

# RIA FORMOSA

## Challenges of a coastal lagoon in a changing environment

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# 7. Metal contamination in Ria Formosa saltmarsh sediments and halophyte vegetation

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Coastal saltmarshes may be defined as areas bordering saline water bodies vegetated by vascular plants (Box 7.1) such as herbs, grasses or low shrubs (Adam, 1990).

Saltmarsh vegetation may retain certain substances from anthropogenic activities in surrounding areas, providing a control of contaminants such as heavy metals, coming from industry, agriculture and urbanization. In the last decades there are been an increase in urbanization and industrialization of the area surrounding *Marim – Ria Formosa*, where this study was performed (Figure 7.1), focused on the metal contents in sediments and in its distribution among *Spartina maritima* and *Sarcocornia fruticosa* organs.

## Box 7.1. What is halophyte vegetation?

Saltmarsh vascular plants are denominated halophyte vegetation due to the resistant to the high levels of salt to which are subject.



**Figure 7.1.** Location of study area, *Marim – Ria Formosa*.

## 7.1. Metals - contamination and toxicity

Soil contamination by metals differs from air or water pollution, because trace metals persist in soil much longer than in other compartments of biosphere (Padmavathamma and Li, 2007) moreover metals tend to be retained more strongly in wetland soils compared with upland soils (Gambrell, 1994). Trace metals rapidly sorb to particulate matter and accumulate in fine-grained sediments of saltmarsh environments, and persist for long periods of time in benthic habitats. Therefore, sediments represent a major repository for trace metals which may be later remobilized to the water column, the concentrations of trace metals are three to five orders of magnitude greater in the bottom sediments of estuaries than in overlying waters (Kennish, 2001).

Anthropogenic inputs substantially augment natural loads and, in some industrialized and urbanized coastal systems, can exceed natural concentrations by orders of magnitude. Included here are such diverse sources as municipal and industrial wastewater discharges, leaching of antifouling paints, dredged material disposal, combustion of fossil fuels, mining of metal ores, smelting operations, refining, electroplating and the manufacture of dyes, paints and textiles. Periodical tidal flooding of saltmarshes provides large quantities of these pollutants to the marsh ecosystem (Reboreda & Caçador, 2007). Biological and geochemical processes as well as tidal cycles control the distribution and behaviour of trace metals. Trace metals pose a significant threat to organisms because above threshold availability, act as enzyme inhibitors. Biota exposed to elevated trace metal concentrations often experience serious physiological, reproductive and development changes (Kennish, 2001).

## 7.2. Sediments and halophyte vegetation

Halophytes that colonize salt marshes have ability to withstand a sediment environment characterized by high salinity and have a well-developed aerenchyma system through which atmospheric oxygen is transported from the leaves to the roots. The oxygen not consumed by root respiration is available for diffusion into surrounding sediment, promoting change of chemical properties, mainly redox status and pH, which condition the availability of trace metals. In addition, the solubility and availability of metals in marshes, in general, and for vegetation in particular, may be affected by other factors, such as concentration and speciation of metals. The characteristics of the sediment are also of major importance, including the grain size, organic matter content, biotic aspects, concentrations of inorganic and organic ligands including plants exudates, cation exchange capacity, etc.

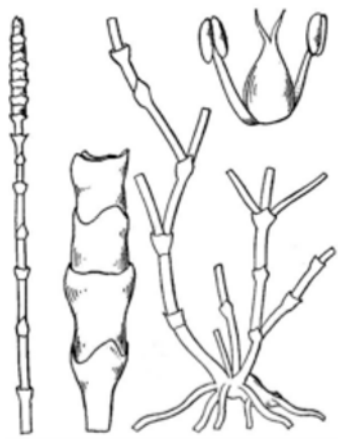
Therefore, mutual interactions between plants and surrounding chemical environment which determine the role-played by plants on trace metal distribution and uptake, may vary among plant species and, for a single plant, among locations with different characteristics.

According Padinha et al., (2000) the dominant producer of the lower salt marshes in Ria Formosa is the small cordgrass *Spartina maritima* (Poales: Poaceae), which is a pioneer specie in the lower marsh areas with a typical zonation forming clear homogeneous stands (Figure 7.2). *S. maritima* is an European cordgrass which has an important role as a primary colonist of intertidal mud flats since it is able to trap and stabilize sediment efficiently, thus facilitating successional development. Its upper limit is typically by subsequent invasion of *Arthrocnemum perenne* (Castillo et al., 2000). In SW Iberian Peninsula *S. maritima* dominates many lower marshes with anoxic sediment exposed to high inundation periods (Castillo et al., 2008). *Spartina* marshes are among the most productive ecosystems in shallow coastal marine environments (Barnes & Hughes, 1995). Nitrogen fixation associated with the roots and rhizomes of *S. maritima* was 41-650-fold higher than in the bulk sediment (Nielsen, et al., 2001). Early studies (in the 1960s) indicated that a *Spartina* marsh in Georgia, was calculated to export 14 kg ha<sup>-1</sup> of organic matter per tidal flushing during periods of spring tide and 2.5 kg ha<sup>-1</sup> during neaps (Barnes & Hughes, 1995).



