

# LONGITUDINAL DISTRIBUTION OF HEAVY METALS IN SEDIMENTS OF PIAVE RIVER ESTUARY (NORTHEASTERN ITALY).

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## ABSTRACT

An investigation on heavy metals in the sediments of the Piave River, one of the main tributaries of the northern Adriatic Sea (Italy), was performed within a research project on the dynamics and physico-chemistry of the 30 km-long estuary. A large number of surface samples were analysed for total heavy metal concentration, grain-size distribution and organic matter content. The distribution of organic matter identifies a clear-cut zoning of the estuary, reflecting the extent of the mixing zone. Metal concentrations and grain-size distribution show instead a larger variability in relation to the different morphologic and hydraulic conditions of the meandering course of the river. A normalisation of concentrations by the content of finer particles ( $d < 62\mu\text{m}$ ) permitted to reveal a common trend of the analysed species and the existence of geochemical anomalies related to the contamination from the urban areas nearby.

## INTRODUCTION

The Piave River (Figure 1) is one of the main tributaries of the northern Adriatic Sea (Italy). It originates in the Dolomite mountain region (eastern Alps) where the larger proportion of its 3827 km<sup>2</sup> drainage basin, mainly constituted by carbonate rocks, is located.

The morphology of the lower course of the river has been modified several times in the past centuries. After the diversion from its original course to avoid silting of the Venice Lagoon, the more important modification was the excavation of a straight channel in the lower reach, to limit the recurrence of overbank flooding.

The estuary has an average

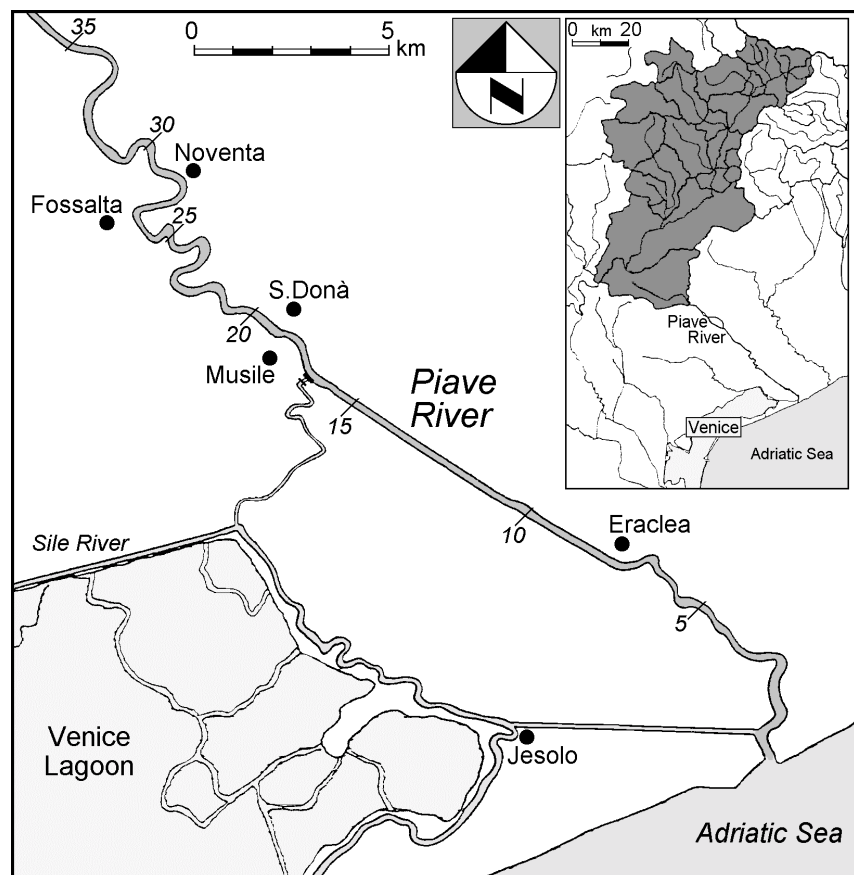


Figure 1. Map of the investigated reach of the Piave River; the distances from the sea (km) are indicated. In the inset, the drainage basin is shadowed.

depth of about 5 m. Local depressions as deep as 10 m are frequent in the outer side of meander bends or in the numerous sites of past sand-extraction activities.

