Trace elements distribution and mobility in estuarine sediments of the Krka River (Croatia)

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Introduction: Historically, estuaries are preferable places for urbanization and industrialization, due to the easy access to freshwater, marine and continental resources. Therefore, the estuarine environment experiences intense anthropogenic pressure and consequent contamination [1]. Among the contaminants present in the aquatic environments, trace metals are ones that pose the highest threat. Unlike organic pollutants which undergo degradation by biological, physical and chemical processes to less harmful components, trace metals are considered as non-degradable pollutants. Once introduced in the aquatic environment, metals are redistributed among abiotic and biotic compartment, with a substantial fraction being quickly associated to inorganic and organic particles, deposited and accumulated in sediments. It is well known that sediments are not just a sink for contaminants, but they may act as a source of contamination to the water column due to the processes of desorption and reductive dissolution of carrier phases [2,3,4].

Our research was conducted in the Krka River estuary, a typical vertically stratified estuary located on the Eastern Adriatic coast. Most of the freshwater part of the Krka River is protected as a national park, thus there is no significant contamination source affecting estuary from upstream. Contrarily to pristine nature of the upper estuary region, the lower part of the estuary (Šibenik Bay) is under the anthropogenic influence of the town of Šibenik. It is the largest settlement in the region (~35 000 inhabitants) and in the past, there were several sources of contamination (a factory of electrodes and ferroalloys, untreated waste waters, port, etc.). Most of the town's sources of contamination are closed or modernized during the last ~15 years. However, in the recent years, nautical tourism is recognized as a serious seasonal anthropogenic threat to the estuary ecosystem [5].

Methods: The objectives of the present study were: (1) to identify existing sources of contamination within the estuary and to evaluate their impact in terms of trace element content and (2) to evaluate trace element mobility in the estuarine sediments. To accomplish the first objective, surface sediment samples were taken on 40 locations along the entire estuary and analysed for major/minor/trace elements. Principal component analysis (PCA) was performed to establish spatial groupings of sampling points and groupings of contaminants with a common origin or behaviour. To achieve the second objective, sediment cores were sampled and sliced every 1 cm under an inert atmosphere. Pore water and solid fractions were recovered and analysed for major/minor/trace elements and particulate/dissolved organic matter. Additionally, the diffusive gradient in thin films (DGT) sediment probes were used to gain information on element lability and geochemical reactions between sediment particles and pore water, with high spatial resolution.

Results and Discussion: According to the trace elements distribution in surface sediments, the estuary is divided into two parts: (1) the non-impacted upper estuary and (2) the lower estuary where the impact of various sources of anthropogenic pollution can be observed. There are three main pollution sources: former ferromanganese industry, harbour and marina; which differently contribute to the sedimentary contamination stock.

The complementary approaches (pore water/solid fraction, DGT) applied for sediment profile analysis, demonstrated the control of early diagenesis processes on the trace metals mobility, with the significant gradient at the sediment/water interface, suggesting potential transfer of some elements (e.g. Cu, Cd and Pb) from sediment to the water column.

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