**Figure 7.2.**  
Illustration of *Spartina maritima* (M. A. Curtis) Fernald.

In the upper *Marim* saltmarsh *Sarcocornia fruticosa* (Caryophyllales: Chenopodiaceae) appears in pure stands normally with less reducing sediments (Padinha et al., 2000; Moreira da Silva et al., 2015) (Figure 7.3). However this high marsh can presents *S. fruticosa* associated with *Halimione* sp. and *Atriplex* sp.. This association reflects the high values of salinity of the lagoonal water throughout the year (35 g/kg) which results from a semiarid precipitation regime and an extremely high renewal rate (80 % and 52 % in spring and neap waters, respectively) every tidal cycles (Andrade et al., 2004). In Family Chenopodiaceae was developed succulence of organs as a mechanism of salt tolerance, with the aim of balancing out ion toxicity created in saline conditions by increasing the total plant water content. As a result of increased growth on the cell size in succulent tissue, a large accumulation of salts is found without any high increase in intracellular salt concentration. The succulence can be expressed in direction of increase in cell size, decrease in extension growth and reduction in surface area per volume tissue. These halophytes accumulate therefore big amounts of salts through their shoots and show the highest degree of succulence (Grigore & Toma, 2007).



**Figure 7.3.**  
Illustration of *Sarcocornia fruticosa* (L.) A. J. Scott.

The photosynthetic system CAM (Crassulacean Acid Metabolism) is strongly associated with succulence, and has the advantage not only the reduction in salt uptake but also the possibility of photosynthesis continuing when the plants are submerged by flooding tides and direct gas exchange to the atmosphere is temporarily curtailed, although there are intertidal halophytes with the  $C_3$  pathway (Adam, 1990).

### 7.3. Metal contents and distribution in sediments of saltmarsh

Non-vegetated sediment can be considered as a sandy sediment, characterized by low fine fraction (FF) in the first 15 cm (1.7-5.8 %), and increasing slightly to deeper layer (max. 12.7 at 30 cm). Aluminium concentration showed a minimum at 5-10 cm, maybe due to the sand transported from nearby clam-culture grounds by tidal currents. The Al content co-varies with the percentage of FF in the sediment at a significant level ( $[Al] = 8 \pm 4 [FF] - 23 \pm 14$ ;  $r = 0.776$ ; Tukey test,  $p < 0.005$ ). Sediments with high clay content (very fine) have higher aluminium content (aluminosilicates) and, usually higher metal concentrations due to the negative charges of the clay particles. The evolution in the last years of levels of Manganese (Mn), Zink (Zn), Copper (Cu), Chromium (Cr), Nickel (Ni), Lead (Pb), Molybdenum (Mo), Cadmium (Cd) and Silver (Ag), in sediments of *Marim* saltmarsh from surface to 30 cm of depth, showed in surface sediment lower metal contents than deeper, except for Ag, Cd and Mo (Moreira da Silva et al., 2015). This is suggesting the remobilisation of these elements from sediments to water column with the flood tide (Roychoudhury, 2007). The environment at sediment surface is always oxidant, which prevents for instance the formation of metal sulphides that in some cases are unsolvable species. Other possibility is the occurrence of metals downward diffusion into the sediment.

Surface level of Pb observed was higher than those found before in other Ria Formosa sampling areas, not far from *Marim*, indicating the presence of new Pb sources in this area. Industrial plants sited in the surrounding area, like those manufacturing batteries and paints, welding operations, ceramic paints, may be possible sources of Pb, because the effluents of the respective waste water treatment plants are discharged into the *Ria Formosa* with run-off waters. Silver, which was studied by the first time in *Ria Formosa*, presented relatively low levels, between 0.12 and 0.21 mg g<sup>-1</sup>, depending on the deep. Levels of Mn, Zn, Ni and Cr seemed to have decreased in the last decade while those of Cu and Cd kept approximately constants. The levels of Pb surpassed the respective Effects Range Low being lower than Effects Range Median (Long et al., 1995), indicating that harmful toxicological effect might occasionally occur. According to the Portuguese classification (DR, 2007), the sediment of *Marim* can be considered as trace/lightly contaminated by Pb, Cr and Ni.

