



# *Salicornia* spp. as a biomonitor of Cu and Zn in salt marsh sediments



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## ARTICLE INFO

### Article history:

Received 24 July 2013

Received in revised form 5 March 2015

Accepted 10 March 2015

### Keywords:

Fal

Halophytes

Mine pollution

Plant sediment relationships

Metals

## ABSTRACT

Macroalgae in estuarine and coastal waters, in contrast to vascular salt marsh plants, have previously been utilised as biomonitors of sediment-held metals. The colonising halophyte *Salicornia* spp., however, occurs in both mudflats alongside macroalgae, as well as in association with salt marsh vascular plants. The present research aims to determine the relationships between fluctuations in sediment-held metals and those in *Salicornia* spp. over the course of a growing season. Samples of the species and corresponding underlying sediment were collected from the metal mine-polluted Restronguet Creek of the Fal Estuary, Cornwall on a monthly basis between March and November, 2000. Oven-dried sediment and vegetation samples were analysed for total Fe, Cu, Zn and Mn. Significant correlations with both the roots and aerial portion of the plant were found with sediment Cu and Zn concentrations. Significant relationships with either Mn or Fe were not observed. Thus, *Salicornia* spp. would appear to be a suitable tool for biomonitoring Zn and, particularly, Cu. Hyperaccumulation of Zn in the aerial portion during initial growth also indicates that *Salicornia* spp. may be useful for alleviating metal contamination through phytoextraction, whilst Cu in the roots is proposed as having potential for phytostabilization.

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## 1. Introduction

Certain metal species, such as Cu and Zn are required as nutrients by vegetation (Kabata-Pendias and Pendias, 1984). However, excessive metals generated by anthropogenic activities, such as mining, can result in toxicity. The impacts of mining are not limited to the immediate vicinity of the mining zone but, when carried by rivers and runoff, can extend to other environments, including estuaries (Álvarez Rogel et al., 2004). This may occur as the result of single pollution incidents, such as the mine tailing spill at Aznacollar, Spain, 1998, where elevated concentrations of metals were found in salt marsh vegetation six years after the incident (Álvarez Rogel et al., 2004). Alternatively, pollution may occur over a period of time as acid mine drainage in, for example, the abandoned Britannia Mine in Vancouver, Canada (Wilson et al., 2005). Coastal marshes are particularly sensitive to anthropogenic metal inputs, such as the ones resulting from present and post mining activities, since they are subject to little turbulent mixing combined with fragile substrates (Venosa et al., 2002).

*Salicornia* spp. exists in both areas of mudflat, alongside *Zostera* spp. and macroalgae, and in the upper salt marsh as a pioneer

species (Watkinson and Davy, 1985). This has been attributed to the ability to tolerate a wide range of climatic conditions, sediment types and water stress regimes (Davy et al., 2001). The upper limit of *Salicornia* spp. has been connected with invertebrate bioturbation (Gerdol and Hughes, 1993). However, in these upper reaches, *Fucus* spp. provided beneficial sites for germination (Costa, 1992). *Salicornia* spp. is limited landward due to being outcompeted by perennial species (Bertness et al., 1992). Germination occurs from March to May (Gerdol and Hughes, 1993), with a delay in growth until summer being attributed as a response to extreme conditions (Jefferies et al., 1979). McGraw and Ungar (1981) observed low dry weight gain from samples collected in April and June, despite germination having taken place. The aerial portion, however, had quadrupled in dry weight from 6 June to 14 August, although no measure was published between these dates. Anoxia and mechanical damage result in shallow rooting (Cooper, 1982), although Schat et al. (1987) found this had no significant impact upon survival and reproductive ability.

Vegetation can be regarded as a more appropriate tool than sediments for measuring contamination as plant–metal concentrations can reflect both chemical availability and bioaccumulation potential—both of which are toxicologically significant (Williams et al., 1994a). A substantial degree of research into vegetation relationships with metal contamination in estuarine and coastal waters using aquatic macrophytes has been attempted. Eelgrass (*Zostera marina*) and other submerged seagrasses (*Z. muelleri* and *Thalassia*

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*testudinum*) have been successfully utilised as metal-bioindicators for certain metals (Carter and Eriksson, 1992; Di Giulio and Scanlon, 1985; Lyngby and Brix, 1987a,b).

In salt marsh, Otte et al. (1991a) found that middle and upper marsh halophytes (*Spartina anglica*, *Bolboschoenus maritimus*, *Aster tripolium*, *Suaeda maritima*, *S. media* and *Triglochin maritima*) collected from metal-contaminated estuaries exhibited higher metal levels than those from less polluted areas. Similar findings have also been reported by Luque et al. (1999) and Cambrollé et al. (2008) for *Spartina* sp. Furthermore, species from the low marsh (*Z. noltii*, *Spartina maritima* and *S. densiflora*) were found to be higher in metal content than those of high marsh areas (*Anthrocnemum macrostachyum* and *Halimione portulacoides*) (Otte et al., 1991a). Vegetation was also found to be higher in concentrations for essential metals than non-essential. Other research has failed to establish such a relationship (Alberts et al., 1990; Padinha et al., 2000).

Although known to be highly salt tolerant, *Salicornia* spp. tolerance to heavy metals has been ill-studied (Rosso et al., 2005). *Salicornia* spp. present in the metal-enriched Restronguet Creek has been observed to accumulate high levels of Cu, Fe, Mn and Zn compared to results from the relatively uncontaminated Avon Estuary (Bryan and Gibbs, 1983). Metals concentrations in the roots exceeded levels present in aerial portions of *Salicornia* spp. However, metals in the sediments did not correlate with plant concentrations. *Salicornia* spp. from two salt marshes in Essex indicated that metals were generally lower in the plant in comparison with the associated sediments (Williams et al., 1994b), although Zn was observed to hyperaccumulate. Williams et al. (1994b) concluded that *Salicornia* spp. could not be utilised for biomonitoring of metals.

