Heavy metals in sediments and halophytes of saltmarshes in the Marano and Grado Lagoon (Northern Adriatic Sea)

UNIVERSITÀ DEGLI STUDI DI TRIESTE

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Introduction and aim of the work

Saltmarshes are important constituents of transitional environments, where they provide several services to the ecosystem and are essential to the sedimentary budget (*Pethick, 1984*). On the other hand, they are subject to the effects of increasing human pressures, especially where anthropogenic activities occur. As a consequence, the accumulation of contaminated sediments (e.g., heavy metals) may affect these fragile environments (*Cacador et al., 1996*).
Plants living in saltmarshes often show their ability to accumulate heavy metals both in roots and shoots, thus providing a natural metal-extraction pathway useful for remediation activities.

The aim of this study was to evaluate the content of some heavy metals (As, Cd, Cr, Cu, Hg, Ni and Pb) of ecotoxicological importance (*WFD/2000/60/CE*) in sediments, rhizo-sediments and in plants (roots, shoots and leaves) from two selected saltmarshes located in the Marano and Grado Lagoon. Enrichment Factors (EF) and metal translocation from the belowground to the aboveground biomass were also considered.

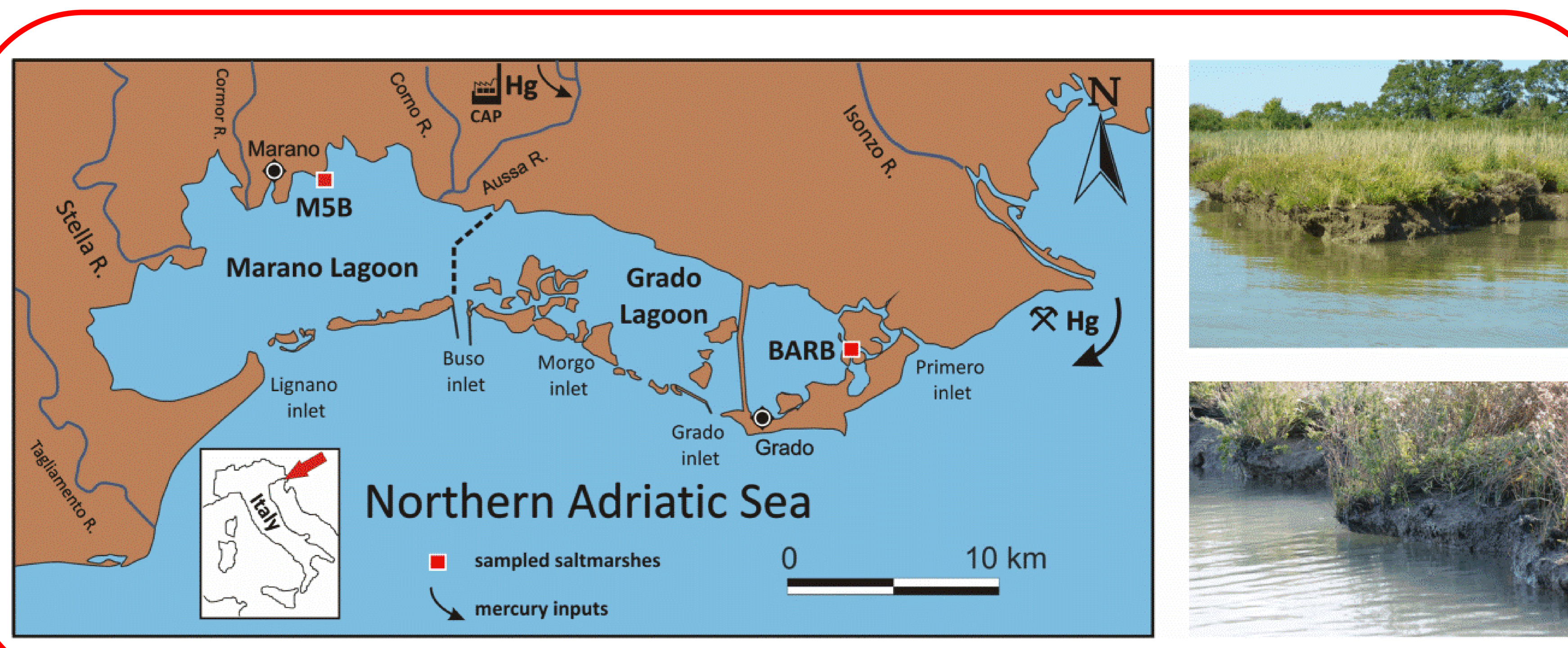

Fig. 1 – The Marano and Grado Lagoon study area. Saltmarshes core sampling sites are indicated.