### 7.4. The role of *Spartina maritima* and *Sarcocornia fruticosa* on metal distribution in saltmarsh

#### ***Rhizosediments - characteristics and metals contents***

Rhizosediment of *S. maritima* was the richest in organic matter, particularly in the first 10 cm depth. In contrast, *S. fruticosa* displayed organic matter depth profile and magnitude rather like that non-vegetated sediments. Enrichment in organic matter at rooting sediment has been usually found (e.g. Caçador and Vale, 2001) and is understandable. Entanglement of roots can act as a trap of small and muddy particles from the surrounding sediment, which flows into the rhizosphere of the plants with water during tidal movements. In addition, dead above- and belowground biomass from plants and dead microorganisms that lived in symbiosis with plants may give also an important contribution for the enrichment of rhizosediments in organic matter, namely humic substances, which have high capability of sorption of trace metals, as well as organic and organometallic chemical species. Nevertheless, this study showed that as organic matter trapper and/or producer *S. maritima* was much more efficient than *S. fruticosa*. Rhizosediment of *S. maritima* was the poorest in silt and clay particles (grain size < 0.063 mm diameter) and, again, only small differences in terms of grain size depth distribution were observed between rhizosediment of *S. fruticosa* and non-vegetated sediment. On the other hand, levels of Si were much

lower in rhizosediment of *S. maritima* than in the other two sediments. The highest Si levels occurred in non-vegetated sediment, the same being observed for Al. However, on the contrary to that happened for Si, *S. maritima* rhizosediment displayed higher Al levels than rhizosediment of *S. fruticosa* [rhizosediment of *S. fruticosa* ( $0.98 \pm 0.19\%$ ) < rhizosediment of *S. maritima* ( $1.76 \pm 0.33\%$ ) < non-vegetated sediment ( $4.26 \pm 0.72\%$ )]. Together these results indicated some significant differences (Tukey test,  $p < 0.005$ ) amongst the compositions of the sediments. Silicon and organic matter displayed opposite tendencies, which was expected, as Si predominates in sandy sediments whereas organic matter is mainly associated with muddy sediments. Such differences may result of a combination of natural and anthropogenic actions, like the dynamic of the lagoon, dredgings, and presence of specific saltmarsh plants, which condition the preferential retention of certain types of particles. Very distinct redox potential depth profiles were observed. Non-vegetated sediment was anoxic (or reductive). *S. fruticosa* rhizosediment presented positive and relatively high redox potential (oxidative sediment) and rhizosediment of *S. maritima* displayed redox potential in between the other two sites. The release of oxygen by roots can cause a decrease of pH in the rooting zone due to, for instance, sulphide oxidation ( $S^{2-}/SO_4^{2-}$ ) and  $Fe^{2+}/Fe^{3+}$  oxidation followed by  $Fe^{3+}$  hydrolysis. In the present case, rhizosediments displayed more acidic conditions than non-vegetated sediment, that is, lower pH values (*S. maritima*: 6.48, 0-5 cm; 6.60, 5-10 cm; 6.70, 10-15 cm depth; *S. fruticosa*: 7.07, 0-5 cm; 7.06, 5-10 cm; 7.02, 10-15 cm depth; non-vegetated: 7.60, 0-5 cm; 7.60, 5-10 cm; 7.70, 10-15 cm depth). These data confirmed results of previous studies, which have showed that more acidic conditions prevail in vegetated sediments than in non-vegetated areas (Caçador et al., 1996; 2000). In all cases some specific variations of redox potential with depth were observed, which are of difficult interpretation. However, it seems clear that the marsh plants could oxidize their rhizosediment in different ways. Visual inspection during sampling showed that main active belowground biomass of *S. maritima* was confined in the first 10 cm depth. In the case of *S. fruticosa* rhizosediment, were observed inorganic precipitates forming rhizoconcretions below 15 cm, which is compatible with the presence of active biomass capable of oxidize the rhizosediment. In addition, *S. fruticosa* showed to have much higher oxidative power than *S. maritima*. Reductive sediment among roots of *S. maritima* and oxidative sediment among roots of *Halimione portulacoides* (another Chenopodiaceae) have been also reported by Reboreda & Caçador (2007) for *Tagus* estuary saltmarsh. The presence of halophyte species changes metal concentration of sediment among roots and that influence is very specific, depending on the plant specie. Much higher level in non-vegetated sediment occurred for Cd: non-vegetated sediment > (5 times higher than) *S. maritima* sediment  $\approx$  *S. fruticosa* sediment (except for depth > 15 cm, where the levels were a little bit high, but still lower than in non-vegetated sediment). Not so drastic differences but still significantly lower levels in rooting sediments of both plants were also found for Mn (only for depth > 10 cm). For other metals, like Cr and Pb, significant and marked differences between rooting sediments of the two plants were observed: metal levels in sediment colonized by *S. fruticosa* were lower than those founded in both non-vegetated and *S. maritima* sediments. Iron occurred in much higher concentrations in rooting sediment of *S. maritima*, whereas *S. fruticosa* rhizosediment displayed levels identical to those of non-vegetated sediment. Significant influence of the plants was not observed for Ag and Mo levels, whereas Zn occurred in much higher concentration in rooting sediments of both plants than in non-vegetated one. Significant differences were found for metal concentrations in depth between non-vegetated sediment, rhizosediment of *S. maritima* and rhizosediment of *S. fruticosa*, except for Cu and Mo.

