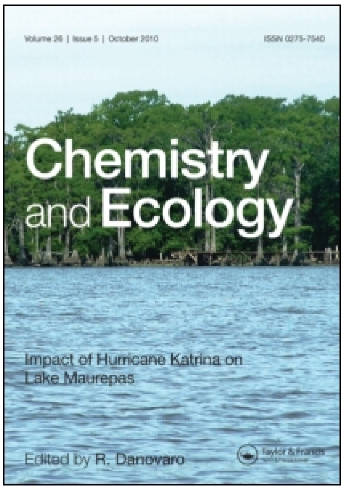

Chemistry and Ecology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455114

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To cite this Article Vukadin, I. , Odžak, N. and Radaĉrić, J.(1994) 'Heavy Metal Pollution in Sediment from the Eastern Adriatic Coast, Croatia', Chemistry and Ecology, 8: 4, 265 — 274
To link to this Article: DOI: 10.1080/02757549408038553
URL: http://dx.doi.org/10.1080/02757549408038553

Chemistry and Ecology, 1994, Vol. 8, pp. 265–274
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HEAVY METAL POLLUTION IN SEDIMENT FROM THE EASTERN ADRIATIC COAST, CROATIA

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(Received 27 January 1992)

Sediment samples were collected from the Adriatic Sea in areas near large coastal towns along the eastern Adriatic coast (Zadar, Šibenik, Split, Ploče and Dubrovnik).

Considerable quantities of untreated effluents are discharged via freshwater runoff and a variety of industrial waste waters, significantly affecting the quality of marine sediments.

Distribution of some trace metals (Pb, Cu, Ni, Cr, Zn, Mn, Cd, and Al) involved in problems related to metal pollution in Adriatic sediment were examined. Values are expressed as a total concentration of heavy metals of sediment dry weight.

Spatial distribution of some trace metal values in sediments and correlation of results for grain size effect were examined. The trace elements in marine sediments generally remain in the fine grained fraction, often in the silt-clay fraction. Higher values of heavy metals in some areas (Split, Šibenik) could be attributed to anthropogenic effects, i.e. to land-based activities. The main cause of higher values of some metals at open sea sites and in some coastal areas are probably caused naturally by sedimentation processes in those areas. Our results show that the sediments undoubtedly play a key role in determining the transport and ultimate fate of contaminants.

KEY WORDS: sediment, heavy metals, pollution, Adriatic Sea

INTRODUCTION

Trace elements are perhaps among major contaminants of the marine environment. In particular those toxic to marine or human life. In this context, their amount, distribution and influence at different levels of the marine ecosystem play an important role in pollution of the Adriatic Sea. Marine sediments are the products of large-scale and complex chemical and physical breakdown processes. The proportions of natural and anthropogenic metal levels in sediments are difficult to determine, since the sediment can be deposited under a wide variety of environmental conditions. The determination of metal concentrations in recently deposited sediments, as compared with those in older strata, has become a common means of assessing the extent to which an area is influenced by anthropogenic inputs (Förstner and Wittman, 1979). The following approach for the interpretation of anomalous metal concentrations in sediment is an assessment of their magnitude in relation to baseline or "natural" levels (Martinčic *et al.*, 1990). A wide variation in metal concentrations of sediments, especially in those from estuaries or rivers or from urban and industrial wastes, may result from differences in grain size of sediment, organic carbon and calcium carbonate content, and mineralogy.

MATERIAL AND METHODS

This paper presents data on heavy metals in surface sediments (0–5 cm depth), collected from several stations in the vicinity of larger urban centres along the eastern

Adriatic coast: Zadar (Zd) and Petrčane (Pč), Šibenik (Ši), Split (St), Kaštelanski zaljev (Kz), Vranjic (Vr) and Stobreč (Sb), Ploče (Pl), Neum (Ne) and Ston (Sn), Dubrovnik (Du) and from an open sea station (9) Stončica (So) island Vis. (Figure 1). Some of the stations are about 1 km off the outfalls from large town outfalls (Zadar, Šibenik, Split, Vranjic and Dubrovnik). The depth of these stations is about 35–40 m. Other stations (Petrčane, Kaštelanski zaljev, Stobreč and Ploče) are also near the town outfalls but at greater distance offshore (about 2 km) at similar depth. The stations Neum and Ston are located in clean waters of a shellfish breeding farm; depth is about 20 m. Stončica (9), a reference station, is in the open sea where depth is about 100 m.

