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Heavy Metals in Sediment Cores from a NW Spain Estuary

R. Barreiro, C. Real, A. Carballeira

Area de Ecología, Facultad de Biología, Universidad de Santiago de Compostela, 15076-Santiago de Compostela, Spain

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Core samples have been used to describe the chronology of heavy metal inputs to aquatic systems. Metal concentration profiles have been investigated to detect pollution (Evans et al. 1983; Loring and Ashmund 1989; Verta et al. 1989), to establish when the polluting event started (Presley et al. 1980; Allen and Rae 1986; DeLaune et al. 1989), and to quantify its magnitude relative to "precivilization" background values (Johnson 1987; Finney and Huh 1989; Mueller et al. 1989). Less frequently, and mainly in studies of coastal systems, the heavy metal nonresidual fraction has been measured to estimate the portion of trace metals potentially available for the biota or remobilization processes, and to assist in identifying the origin of metal inputs (Morris and Kwain 1988; Brügmann and Lange 1990).

This work is part of a wider study of metal concentrations in organisms and superficial sediments from a small estuary in NW Spain (Barreiro 1991). The aims of this research were to detect any potential pollutant input to the sediments of the estuary, and to establish the influence of postdepositional redistribution on the heavy metal concentrations of oxidized surface sediments.

MATERIALS AND METHODS

Pontedeume is a small estuary (7 km long) in NW Spain divided bathymetrically and morphologically into two zones by a sandbank. The outer zone is predominantly infralittoral, whereas the inner zone is dominated by intertidal mudflats. Samples were taken with a gravity corer in the outer zone, and twisting the corer by hand in the inner zone. All corers were equipped inside with a PVC tube. Cores were dissected into 5-cm slices. Sieved sediment aliquots (0.063 mm nylon mesh) were analyzed for dry weight (105ºC), total metal concentration (hot nitric acid digestion under high pressure), and nonresidual metal concentration (1N HCl extraction)

Correspondence to: R. Barreiro

(Barreiro 1991). The total concentration analytical procedure was controlled by parallel analyses of certified reference material (estuarine sediment-MESS 1, National Research Council of Canada). Recoveries were >95% for Zn, Cu and Pb, and >65% for Fe and Mn. A lower recovery for Fe and Mn was expected since the digestion procedure did not include hydrofluoric acid. Grain size distribution was analyzed by sieving and settling after H_2O_2 digestion.

RESULTS AND DISCUSSION

Although eight core samples were collected, this paper is restricted to only two of them: one from the outer zone and another from the inner one. Both were selected seeking a longer timescale and better resolution since they were the longest profiles (55 and 50 cm respectively). Sedimentological analysis of the cores showed remarkable differences in the sedimentation rates between both zones (Vilas et al. 1989). It is highly probable that both cores span over different time periods.

Both cores showed different enrichment levels (Fig. 1). Zinc, Ni and Cu concentrations in the inner zone core were consistently higher than in the outer zone sample. Iron showed a less pronounced difference, while Mn was almost identical in both cores except for the surficial layer. Trace metal concentrations never yielded similar values, even for the supposedly older layers, contrasting with observations from other studies (Håkanson et al. 1989; Mueller et al. 1989). This fact reflects the close relationship between sediment composition and its heavy metal carrying capacity. Such relationship was previously noticed for surface sediments (Barreiro 1991). A greater marine influence in the outer zone yields sediments with higher carbonate content and lower amounts of metal-reactive components (clay minerals, mainly). Establishing background values based on deep (nonpolluted) sediment layers must account for this effect of the sediment composition when comparing heterogeneous sediments as those from estuaries. Geochemical normalization has sometimes been used to improve the comparability of metal concentrations in sediments of different textures or different composition (Allen and Rae 1986; Pardue et al. 1988). We tried total iron concentration as a normalizing parameter without satisfactory results. Iron´s normalizing action is probably inadequate to account for the effect of other sediment variables (i.e., organic matter).

Manganese and Zn were the only elements clearly increasing towards the water/sediment interface in both samples. This feature was less pronounced for Cu in the outer zone profile.

