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Deposition of trace metals in sediments of the deltaic plain and adjacent coastal area (the Neretva River, Adriatic Sea)

I. Jurina [a], M. Ivanić [a], N. Vdović [a], T. Troskot-Čorbić [b], S. Lojen [c,d], N. Mikac [a], I. Sondi [e,*]

[a] Division for Marine and Environmental Research, Ruđer Bošković Institute, Bijenička cesta 54, 10000 Zagreb, Croatia
[b] Laboratory Department, Exploration Sector, INA-Industrija nafte d.d., Lovinčićeva 4, 10002 Zagreb, Croatia
[c] Department of Environmental Sciences, Jožef Stefan Institute, Jamova cesta 39, 1000 Ljubljana, Slovenia
[d] Faculty of Environmental Sciences, University of Nova Gorica, Vipavska 13, 5000 Nova Gorica, Slovenia
[e] Faculty of Mining, Geology and Petroleum Engineering, University of Zagreb, Pierottijeva 6, 10000 Zagreb, Croatia

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ABSTRACT

The deposition and distribution of trace metals in surface sediments of the karstic, microtidal and low-wave energy environment of the Neretva River delta and the adjacent coastal region were investigated. These processes were studied in relation to the sedimentological characteristics of the deposits, their surface physico-chemical properties, i.e., specific surface area (SSA) and cation exchange capacity (CEC), and the content, characteristics and origin of sedimentary organic matter (SOM). The results indicate two principal mechanisms governing the spatial distribution of trace metals in the delta plain and adjacent marine surface sediments. Firstly, the presence of SOM in the delta plain freshwater sediments exerts a significant effect on their surface properties, thus influencing the distribution of trace metals, particularly Cd. In the Neretva Channel, the highest share of the terrestrial component of SOM (estimated from $\delta^{13}C$ values of organic carbon) was found in the proximity of the river mouth. This coincides with the markedly elevated concentrations of Pb, Cu and Cd, indicating their association with organic substances of terrestrial origin. Secondly, the spatial distributions of Ni, Co and Zn in the surface marine sediments of the Neretva Channel are closely related to the sedimentation dynamics and deposition pattern of the river-borne fine-grained particles. The strong correlation between the concentrations of Ni, Co and Zn and the content of Al, Fe and Mn indicates their binding on Mn and Fe oxide and oxyhydroxide coatings at the clay mineral surfaces. The results indicate a low level of anthropogenic metal contamination in the investigated area.

1. Introduction

A variety of overlapping physical, chemical and biological processes govern the transport, transformation and deposition of the river-borne particulate and dissolved inorganic and organic compounds in transitional land–sea environments (Dagg et al., 2004; Geyer et al., 2004; Sondi et al., 1994). These processes, often affected by anthropogenic activities, have immense importance in global biogeochemical cycling, particularly since sediments deposited in the proximity of river mouths act as sinks for various anthropogenic pollutants (Batista et al., 2012; Roussiez et al., 2006).

River deltas are considered to be the most complex transitional environments characterized by the deposition of large amounts of river-borne sediment materials. The literature abounds in studies of the fate of contaminants in the sediments of deltaic environments worldwide, particularly those dealing with trace metals, and with respect to their deposition, distribution, association, and the historical record of their accumulation (Cenci and Martin, 2004; Heise et al., 2013; Shumilin et al., 2002; Swarzenski et al., 2006). Among several deltaic systems in the Adriatic region, only the Po River delta has been investigated and described in detail (Provini and Binelli, 2006). However, the distribution of trace metals has been examined in small estuarine environments of the eastern, karstic Adriatic coast (Cukrov et al., 2008; Sondi et al., 1994, 2008). These studies revealed that the heterogeneity of sediments imposes considerable difficulties in identification of the dominant processes and mechanisms governing the binding of trace metals to mineral particles and their transport and deposition in transitional land–sea environments.

