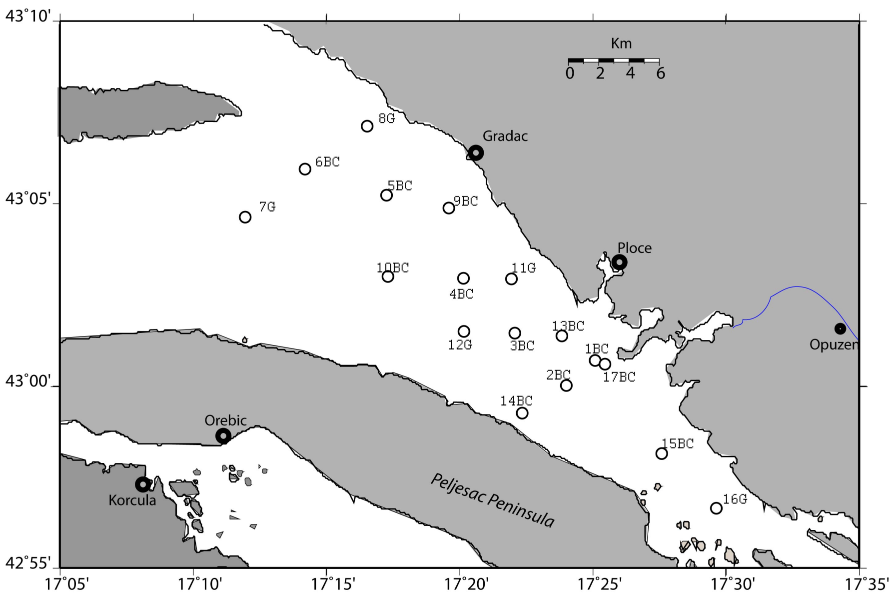

Fig.1 - study area and sampling location.

12 light box cores (subscript “BC”, Fig. 1) and 9 grab samples (subscript “G”, Fig.1) were collected in May 2006 in order to sample both surficial and subsurficial sediment along tree transect SE-NW oriented.

The short cores were radiographed, scanned for magnetic susceptibility, described for visual characteristics, then subsampled to obtain sections 2 cm thick for chemical and radiochemical analyses.

Sediments were dried at 60°C and porosity was calculated assuming a particle density of 2.5 g cm^{-3}. OC and TC contents were determined using a Fisons Elemental Analyser NA2000. To obtain OC concentrations, the carbonate fraction was eliminated through a pre-treatment with 1.5 M HCl.

$\delta^{13}C$ values were obtained from the same samples by using a FINNIGAN Delta Plus mass spectrometer directly coupled to the FISONS NA2000 EA (Tesi et al,, 2008).

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

^{210}Pb was analysed by alpha spectrometry of its daughter ^{210}Po, assuming secular equilibrium between the two isotopes (Frignani et al. 1993).

Metal analysis were performed on wet sediments. The materials were leached with HNO_3 8N and H_2O_2 under reflux (Bellucci et al., 2002).

Cr, Ni and Pb concentrations were determined by Furnace Atomic Absorption Spectrophotometry with accuracies of 11.5, 4.48 and 0.97 %, respectively. Precisions were 19.6%, 9.80% and 13.3%. The Accuracy and precision were tested according the values suggested for the leachate of NIST 2709 soil. All values are reported with respect to dry weight.

The data relative to surficial samples were analyzed for correlation through the Pearson coefficient. STATISTCA software packages were used for the statistical analysis

RESULTS AND DISCUSSION

Core radiographies show no evident inner sedimentary structures and many of the samples seem to be mixed by bioturbation.

The sediment is composed principally by silty-clay and seems to be quite uniform all over the study area (Fig. 1), with grain size slightly coarsening with increasing distance from the delta. A sandy fraction was recognized only at the NW and southernmost sites (station 7G and 16G respectively).

The plot of $\delta^{13}C$ composition vs N/C ratio (Fig. 2) provide information on sediment distribution. As expected, particulate materials move northward from the river mouths driven by marine currents.

The sites close to the river inlet show a strong terrestrial input characterized by very low $\delta^{13}C$ values. On the contrary, at the farthest site the marine input of OC 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 BC10.