Samples were collected by the research vessel "Bios" in December 1990 and January 1991. Sediment was sampled with a gravity corer of 35 mm internal diameter in perspex tubes. Surface sediments were immediately sectioned into 5 cm lengths and stored frozen until analysis. The samples from all stations were screened through sieves (Fritsch, Analytical Sieves) of pore diameters: 0.040, 0.063 and 0.080 mm. About 0.5 g of sediment from each size fraction was wet digested overnight with a mixture of concentrated HF, HNO_3 and $HClO_4$ (5, 10 and 1 ml respectively) in closed Teflon crucibles at 180°C.

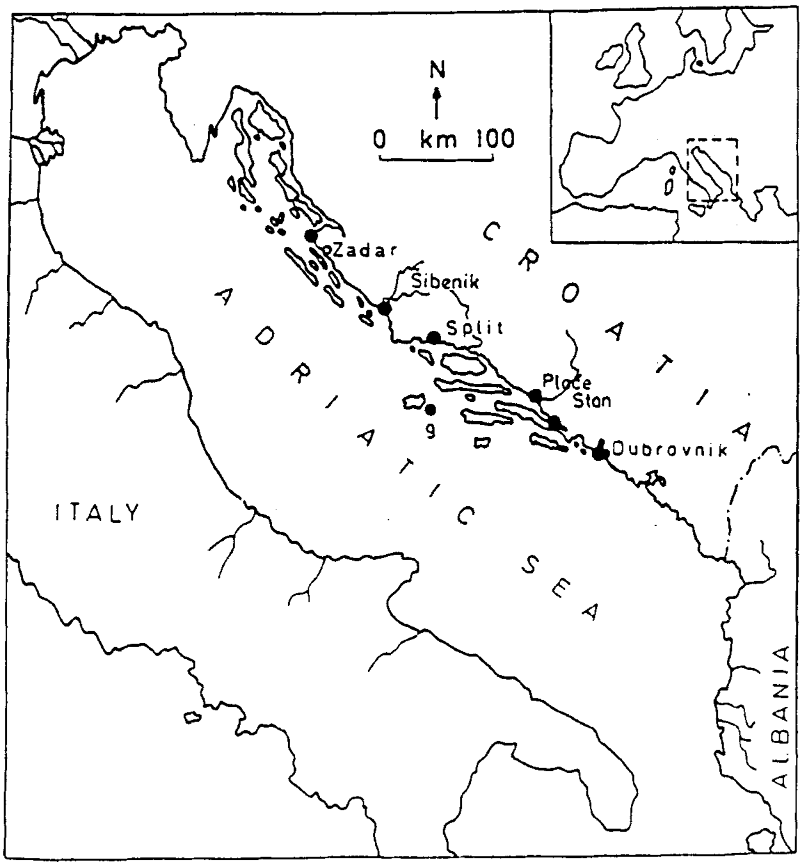

Figure 1 Study area and sampling sites on the eastern Adriatic coast.

Trace elements were determined by atomic absorption spectrometry (AAS) using a Perkin-Elmer Model 1100B, equipped with a HGA-700 graphite furnace and an AS-60/70 autosampler system.

RESULTS

The levels of dissolved Cd, Cu, Zn, Ni, Pb, Mn, Al and Cr in relation to different grain-size fractions and stations sampled are summarized and illustrated in Figures 2, 3, 4, and 5.

The results for individual elements are separated on the basis of concentration gradients reflecting sediment grain size.

Cadmium content (Figure 2) had lowest values in all sediment fractions at stations Zadar (Zd), Ston (Sn) and the open sea station Stončica (So). Maximum cadmium values were recorded from the stations in the vicinity of Split, near the Vranjic area (Vr) which receives most of the sewage effluents of the town of Split. There is no significant regular pattern of distribution of this element with respect to sediment grain size. However, maximum values were recorded from the finest sediment fractions.