Special emphasis has been placed on the investigation of fine-grained, clayey sediments since trace metals are commonly associated with clay mineral particles and/or coprecipitated Fe and Mn oxide/oxyhydroxide coatings (Bradl, 2004; Dong et al., 2007). Organic matter was also considered to be an important vehicle in the transport and deposition of trace metals (Charriau et al., 2011; Liu and Gonzalez, 1999). The surface physico-chemical properties of mineral particles, i.e., specific surface area (SSA) and cation exchange capacity (CEC), exhibit, to a certain degree, their surface reactivity. Various organic compounds bound on mineral particles can significantly alter these parameters

* Corresponding author at: Faculty of Mining, Geology and Petroleum Engineering, Pierottijeva 6, 10000 Zagreb, Croatia.
E-mail address: ivan.sondi@rgn.hr (I. Sondi).

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and the transport mechanisms of trace metals (Bišćan et al., 1991; Sondi and Pravdić, 1998). Accordingly, investigation of the trace metal distribution in complex transitional environments also requires assessment of the surface physico-chemical properties of sediments and the content and characteristics of SOM (Sondi et al., 2008).

The Neretva River is the 5th largest Mediterranean river, ranked by annual water discharge (Ludwig et al., 2009). The river delta represents a still intact remnant of Mediterranean coastal wetland protected by the Ramsar Convention. Consequently, the Neretva River mouth and its adjacent semi-enclosed marine environment provide a good example of land–sea interactions, particularly the interactions between sediments, SOM and trace metals in a microtidal, low-wave energy, and river-dominated coastal sedimentary system. The geochemical characteristics of the floodplain soils were examined by Romić et al. (2012), but a sedimentological and geochemical investigation of the delta plain stream sediments and subaqueous deltaic deposits was not systematically performed.

The main objective of this study was to provide insight into the leading processes that govern the transport and deposition of trace metals and SOM in the transitional system of the Neretva River mouth and its adjacent semi-enclosed karstic marine environment. In particular, the study aimed to clarify the influence of the granulometric characteristics, as well as the content and the origin of SOM, on the surface physico-chemical properties of sediments and the fate of trace metals in this microtidal deltaic environment of the Adriatic. The results should complement existing knowledge of the transportation and deposition processes of clayey mineral particles, SOM and associated trace metals in low-energy deltaic marine environments worldwide.

2. Study area

The Neretva River is 255 km long with a catchment area of about 12,000 km^2. The Eocene flysch deposits (marls and sandstones) which predominate in the upper part of the river basin are subject to intense weathering, providing large amounts of sedimentary material (Juračić, 1998). The lowland part of the Neretva River is only 36 km long and flows through Quaternary alluvial deposits (Fig. 1).

The Neretva River delta covers approximately 120 km^2. There are several watercourses flowing through the delta plain: the main channel of the Neretva River and the Mala Neretva distributary channels, as well as local tributary streams (Fig. 1). The physical and chemical parameters of the Neretva River water column indicate a stratified system with the seawater intrusion extending several kilometers upstream all the way to the town of Metković (Fig. 1). Other delta plain watercourses are mostly freshwater environments (Jurina et al., 2010). The Neretva River discharges its water and sediment load into the semi-enclosed microtidal environment of the Neretva Channel. The average annual water discharge is 332 m^3 s^{-1} (Orlić et al., 2006).

3. Methods

3.1. Sampling and sample preparation

Sediment cores up to 50 cm long were collected using a gravity corer (Uwitec, Austria) at 19 stations in the area of the river delta (stations N1–N19, Fig. 1). The Neretva River profile consists of 7 sampling stations (N1–N7); 6 in the river itself (N2–N7) and one in front of the river mouth (N1). Additional sampling of the delta plain sediments included the Mala Neretva distributary (N11–N13), the Norin River (N14–N18) and other local tributaries (N8 and N10), the Lake Kuti (N9), and the intact wetland area (N19). At additional 31 locations in the Neretva Channel (stations C1–C31, Fig. 1) surface sediments (uppermost 5 cm) were collected. Sediments were frozen immediately after sampling and stored at −20 °C.