Study area

The Marano and Grado Lagoon (Northern Adriatic Sea) is the second largest lagoon area of the Adriatic after Venice. The Lagoon is generally considered a well-preserved area where conservation of the natural environment must coexist with several human activities such as fishing, shipping and industries.
The main source of contamination in the Lagoon is represented by the inflow from the Aussa-Corno river system which is impacted by industrial discharges from several industries and is connected to the open sea by a navigable channel. Another source of contamination is given by the Isonzo River, the largest contributor of mercury into the northern Adriatic Sea since the 16th century, due to its transport of cinnabar (HgS) rich tailings from the Idrija (Slovenia) mining district (*Covelli et al., 2012*).

Field and laboratory work

Sampling operations took place in July 2011. Two saltmarshes were investigated: M5B in the Marano Lagoon and BARB in the Grado Lagoon. The saltmarshes differ for morphology and heavy metal contents and are representative of a highly impacted area (Marano Lagoon) and a moderately (except for high Hg contents) contaminated area (Grado Lagoon). In both saltmarshes, individuals of *Sarcocornia Fruticosa* and *Limonium Vulgare*, two of the most abundant halophytes in this environment, were considered.

- Shoot and leaves were collected in two selected saltmarshes
- Rizhosediment and sediment cores were manually collected by hand corer and subsampled on site; roots were separated fom sediments in lab
- Grain-size analyses (Malvern Mastersizer 2000 Laser Diffraction Particle Size Analyzer)
- Total C and N, organic C (CHN Perkin Elmer Elemental Analyzer)
- Trace elements (As, Cd, Cr, Cu, Mn, Ni, Pb, Zn) content were determined by ICP-OES following total digestion procedure in a closes microwave system
- Total Hg was determined by DMA-80 (Milestone)

Results and Discussion

The heavy metal content in the sediments was quite high at both saltmarshes. M5B was the most contaminated site, showing higher concentrations especially for As, Cd, and Pb (**Tab. 1**). On the other hand, Hg was highest in BARB. Such results reflect the different contamination history of the two areas: M5B is directly influenced by the industrial area that insists on the Marano basin, while BARB was affected by Hg contamination due to Hg -rich particulate matter inflowing from the Isonzo River.

***Tab. 1** – Metal concentrations in saltmarsh sediment*

TRACE METALS	M5B		BARB		EQS WFD 2000/60 EC
mg kg^{-1}	mean±sd	range	mean±sd	range	mg kg^{-1}
As	20.4±6.9	10.6-31.8	17.5±2.3	14.4-21.6	12
Cd	1.5±0.2	1.1-1.8	0.7±0.1	0.5-0.9	0.3
Cr	126±134	102-140	100±14	83-123	50
Hg	2.64±1.43	<lod-3.96	13.7±4.2	9.4-23.9	0.3
Ni	62.8±15.6	43.7-97.5	40.0±15.2	25.4-67.4	30

***Tab. 2** – Metal concentrations in plant tissue (in roots, values are the average calculated on the first 15 cm)*

plant	tissue	As	Cd	Cr	Hg	Ni	Pb	Zn
		mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}
Limonium vulgare	roots	18.1	1.64	4.73	0.57	6.79	7.31	47.5
	shoots	9.39	< 0.2	17.9	0.03	< 2	< 2	14
	leaves	9.5	< 0.2	3.38	0.08	< 2	2.58	23.1
Sarcocornia fruticosa	roots	30.1	0.87	69	2.36	15.6	24	131
	shoots	10.6	< 0.2	182	0.55	9.09	4.92	22.1
	leaves	8.77	< 0.2	2.38	0.08	< 2	1.98	12

***Tab. 3** – Metal Enrichment Factors in roots compared to rhizosediment*

Site	plant	EF_r (Min-Max)						
		As	Cd	Cr	Hg	Ni	Pb	Zn
M5B	*Limonium vulgare*	0.56-1.74	0.61-6.10	0.02-0.07	0.10-2.46	0.10-0.24	0.19-0.43	0.37-1.24
	Sarcocornia fruticosa	0.31-1.48	1.70-37.3	0.04-0.46	0.11-2.62	0.15-0.95	0.13-2.46	0.36-1.79
BARB	*Limonium vulgare*	0.73-1.41	0.38-4.86	0.03-0.08	0.03-1.83	0.12-0.32	1.65-0.35	0.30-1.30
	Sarcocornia fruticosa	0.90-2.56	nd-3.21	0.20-2.32	0.03-2.69	0.12-0.85	0.67-4.83	0.30-3.31