According to Fernex *et al.* (1984), dissolved cadmium in sediment is rather rapidly precipitated as carbonate or sulphides, as $CdCO_3$ or CdS. It is well known that Adriatic sediments are very rich in carbonates (Juračić *et al.*, 1984).

Figure 2 also depicts copper distribution. The areas are also grouped on the basis of concentration. The lowest values were recorded from stations Stobreč (Sb), Ploče (Pl), Kaštela Bay (Kz) and Petrčani (Pč) near Zadar, whereas the highest values were recorded from the vicinity of Split (St), Zadar (Zd) and Neum (Ne). It should be emphasized that these highest values were mostly recorded from the finest sediment fractions, i.e. <0.04 mm. Copper distribution is highly affected by grain size. The smallest grains almost always had maximum concentrations of this element. Presumably, this is due to the fact that a large part of the copper is bound to the organic sediment fractions. The principal form of dissolved copper is bound as soluble complexes (Stumm and Morgan, 1970).

The spatial distribution of zinc (Figure 3) in the study area shows highest values in individual, enclosed and isolated areas such as Šibenik (Ši), Vranjic (Vr) (the area of Split) and Neum (Ne) (Mali Ston Bay). This may be attributed to the effects of sewage effluents carrying considerable quantities of this element. The lowest values were recorded from the Zadar area (stations Zadar (Zd), Petrčane (Pč) and the reference open sea station So (9). Rather high zinc levels in the finest sediment fractions from the open sea station are surprising.

Zinc and nickel belong to a group of elements entering the sea mainly by terrigeneous discharges; zinc and nickel behave similarly in marine ecosystems.

The spatial distribution of nickel (Figure 3) showed rather low values at stations in the Zadar area, (Petrčane, (Pč), Ploče, (Pl)) and rather surprisingly, in the Šibenik (Ši) area. In general, the stations in the northern part of the eastern Adriatic coast showed lower values than those in the southern part. This may be accounted for by either a larger natural background of this metal in the south, inputs by river or submarine springs, or by sedimentation processes in this area (Paul *et al.*, 1976; Stegnar *et al.*, 1980). The distribution of nickel in relation to sediment particle size showed that smallest particles contained the highest nickel levels.