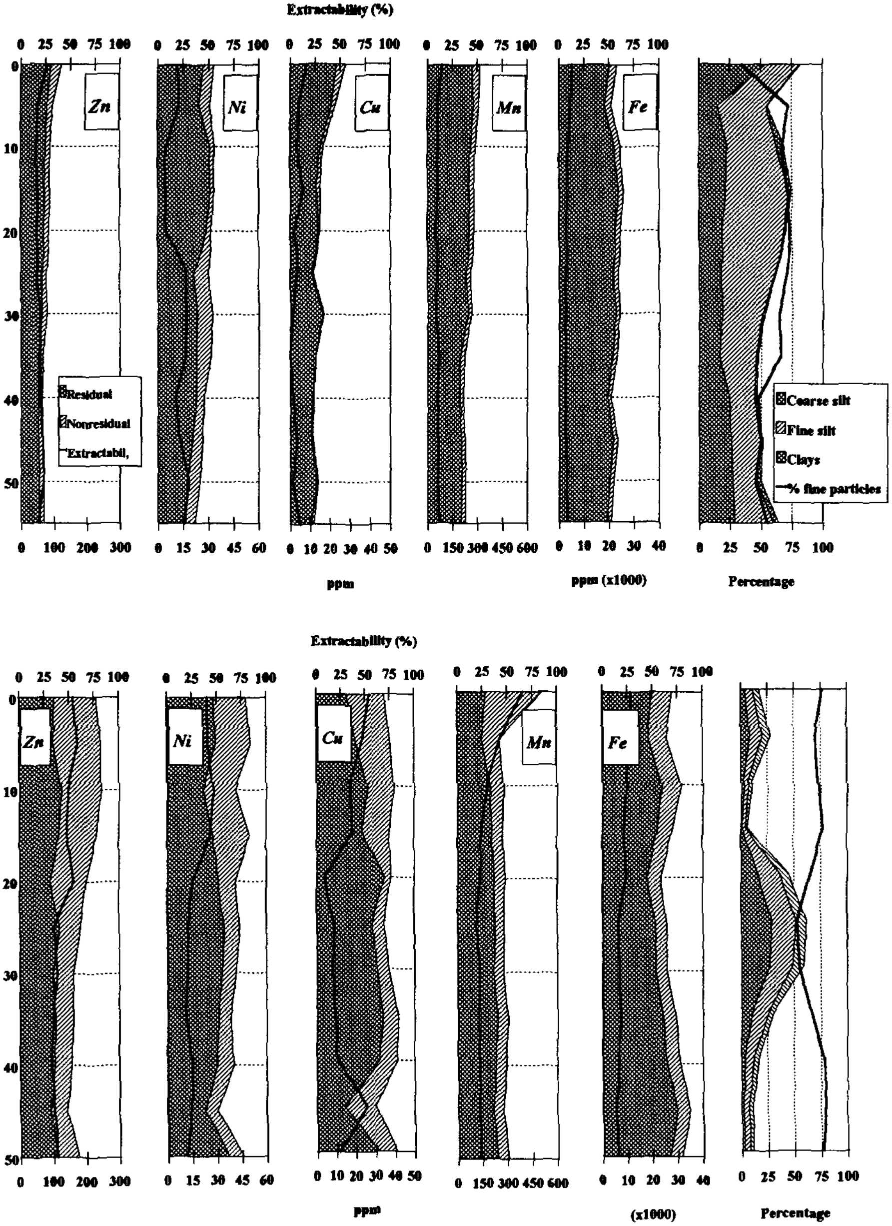

Figure 1. Outer (*top*) and inner (*bottom*) zone metal profiles. Residual (dark grey area) and nonresidual (light grey area) concentrations in ppm (*bottom axis*), extractability (line) in percentage (*top axis*), and depth (*vertical axis*) in cm. Grain size distribution shown on the right for each profile. Percentage of fine particles (line) refers to the portion of fine material (clays + fine silts) in the analyzed sample (clays + fine silts + coarse silts).

Metal enrichment was of a small consequence in the outer core (about 40 ppm Zn, 50-80 ppm Mn, 12 ppm Cu). Extractability (percentage of total metal extractable by 1N HCl) remained fairly constant along the core and lower than 25% for all the elements analyzed, indicating that no change in sediment composition could be detected, at least for metal-reactive compounds (i.e., organic matter, Fe and Mn oxides).

The enrichment profile was more pronounced in the inner zone sample for Zn and Mn. Zinc showed elevated total concentrations in the upper 20-cm, while Mn enrichment affects only the uppermost 5-cm. Manganese enrichment in the uppermost layer was due exclusively to the easily leachable fraction, in accordance with previous observations (Presley et al. 1980; Morris and Kwain 1988; Brügmann and Lange 1990). The profile of Mn in the inner zone typically corresponded with a postdepositional upward migration (Davison 1982). Manganese would be released from deeper reduced layers, precipitating at the oxic-anoxic interface.

Zinc enrichment also paralleled a change in extractability yielding a residual fraction constant throughout the whole core. Nickel and Cu extractabilities underwent a similar trend while their total concentrations remained nearly unchanged. In fact, Cu showed a slight inverse relationship between extractability and residual concentration. Cu concentration remained uniform along the core while Zn and Ni increased in the upper 25-30-cm (about 80 ppm for Zn and 10 ppm for Ni). Both the parallel change in copper´s extractability without a total concentration enrichment and the minimum magnitude of Ni enrichment suggest that the Zn enrichment profile could be due to differences in sediment type along the core and not to an increase in recent metal inputs to the estuary. Grain-size distribution does not seem responsible for this change since it follows a quite different pattern. However, it suggests a high variability in the characteristics of the particles settling over the time recorded by the core. Two big dams have been built in the Eume River (main source of freshwater and fluvial particulate matter to the estuary) in the last 25 years. They have brought about a decrease in the amount of suspended fluvial matter as well as change towards finer particles in its grain-size spectrum (Vilas et al. 1989). Also, the influence of postdepositional mobility of heavy metals cannot be excluded. Ridgway and Price (1987) showed that the present distribution of metals in sediments can be controlled by organic matter diagenesis, especially where Mn and Fe are not prevalent. Sediment organic matter differed greatly between the inner and the outer zones. Lost on ignition (an estimate of the sediment organic content: weight lost by a dried sediment aliquot after ashing at 400ºC for 6 h) ranges from 5.4% to 13.8% in the inner zone surficial sediments, while outer zone ones only showed values from 1.2% to 8.4% (Barreiro 1991). Such differences could partly explain the different enrichment levels observed in both zones as well as the different chemical behavior of trace metals within the profiles. Heavy metal chemistry could be more dependent on the organic matter diagenesis in the inner zone yielding enrichment profiles (Zn) enhanced by a postdepositional upward migrations.

In conclusion: (a) it is not possible to establish a background value for the whole estuary based on deep sediment layers since the composition and origin of the sediment seem to significantly influence its metal concentrations. (b) Inner zone sediments show clear signs of diagenetic remobilization of Mn yielding high levels in the uppermost oxidized layers. (c) The increase in Zn and Ni measured in the more recent sediment layers of the inner zone could be due to a change in the characteristics of the particles settling in this part of the estuary and not to an increase of the metal inputs to the estuary. Diagenetic mobilization could also have had some effect on the enrichment and metal extractability changes recorded. It is clear, however, that the enrichment of these metals was of minor importance.

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