A ferric oxide/hydroxide precipitate, commonly known as iron plaque, envelops the roots of a number of wetland plants, including *Salicornia* spp. The presence of plaque may in turn immobilise other metal and metalloid species via co-precipitation (Hansel et al., 2001) or increase bioavailability through sequestration (Blute et al., 2004). Plants capable of accumulating metals within their root zone therefore reduce the bioavailability of metals within the system. Halophytes have been suggested as having good potential for this phytostabilization (Almeida et al., 2011; Cambrollé et al., 2012). Although the presence of iron plaque is subject to temporal variation, uptake of Cu, Zn and Cd into aerial portions by the halophytes *Sarcocornia fruticosa*, *S. perennis*, *H. portulacoides* and *Spartina maritima* was found to be non-seasonal (Caçador et al., 2009), suggesting a lack of influence of root plaque on metal uptake. Despite iron plaque being present in *Salicornia* spp., no observations have been undertaken on the seasonal cycling of metals on this species.

Halophytes are able to survive in saline environments due to physiological adaptations. Plants may exclude salt from their tissues. Many of these excluders restrict entry to the aerial portion whilst hyper-accumulating element(s) within roots (Thurman, 1981). Other accumulator species biomagnify salts within the aerial portion (Williams et al., 1994a) yet suffer no damage to essential processes. The ability of halophytes to survive in saline environments renders these species with an ability to survive in locations with high metal contamination (Mendez and Maier, 2008). Accumulator species, such as the salt marsh plant *H. portulacoides*, have been highlighted as having the potential for phytoextraction (Milić et al., 2012), that is, a remediation process where elements are concentrated in aerial portions, then removed to reduce soil contamination.

*Salicornia* spp. is a hyperaccumulator of salts and nutrients (Ozawa et al., 2009) in the aerial portion. Plots experimentally polluted with Ni, As and Cd produced a significant increase in these metals and metalloid in aerial tissues (Sharma et al., 2010). This

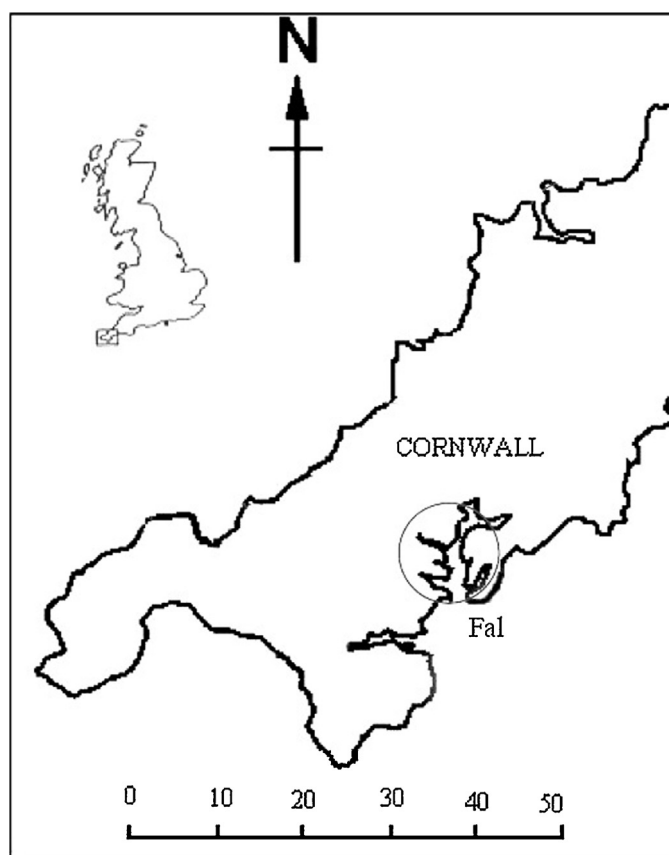


Fig. 1. The Fal Estuary, Cornwall, UK.

species, thus, has been suggested as having potential for phytoextraction purposes.

The primary aim of this investigation is to determine whether *Salicornia* spp. is a suitable candidate for biomonitoring fluxes in metal concentrations within sediments. Although salt marsh plants have generally proved unsuitable for biomonitoring, *Salicornia* spp. is of interest due to its successional position alongside species that have been recorded as biomonitors, such as *Zostera* spp., at the most seaward end of its habitat. By monitoring concentrations over a growing season, fluxes in Fe, Cu, Zn and Mn uptake will be examined, as will potential for phytoextraction, as previously suggested for a different suite of metals.

## 2. Materials and methods

The Fal Estuary (Fig. 1) has been receiving waste from deep mining for hundreds of years (Younger, 2002). Alluvial tin has, however, been recovered for several thousand years until recently (Bryan and Gibbs, 1983), whilst underground mining occurred during the nineteenth century (Dines, 1956). The catchment area of the Fal Estuary in the nineteenth century was considered the major world source of Cu, Sn and As (Bryan and Gibbs, 1983).

Restronguet Creek receives the outflow of the Carnon River, which drains the historical Cu and Sn mining districts served by the County Adit tributary (Bryan and Gibbs, 1983). The Carnon River receives around 50% (dependent upon seasonal variations) of its flow from the County Adit, which typically has a pH of less than 4 and exceptionally high metal loadings (Environment Agency, 1997). The drainage from old Cu mines provides a source of dissolved Cu, whereas drainage from Wheal Jane Sn mine is a source of dissolved Zn (Bryan and Gibbs, 1983). Other studies (Hosking and Obial, 1966; Pirrie and Camm, 1999; Pirrie et al., 2003) suggested

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