

SELECTIVE EXTRACTIONS OF HEAVY METAL IN THE SEDIMENT OF THE CONA MARSH

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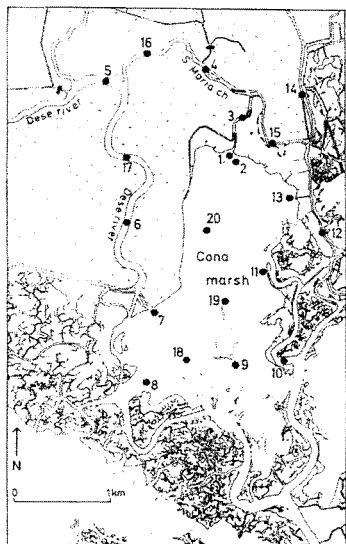


Fig.1. Map of Cona Marsh. Sampling sites are indicated.

- 1) Interstitial water and exchangeable metal (GPH1), by 1M deaerated ammonium acetate solution at pH=7 for 2 h.
- 2) Metal bound or specifically adsorbed to carbonates (GPH2), by 1M deaerated ammonium acetate solution adjusted to pH = 4.8 with acetic acid, for 6 hours.
- 3) Metal bound to Fe-Mn oxides (GPH3), by 0.04 M hydroxylamine hydrochloride in a 25% (v/v) acetic acid solution at 96°, for 6 hours.
- 4) Metal bound to organic matter and sulfides (GPH4), by 0.02 M nitric acid and 30% hydrogen peroxide at about pH=2 at 96° for 5 hours, and then at 25°C for 30 minutes after addition of 3.2 M ammonium acetate in 65% nitric acid diluted 1:4.

Concentration in leachates for eight metals were determined by atomic absorption spectrophotometry, and calculated on a dry weight basis. The grain-size distribution was also determined in the samples - after organic matter removal by oxidation with hydrogen

peroxide - to permit a comparison with metal distribution for each GPHs. Volumetric percentages in 15 diameter classes, that correspond to one-half phi interval, in the $0.7 < d < 125 \mu\text{m}$ range were recorded by a Microtrac laser particle analyzer. The spatial distribution of the sum (Σ) of the four GPHs concentrations well reproduces the previously observed spatial distribution of total anthropogenic heavy metals in the marsh. Heavy metal partitioning generally differs from site to site. The coefficient of variation $CV = (GPH_s^* / \Sigma) / \sigma$ - where the numerator is the percentage concentration in the s-th phase referred to Σ - ranges in fact from 0.17 for Cu in GPH4 to 1.27 for Cd in GPH1. Nevertheless, the partitioning obtained with the average percentage in the 20 sites (Fig.2) may be considered sufficiently representative of the metal-sediment association in the whole marsh. Cd, Cr, Cu, Fe and Ni have a percentage lower than 1.0 in the interstitial water and exchangeable phase, while Pb (1.2%), Zn (2.0%) and Mn (5.6%) show significant values. These three metals also have a noticeable concentration associated to carbonates, particularly Mn and Pb which account for about 60% and 50% respectively; Cd is well represented (29%) while percentages of the other five metals are around 10. Fe-Mn oxides (GPH3) represent the principal association phase for Cd, Cr, Ni and Zn. About 78% of the Cu is in the GPH4, as it may be expected because of its strong affinity with organic matter. GPH4 also comprises about 40% of Fe, Ni and Cr, and from 10% to 20% of the remaining four metals; a significant part of these concentrations could be associated to sulfides (ZONTA *et al.*, 1993). The comparison between grain-size and metal spatial distributions emphasizes the role of finer particles for the accumulation of contaminant in the marsh sediment. Fig. 3 reports, as an example, the regression between Zn in GPH3 and particle content in the size interval $1.4 < d < 31 \mu\text{m}$. To a greater presence of finer particles in the sediment a higher metal concentration corresponds, evidencing the role of oxide coatings - that are generally present onto finer particles - as metal ligand. Fig. 3 also permits to show identify a zoning of the marsh with respect to either metal accumulation and finer particle content, with an increasing trend from the southern (S) to the central (C) and to the northern (N) zones and maxima in the correspondence of the zone dominated by the fresh water input (F).