However, we can assume that the particles material is moved quickly by surficial currents but is released not far from the river mouth and in particular in the area close to the coast. However, it is important to point out that our surficial sediment could represent just a particular seasonal condition that can be very different in other periods due to the physical and biological reworking of the sediment.

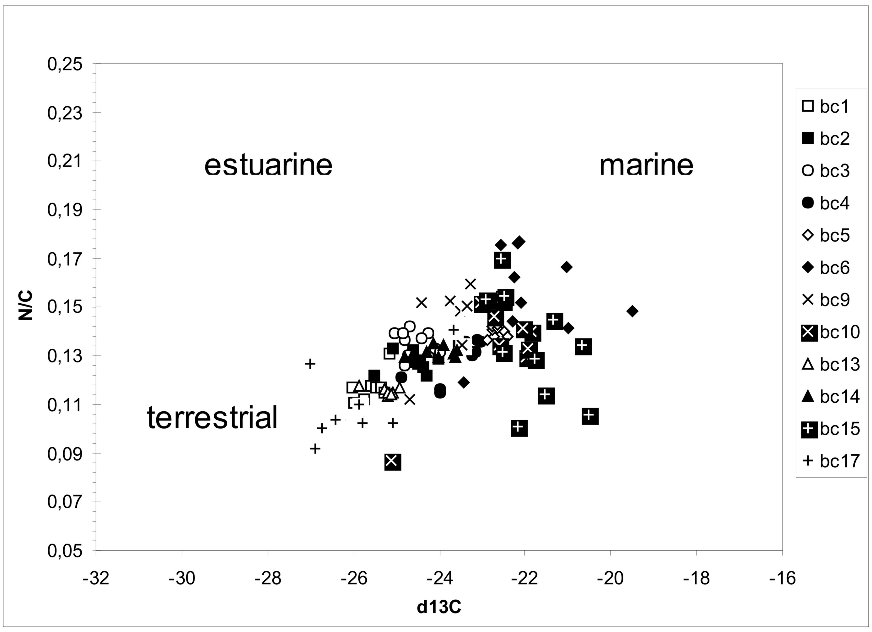

Fig. 2 - δ13C vs N/C Plot.

Fig. 3 shows RX, porosity, metal concentration, grain size and ^{210}Pb activity depth profiles for the box cores BC10 (distal from the inlet).

The metal concentration-depth profiles are related to both characteristic of the inputs and sedimentation mechanisms in the study area, and could be occasionally affected by mixing processes. Actually, the profiles of all analyzed box cores do not show any clear variation in concentration with depth and present similar trends for the three metals. Moreover the grain size composition is constant with depth. This may suggest at some stations the influence of biological or physical mixing that cover the subsurficial structure of the sample (as shown by Rx (Fig. 3). On the other hand the most of core chronologies, based on ^{210}Pb data, there are not evidence of mixing and post depositional reworking processes. except for some stations (BC05; BC14; BC15).

The box core show a typical profile of slow sedimentation profile. As first approximation we can assume that the depth of ca 16 cm where ^{210}Pb reaches the background values (that supported the *insitu* ^{226}Ra decay) correspond to 100 year. This provide a mean sediment accumulation rate of 0.11 cm y^{-1}. Anyway since neither physical mixing nor bioturbation were taken into account these apparent average rate could be considered upper limits valid only for year of collection.