Prior to analyses, sediment cores from stations N1–N19 were subdivided into 2 cm segments. The surface sediments from stations N1–N19 and from the Neretva Channel were then freeze dried (FreeZone 2.5, Labconco, USA). A small amount of the dry sample, intended for XRD and metal analyses, was ground to a fine powder using a ball-mill (Pulverisette 7, Fritsch, Germany).

3.2. Analyses

Sediment samples were granulometrically characterized by a laser diffraction particle size analyzer (LS 13 320, Beckman Coulter, USA). The mineral composition of the surface sediments was analyzed by X-ray diffraction (D4 Endeavor, Bruker AXS, Germany). The carbonate content of sediments was determined volumetrically with Sheibler's

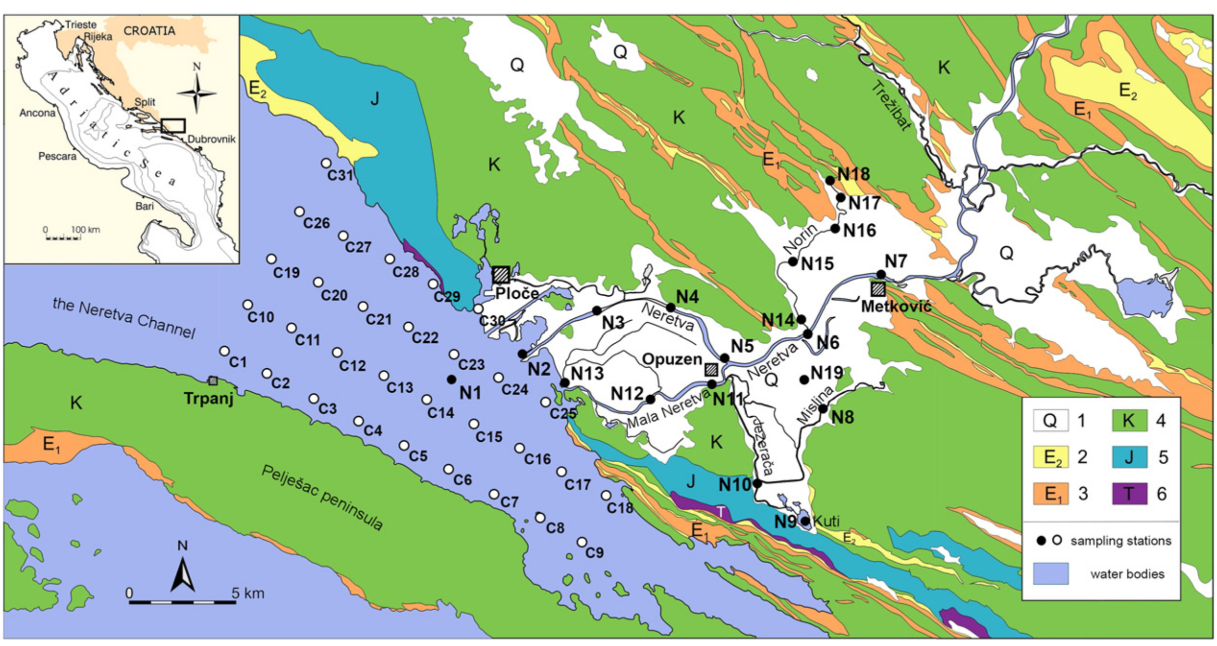

Fig. 1. Geological map of the Neretva River delta and the Neretva Channel showing the investigated area and sampling stations (N1–N19 and 31 stations in the channel). Legend: 1 — Quaternary alluvial deposits; 2 — Eocene flysch; 3 — Eocene limestones; 4 — Cretaceous limestones and dolomites; 5 — Jurassic limestones and dolomites; 6 — Triassic limestones.