At the end of the mountain area the mean discharge is about  $50 \text{ m}^3\text{s}^{-1}$ , while peak flood may be as high as  $3000 \text{ m}^3\text{s}^{-1}$ . In this reach, characterised by a gravel-paved channel developed over highly permeable deposits, the river flow undergoes a considerable dispersion by infiltration in the multi-layered aquifer of the floodplain. The riverbed finally grades into a sandy channel that characterises the entire lower course down to the sea.

The combined effect of flow controls by the intense use of water resources (hydroelectric power production and land irrigation) and channel dispersions strongly affects the fluvial regimen, determining long periods of low discharge during which the tide (average spring tide excursion is about 80 cm) has a marked influence on the dynamics of the whole estuary. The salt wedge intrusion can therefore extend for several kilometres upstream, up to the end of the meandering course, at approximately 30 km from the sea (Zonta et al., 1996). During the periods of low discharge, the channel of the studied reach is covered by finer deposits, mostly fine silt and clay, which are flushed seaward by flood events. However these deposits may be preserved in the lee of flow obstructions, in the inside of meander bends and in channel depressions.

As a part of a research on the dynamics and physico-chemistry of the Piave estuary, heavy metal, organic matter and grain-size distributions were investigated in bottom sediments of the lower reach of the river.

## METHODS

A total amount of 100 surface samples (from 0 to 5 cm) were collected in June 1997 using a box corer operated from the surface by a survey boat. Each sample was collected every 300 meters alternatively on the left and right side of the channel, for an overall distance of 36 km from the sea. Materials were stored in sealed PE containers and kept at  $4 \text{ }^\circ\text{C}$  until the transfer to the laboratory, where the samples were homogenised and subdivided into three aliquots for the different analytical determinations. A  $\text{HNO}_3\text{-HCl}$  1:1 cold digestion was adopted for sample mineralisation and the extracts were analysed for Cr, Cu, Fe, Mn, Ni and Zn concentrations by A.A.S. Grain-size distribution was determined with a laser particle analyser that provided high resolution spectra (50 contiguous size classes from 700 to  $0.15 \text{ }\mu\text{m}$ ). Finally, the water content and the organic matter percentages were respectively estimated by weight loss after heating at  $105 \text{ }^\circ\text{C}$  and  $550 \text{ }^\circ\text{C}$ .

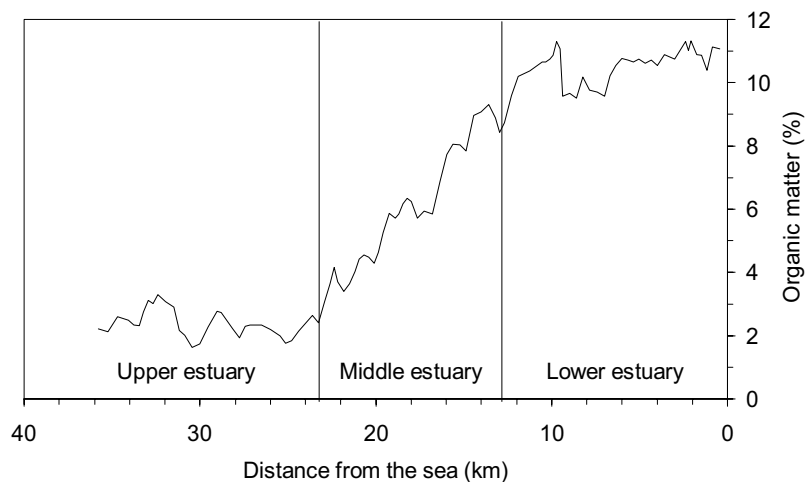


Figure 2. Longitudinal trend of the organic matter content (as percentage) in the sediment of Piave River estuary.

## RESULTS AND DISCUSSION

The longitudinal trend of the organic matter content in the sediment of the river is shown in Figure 2. From the upper part of the investigated reach to a distance of 23 km from the sea, the percentage is relatively low, with an average value of about 2.5%. It progressively increases downstream, reaching a value of approximately 10% at 13 km from the sea. This value remains nearly constant up to the river mouth.