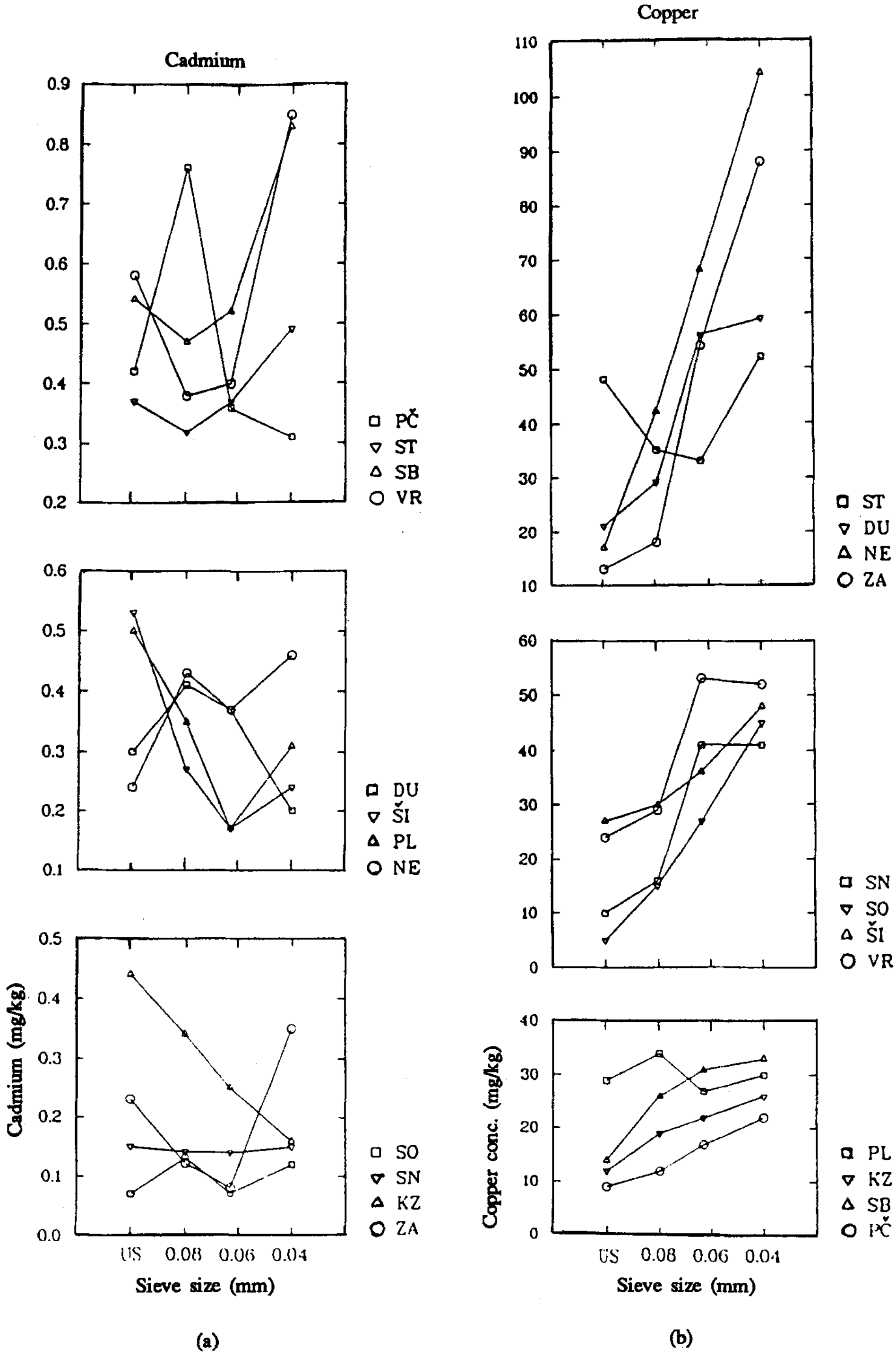

Figure 2 Cadmium (a) and copper (b) in unseived sediments (US) and different sediment fractions at the study sites.