### **Metals in Biomass of *S. maritima* and *S. fruticosa***

Most of metals coming from surrounding areas to saltmarsh are accumulated in roots of both halophyte species, and also in rhizomes of *S. maritima*. There are significant differences (*Student t-test*,  $p < 0,05$ ) in metal

concentrations between below- and aboveground parts for all studied metals except for, Fe and Mn in *S. fruticosa* and for Mn in *S. maritima* (Box 7.2).

Enrichment factors higher than 1 have supported the idea that saltmarshes can act as metal phytoestabilizers (Caçador & Vale, 2001; Caetano et al., 2008) thus contributing for decreasing ecosystem metals availability. In *Marim* saltmarsh EF were higher

than 1 for Ag, Cd, Mo, Cu, Pb, and Zn, for both halophytes. *S. maritima* displayed lower EF than *S. fruticosa* for Cr, Ni, Zn, Al and Fe and higher for Cu and Pb. Differences in chemical speciation of the different elements, physico-chemical characteristics of the rhizosphere and biomass characteristics, all together

### Box 7.3. Why these two halophyte have behave differently in metals remediation?

Why these two halophyte have behave differently in metals remediation? *S. maritima* is a monocotyledonous and *S. fruticosa* is a dicotyledonous, having unlikeness in density and structure of belowground biomass and biological response, these differences in the plant characteristics influence their role in metals remediation.

magnitude of translocation for Fe and Mn was very much distinct of that for the remaining studied metals. Iron in aerial organs is closely related to chlorophyll formation and all plants have iron-containing enzymes (Almeida et al., 2005).

Manganese is an activator of a number of enzymes involving in the tricarboxylic acid cycle.

### Box 7.2. How to evaluate the ability for phytoremediation?

To evaluate whether plants can accumulate trace metals in belowground biomass, enrichment factors (EF) can be calculated,  $EF = \text{Metal concentration in belowground tissues} / \text{Metal concentration in rhizosediment}$ .

will condition the observed results. For instance, *Sarcocornia fruticosa* removed Cr from sediment to roots at all depths, while *S. maritima* didn't show the same behaviour (Moreira da Silva et al., 2015) (Box 7.3).

Once inside the plants, metals can be translocated from belowground vegetal tissues to the aerial organs, leaves and stems for *S. maritima* and chlorophyllin and non-chlorophyllin organs for *S. fruticosa* (Figures 7.4 and 7.5).

Metal translocation (Box 7.4) to both kinds of aboveground organs was significantly higher in *S. fruticosa* than in *S. maritima*, for all metals. The

### Box 7.4. Is the metal translocation a relevant information to phytoremediation?

Metal translocation to aboveground tissues may be very valuable for phytoremediation of areas where the plants can be cultivated and harvested, thus removing the pollutant from the soil or sediment.



**Figure 7.4.** Metal distribution (%) among the roots, rhizomes, stems, and leaves of *S. maritima* (Photo by Nuno Serrano, 2011).



**Figure 7.5.** Metal distribution (%) among the aerial chlorophyllin and non-chlorophyllin organs, and roots of *S. fruticosa* (Photo by Nuno Serrano, 2011).



There are few studies on the capacity of saltmarsh species to accumulate and translocate Ag to aboveground tissues. Further efforts are needed to study the Ag uptake by other plants, having in mind the possibility of using phytoremediation for cleaning Ag contaminated sediments. Silver residues may occur as a result of some industrial activities, such as photographic films and paper, batteries, mirrors, photosensitive glass, etc.

Previous studies (Reboreda & Caçador, 2007) about Cu, Cd, and Pb, concluded that areas colonized by *Halimione portulacoides* (also from Chenopodiaceae family) are potential sources of metals to the marsh

### **Box 7.5. How does metal translocation contribute to its phytoremediation in the saltmarsh?**

Metal translocation by halophytic vegetation, may result in a drawback for saltmarsh metal remediation. Metal in aboveground tissues may be accumulated in leaf and stem litter, returning to the marsh system and thus acting as a potential source of metals.

ecosystem, *S. maritima* seeming to contribute more effectively to the metal stabilization in saltmarsh sediment (Box 7.5).

During the last decades, wetland plants have been shown to play important roles in constructed wetlands to remove metals from wastewater. Therefore phytoremediation on wetlands can be considered an important type of ecosystem services to society, based on 'green' technologies and low energy consumption (Min et al., 2007; Rahmana et al., 2014).

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