This clear-cut zoning of bottom materials is in relation to the characteristics of the estuarine circulation. Due to the range of variations of river discharge, in fact, the extent of the mixing zone varies considerably in response to the river regime and tide excursion. From the results of previous investigations (Zaggia et al., 1998), the central part of the studied system is more frequently affected by the saltwedge expansion. In this reach, that can be identified as the middle estuary, flocculation of dissolved organic compounds is responsible for the observed seaward increase of the organic matter content in the sediment. In the downstream reach (lower estuary) the riverbed bathymetry is such that saltwater can propagate at bottom even under moderate floods. The saltwedge is therefore present for most of the time, determining the measured maximum of organic matter content.

The large amount of data relative to the concentration of the analysed species are resumed in Table 1. If compared to the typical values found in highly contaminated estuaries, the average concentrations found in the sediments of Piave River rank at low levels. Despite the metal distribution in the system is characterised by a large variability, there is no evidence of a significant pattern along the estuarine transition.

Figure 3 shows, for example, the longitudinal distribution of Zn and Mn concentrations, emphasising the intrinsic variability that characterises the analysed metals in the investigated system.

This trend is to be ascribed to the large variations of grain-size distribution of the sediment samples.

	Fe	Mn	Zn	Cr	Cu	Ni
Average	7766	275	125	3.6	19.8	21.2
Max	13083	484	370	8.9	37.7	24.4
Min	4857	137	68	1.8	10.7	18.2
Max/Min	2.7	3.5	5.4	4.9	3.5	1.3

Table 1. Average heavy metal concentrations (mg/kg, d.w.) and descriptive parameters of the whole set of data.

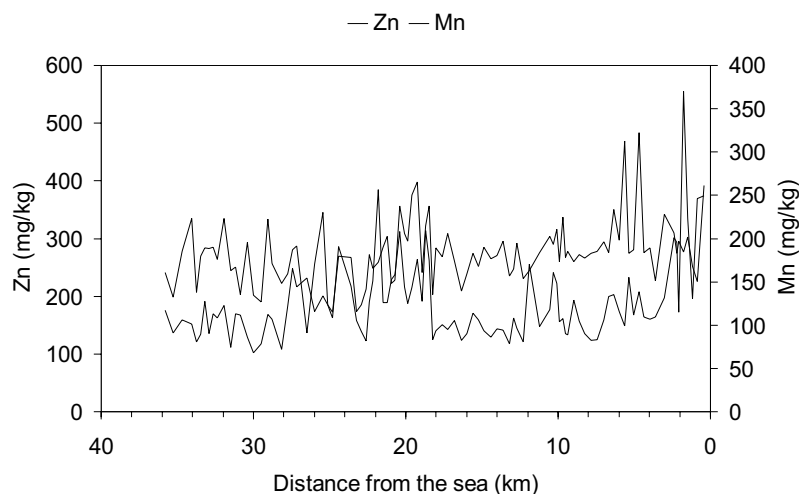


Figure 3. Longitudinal trend of Zn and Mn concentrations.

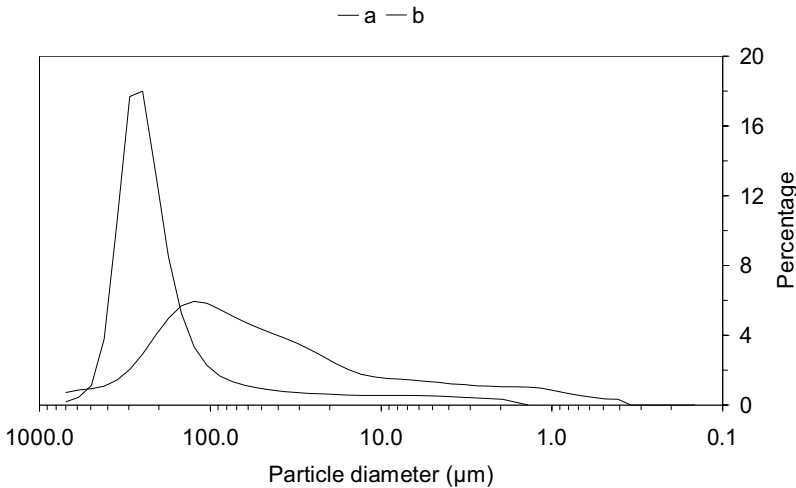


Figure 4. Grain-size distribution of two sediment samples collected in two contiguous sites located respectively at 24.8 (curve a) and 24.4 (curve b) km from the sea.