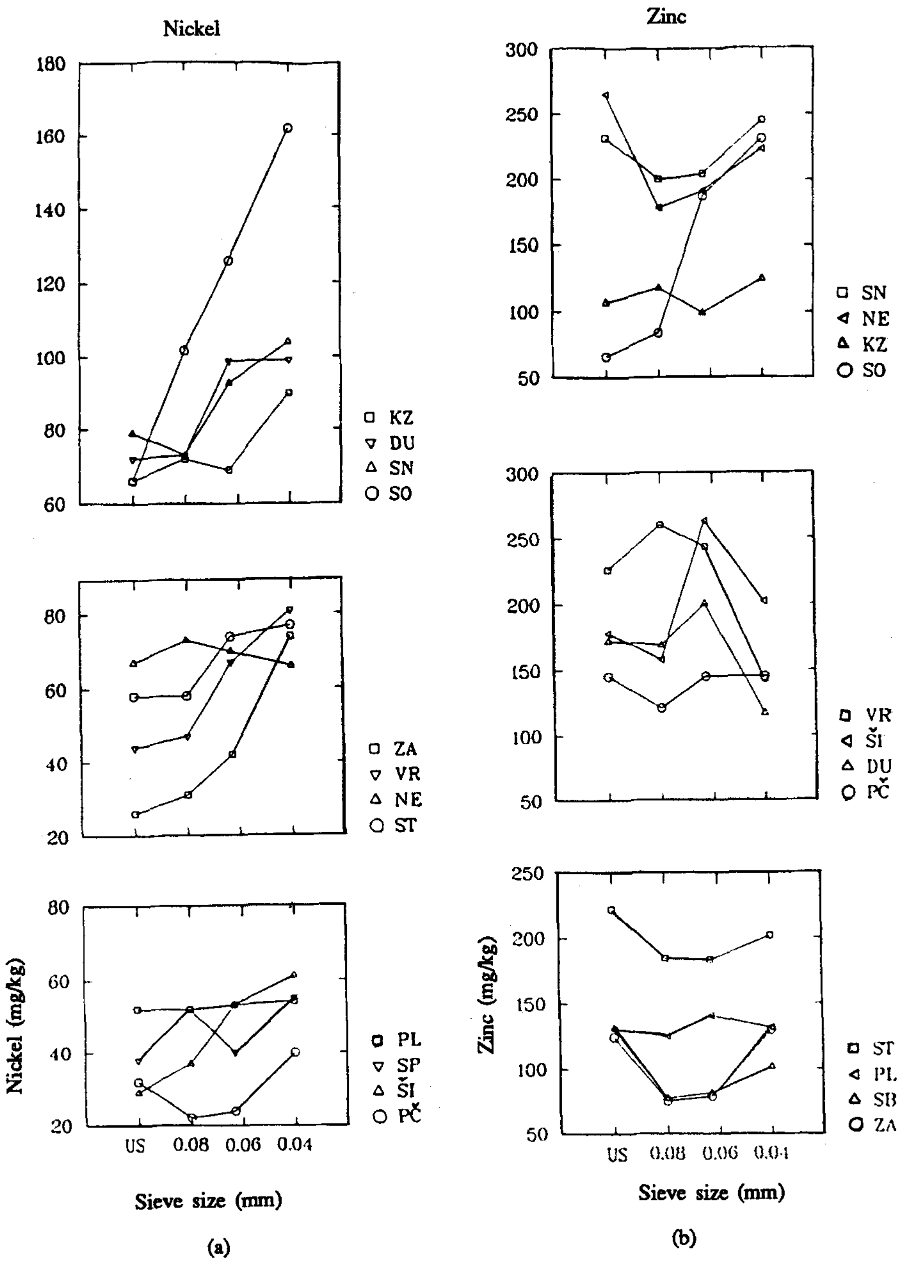

Figure 3 Nickel (a) and zinc (b) in unseiveu sediments (US) and different sediment fractions at the study sites.

Spatial distribution of lead (Figure 4) in sediments of the eastern Adriatic shows that open sea stations or those closer to the open sea had considerably lower values than sediments of enclosed areas or areas in the vicinity of town outfalls. This particularly applies to the station in the vicinity of Šibenik (Ši) and Split (St).

The distribution of this element in different sediment fractions did not show significant gradients. The smallest sediment particles had slightly higher values than the remainder. Juračič *et al.* (1984) reported lead in surface sediments from estuaries and coastal sea to be bound to a reducible and organic sediment fraction, where this element is present and bioavailable.

The distribution of manganese (Figure 4) both spatially and in different fractions did not show any significant differences. The values are almost identical in all sediment fractions. Manganese values were recorded from the station in Šibenik (Ši) area presumably due to the vicinity of smelting factories. Figure 5 shows the distribution of aluminium and chromium in the study area. Neither spatial nor sediment size distribution showed any regular pattern. It is not easy to explain why some relatively clean areas showed considerably higher values of aluminium and chromium. The stations in the southern area (Ston (Sn), Neum (Ne), Dubrovnik (Du)) showed slightly higher values than those in the northern area. The values of chromium were also surprisingly high at the reference station, Stončica (So), possibly attributable to coastal drainage of this element in the southern Adriatic (Paul *et al.*, 1976; Vukadin, 1980).

DISCUSSION

The study of the content and distribution of some heavy metals (Pb, Cu, Ni, Cr, Zn, Mn, Cd and Al) in total sediment and in different sediment fractions obtained by sieving through 0.040, 0.063 and 0.080 mm pore size sieves confirmed that some areas of the Adriatic are very strongly affected by land activities e.g. sewage effluents, industrial effluents, agricultural waste waters, river runoff. These discharges affect both the content and distribution of heavy metals. Elevated values of almost all heavy metals were recorded from the areas of Šibenik and Split, that is at the Kaštela Bay station in the vicinity of Vranjic.

Higher values of some metals (Cr, Al, Ni and Zn) at stations in the bay of Mali Ston (Ston and Neum) are presumably due to submarine inputs either from the Neretva River or submarine springs, as well as to sedimentary and geological processes (Stegnar *et al.*, 1980).