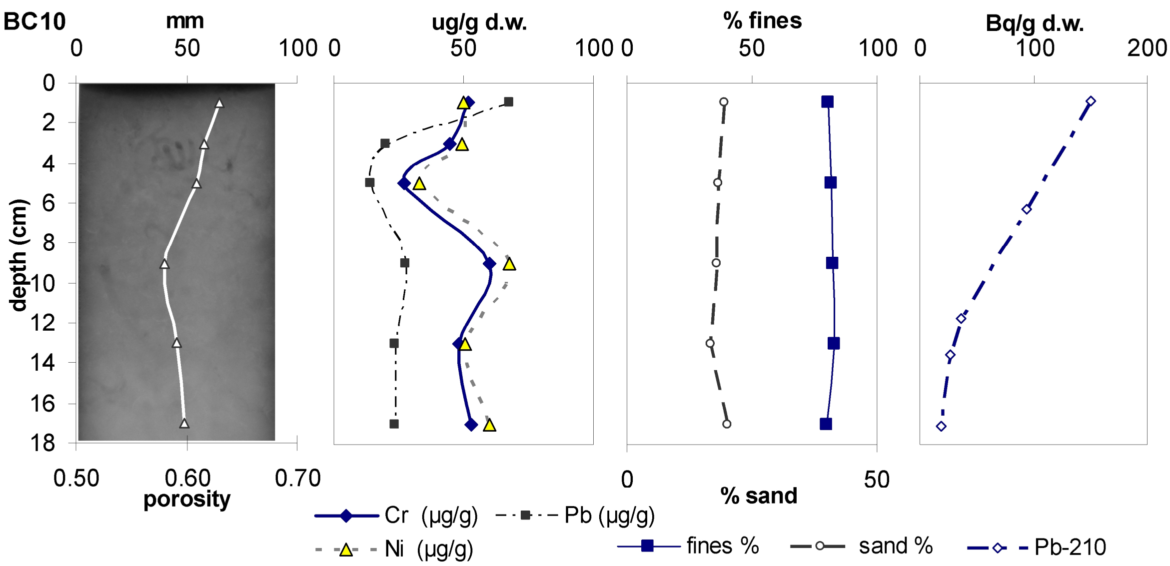

Fig. 3 - RX, porosity, metals depth concentration, grain size and 210Pb activity depth profile for the box cores BC10.

Sometime the low range of variation in concentration with time may also highlight, in 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 comm.).

The Pearson correlation analysis (product-moment correlation r), applied on all data shows a highly significant positive correlation ($p < 0.001$) between Cr and Ni, whereas highly significant negative correlations were observed between these metals and both TC and inorganic carbon; Pb does not show any significant correlation. On the other hand, the sediment accumulation rate is significantly correlated with both $\delta^{13}C$ and C/N ratio.

These results could indicate that Pb has a different source and/or is affected by different mechanisms of transport and deposition than Cr and Ni. In particular, the source of Cr and Ni could not be the river but rather the runoff from the South Dalmatia coast. Actually, Cr and Ni levels are in the range of concentration reported for the soil of South Dalmatia (Miko et al., 2001).

Table 1 lists average metal concentrations in surficial sediments together with minimum and maximum values in cores. Some indications of potential contamination in the present sediments may be obtained by comparing their concentration with pre-industrial levels and with some internationally recognised concentration benchmarks.

	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.

Tab. 1 - Average metal levels in surficial sediments, min and max concentration in cores and international benchmark values. for selected metals.

In particular, the surficial concentrations are compared with Sediment Quality Guidelines (SQG): Threshold Effect Level (TEL), Effect Range Low (ERL), Probable Effect Level (PEL), Effect Range Median (ERM) (Long et al., 1998). Other benchmarks (Base Chemical Level, LCB and Limit Chemical level, LCL) derived by APAT and ICRAM (2007) for Italian coastal areas with similar geochemical characteristic are listed as well.

All these guidelines are screening tools to predict potential sediment toxicity, linking sediment concentrations of contaminants to any adverse biological effect resulting from biota exposure to various chemicals.

Pb and Cr levels in surficial samples usually do not reach any lower benchmark (PEL, ERM, LCB). There are some exceptions but the effect incidence for these samples can be considered low (8-30% for Pb and 2.9-21.1% for Cr; Long et al., 1995).

Ni surficial concentrations at all stations exceeded both PEL and ERM guidelines but not the LCB. This means that these elements might cause adverse biological effect, although their levels are similar to natural soil concentrations (mean 84 $\mu g\ g^{-1}$) in the area (Miko et al., 2001), and in generally lower than the Italian benchmarks referred to similar geological settings. However, for Ni, the incidence of effect for exceeding ERM it is only 16.9 % (Long et al., 1995).

FINAL COMMENT

Grain size results and the plot of $\delta^{13}C$ composition vs N/C ratio highlight that the Neretva river influence on sediment distribution decreases northward. Pb concentrations in surficial sediments show a similar behaviour, whereas Ni and Cr distributions account for another source, different from the river. The comparison with SQG shows that surficial concentrations have a low toxicity. Metal concentration-depth profiles do not show any significant variation or trend. Very likely the bioturbation activity in the area masks the sediment record and hence the process dynamics that have influenced the area in the past. Moreover, one the key phenomena to be study is the saline ingression which could serve as a physical barrier to the transport of contaminants into the Neretva channel.

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