the fine silt-clay diameter range ( $d < 62 \mu\text{m}$ ). This procedure is commonly achieved by measuring concentrations in sieved samples or by extrapolation from regression curves (Förstner and Wittmann, 1979). However, the technique adopted for grain-size distribution analysis permitted a definition of several size classes that can be statistically compared with metal concentrations determined in non-fractionated samples (Zonta et al., 1994). The more representative diameter range can be therefore identified and used for the normalisation.

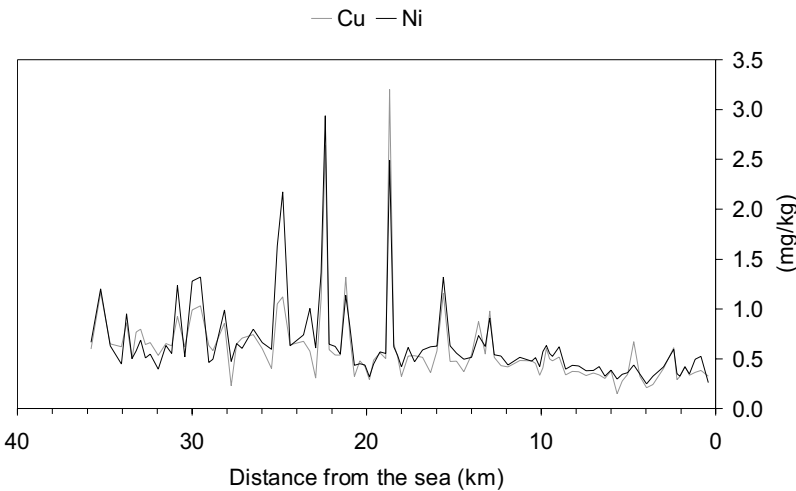


Figure 5. Longitudinal trend of the normalised concentrations of Cu and Ni (mg/kg, d.w.).

In the upper reach, values are affected by a certain variability and are generally high on average, while in the downstream reach, corresponding to the area occupied by larger urban centres, the variability is higher, even if average values are similar to those determined upstream. The highest peaks, resulting from a high metal content in relatively coarser sediments, are related to the presence of local contamination by point sources. Finally, in the lower estuary, the normalised concentrations are lower and generally show a more regular trend, with only limited deviations. The

Noticeable differences are in fact observed even for materials collected in contiguous sites (Figure 4). Besides masking any eventual trend of metals along the river course, the variability of grain size-data also minimises the significance of the correlation between the particle size and metal concentrations.

In order to obtain a better description of the space distribution of contamination in the investigated system, data were normalised for the percentage of particles in the

The examples of Figure 5 show that by normalising concentrations the longitudinal distribution of metals becomes similar, being primarily governed by the trend of percentages in the diameter range selected for the normalisation. Furthermore, the overall trend shows the existence of three zones with peculiar distribution. In the upper reach, values are affected by a certain variability and are generally high on average, while in the downstream reach, corresponding to the area occupied by larger urban

so identified zones of the estuary are approximately coincident with those recognised on the basis of the distribution of organic matter content. Therefore, the relatively higher average values determined in the upper and middle estuary can be related to the presence of contaminant sources and accumulation in the sediment caused by biogeochemical processes occurring in the freshwater-saltwater mixing zone.

Despite the relatively low contamination levels found in the Piave River estuary, the normalised concentrations permitted the spatial zoning of the estuary and to recognise local enrichment related to anthropogenic inputs.

## **REFERENCES**

Forstner U, Wittmann GTW (1979), *Metal Pollution in the Aquatic Environment*. Berlin, Springer-Verlag.

Zonta R, Zaggia L, Argese E (1994), *Sci. Tot. Environ.* 151:19-28.

Zonta et al. (1996), CNR-ISDGM, Venice, Technical Note n. 169.

Zaggia et al. (1998), CNR-ISDGM, Venice, Technical Note n. 186.