Heavy metal distribution in individual sediment fractions is also of interest. The smallest fractions contained highest metal levels (diameter pore size 0.04 mm), representing the mud–clay fraction of sediments. Some elements, such as chromium, cadmium, zinc and aluminium show a rather irregular distribution as to the sediment particle size. This may be accounted for by the chemical structure of sediment of individual areas. Unfortunately we are not yet able to determine mineralogical and chemical sediment composition, so that this question cannot be answered properly. Future studies should therefore give special attention to this problem. This means that complete sediment analysis is needed (granulometric, mineralogical and chemical sediment composition). This is clearly shown by Figure 6 which depicts the levels of heavy metals studied and percentage of organic matter in unsieved sediment from all stations. It is quite obvious that high levels of organic matter at a particular station are accompanied with high concentrations of some heavy metals (manganese, lead, aluminium and nickel) particularly at Šibenik.

Some areas show rather large ranges of some metals, which may be accounted for by a defined sediment type containing different quantities of organic matter and certainly organic carbon. Sediment types and their organic matter content point to

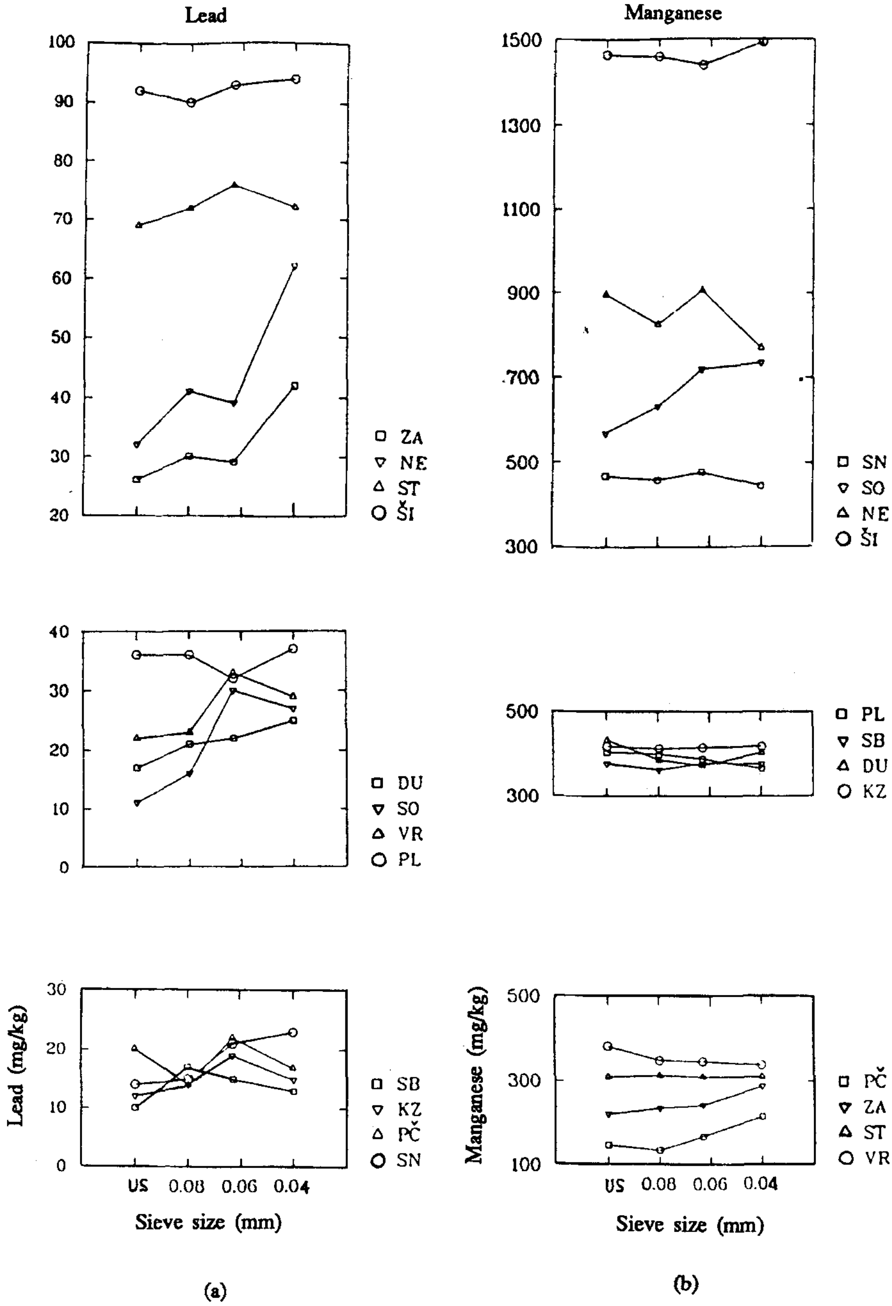

Figure 4 Lead (a) and manganese (b) in unseived sediments (US) and different sediment fractions at the study

the fact that their distribution is closely related to the total biological activity of organisms in given areas.