REFERENCES

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Based on the results of a previous research on total anthropogenic heavy metal and grain-size distributions (ZONTA *et al.*, 1994), a sediment sampling was performed in the Cona Marsh (Venice Lagoon, Italy) to acquire a detailed description of metal accumulation and partitioning by a selective extraction sequence. The marsh (Fig. 1) is the shallow water estuarine system of the Dese River, one of the main tributaries of the lagoon basin. Morphology, tidal exchanges and the discharge of fresh water renders it a spatially diversified ecosystem with a complex hydrodynamical behaviour. Surface sediment samples (5 cm long) were collected by a syringe-type corer in the 20 sites indicated in Fig. 1, and immediately transferred in pyrex bottles containing the first extractive solution. In order to limit perturbation in the metal partitioning, the contact between the sample and atmospheric oxygen was avoided until the third extraction were performed. The adopted extraction sequence provided metal concentrations (GPHs) in four geochemical phases, as indicated in the following scheme :

1) Interstitial water and exchangeable metal (GPH1), by 1M deaerated ammonium acetate solution at pH=7 for 2 h.

2) Metal bound or specifically adsorbed to carbonates (GPH2), by 1M deaerated ammonium acetate solution adjusted to pH = 4.8 with acetic acid, for 6 hours.

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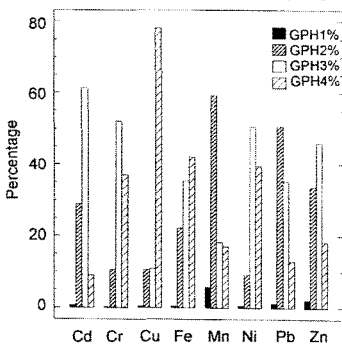


Fig. 2 Average partitioning of metals in the marsh.

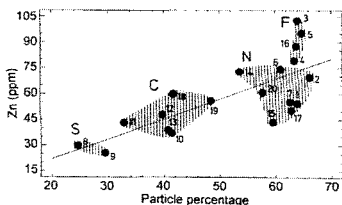


Fig. 3. Regression between Zn in GPH3 and particle content in the range $1.4 < d < 31 \mu\text{m}$. The marsh zoning is indicated.

peroxide - to permit a comparison with metal distribution for each GPHs. Volumetric percentages in 15 diameter classes, that correspond to one-half phi interval, in the $0.7 < d < 125 \mu\text{m}$ range were recorded by a Microtrac laser particle analyzer. The spatial distribution of the sum (Σ) of the four GPHs concentrations well reproduces the previously observed spatial distribution of total anthropogenic heavy metals in the marsh. Heavy metal partitioning generally differs from site to site. The coefficient of variation $CV = (GPH_s^* / \Sigma) / \sigma$ - where the numerator is the percentage concentration in the s-th phase referred to Σ - ranges in fact from 0.17 for Cu in GPH4 to 1.27 for Cd in GPH1. Nevertheless, the partitioning obtained with the average percentage in the 20 sites (Fig.2) may be considered sufficiently representative of the metal-sediment association in the whole marsh. Cd, Cr, Cu, Fe and Ni have a percentage lower than 1.0 in the interstitial water and exchangeable phase, while Pb (1.2%), Zn (2.0%) and Mn (5.6%) show significant values. These three metals also have a noticeable concentration associated to carbonates, particularly Mn and Pb which account for about 60% and 50% respectively; Cd is well represented (29%) while percentages of the other five metals are around 10. Fe-Mn oxides (GPH3) represent the principal association phase for Cd, Cr, Ni and Zn. About 78% of the Cu is in the GPH4, as it may be expected because of its strong affinity with organic matter. GPH4 also comprises about 40% of Fe, Ni and Cr, and from 10% to 20% of the remaining four metals; a significant part of these concentrations could be associated to sulfides (ZONTA *et al.*, 1993). The comparison between grain-size and metal spatial distributions emphasizes the role of finer particles for the accumulation of contaminant in the marsh sediment. Fig. 3 reports, as an example, the regression between Zn in GPH3 and particle content in the size interval $1.4 < d < 31 \mu\text{m}$. To a greater presence of finer particles in the sediment a higher metal concentration corresponds, evidencing the role of oxide coatings - that are generally present onto finer particles - as metal ligand. Fig. 3 also permits to show identify a zoning of the marsh with respect to either metal accumulation and finer particle content, with an increasing trend from the southern (S) to the central (C) and to the northern (N) zones and maxima in the correspondence of the zone dominated by the fresh water input (F).