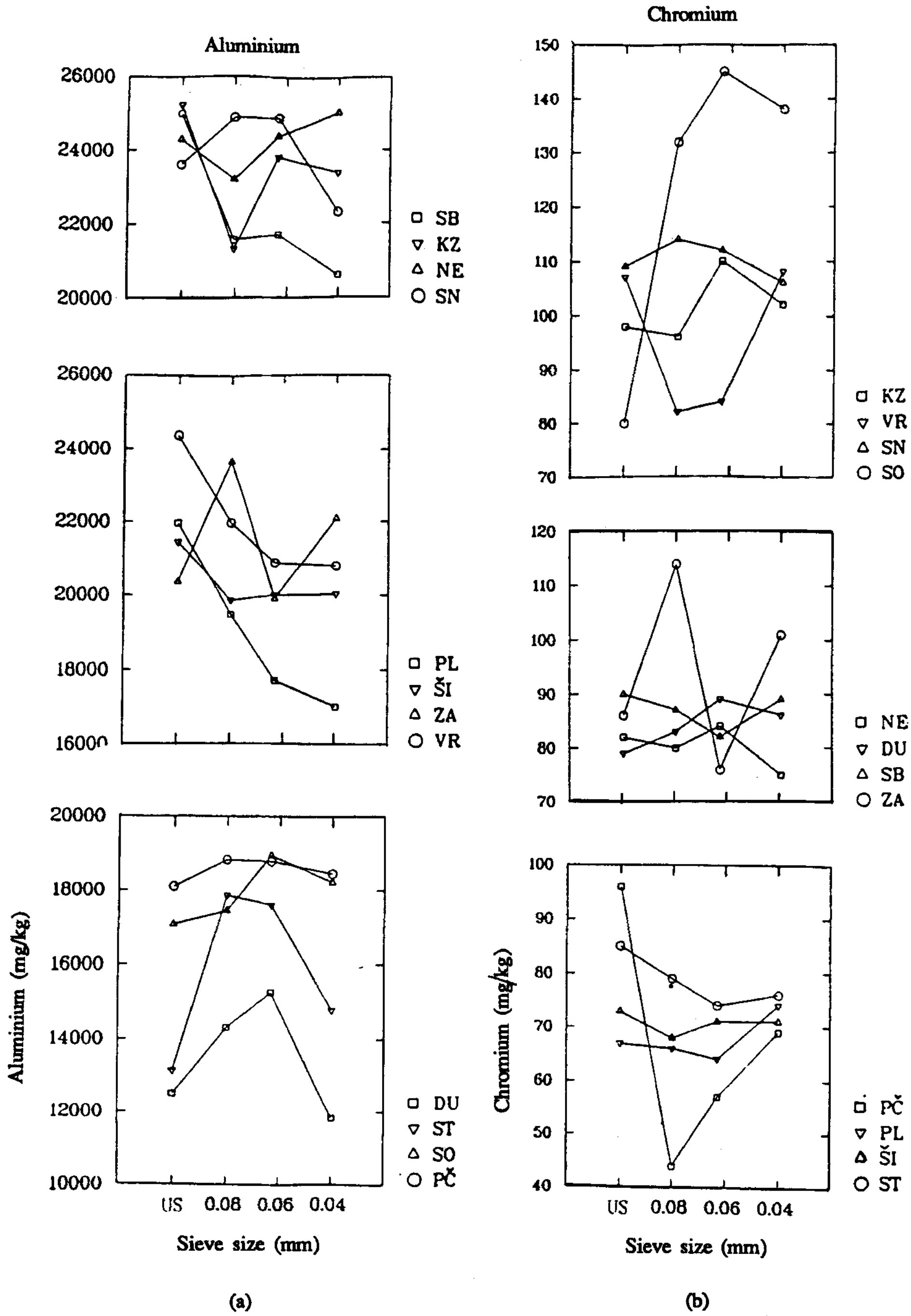

Figure 5 Aluminium (a) and chromium (b) in unseived sediments (US) and different sediment fractions at the study sites.

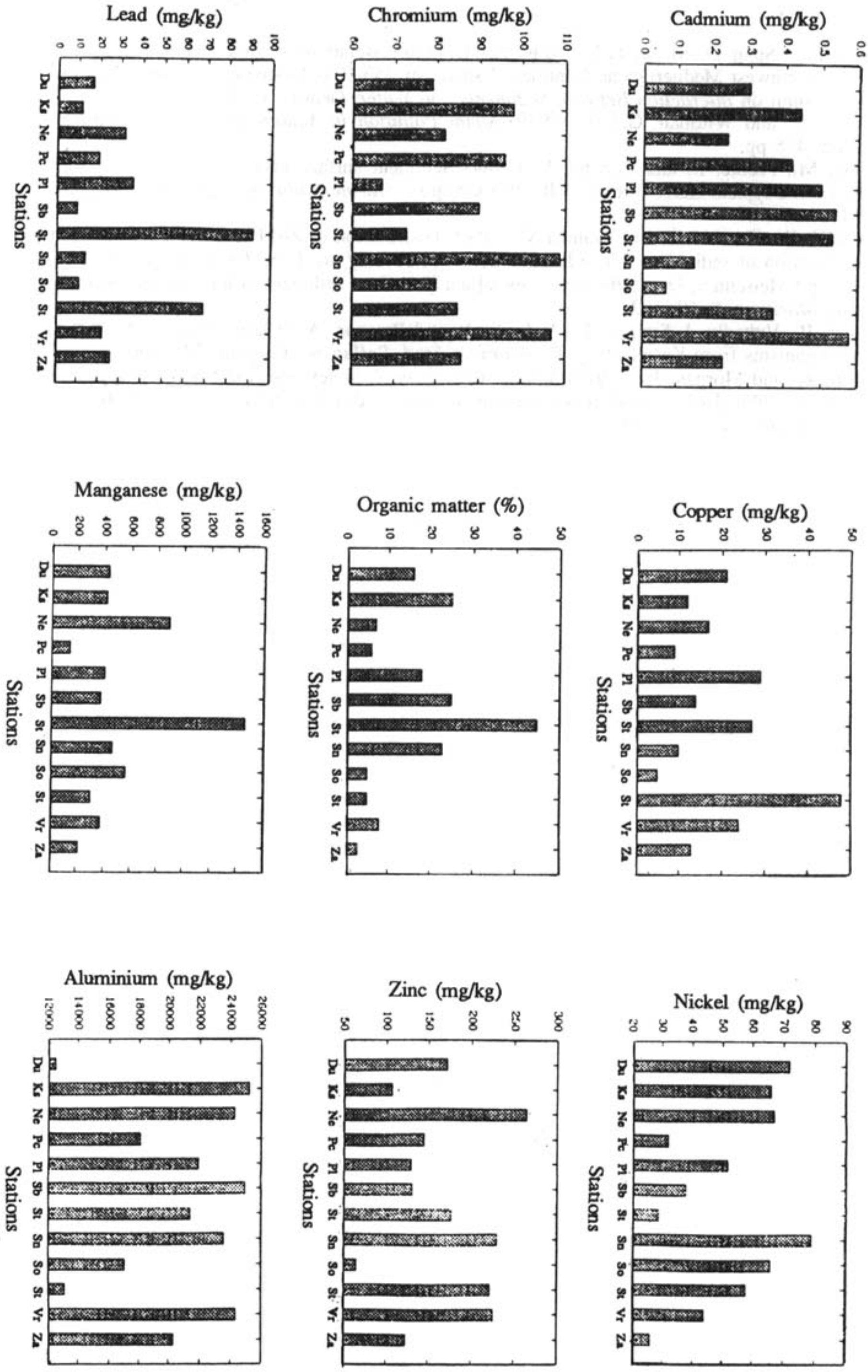

Figure 6 Trace metals and percent organic matter in unsieved sediments at stations in the study area.

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