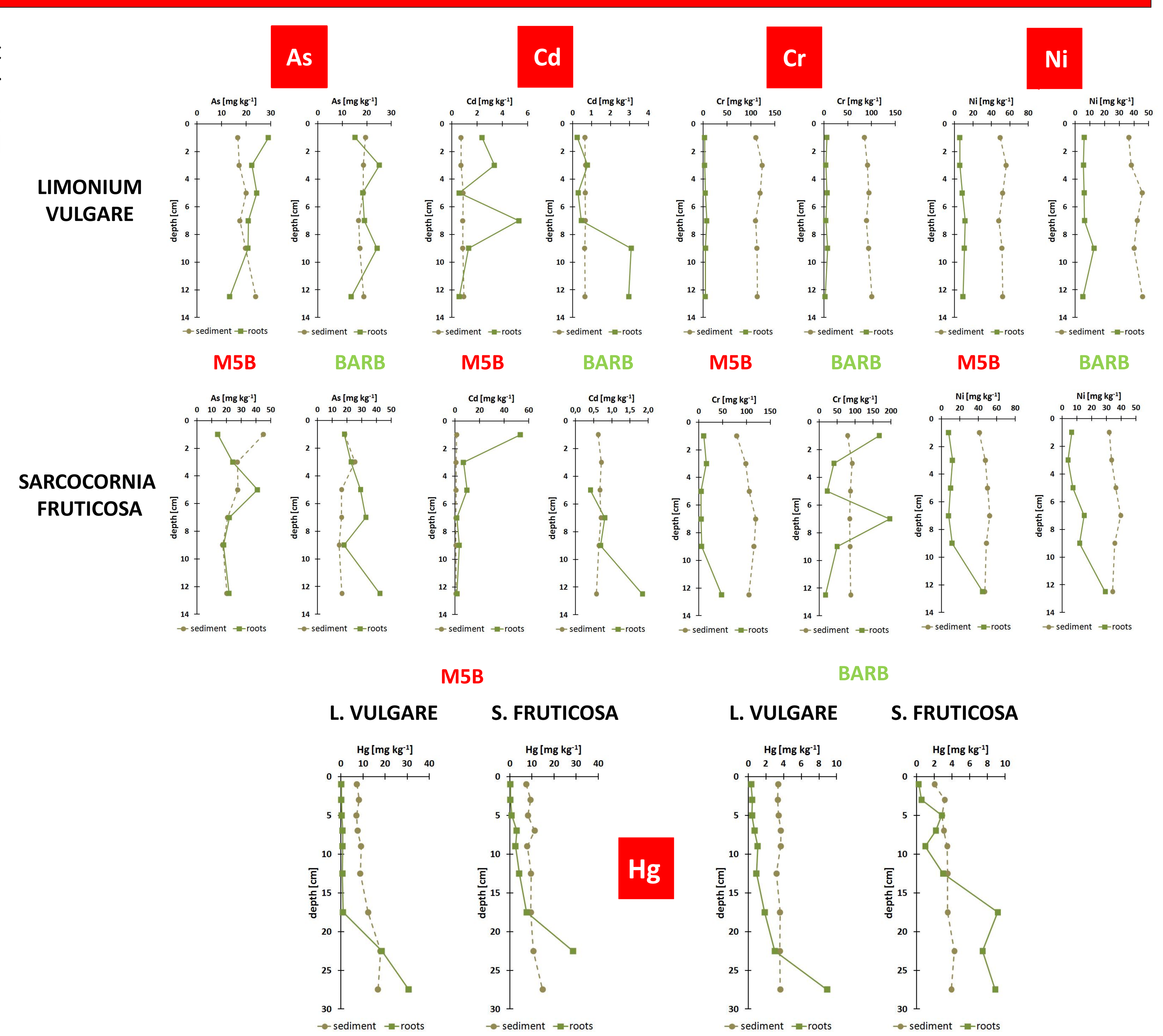

***Fig. 2** - Vertical concentration profiles for As, Cd, Cr, Ni and Hg in rhizosediments and roots of the halophytes S. fruticosa and L. vulgare in the Marano and Grado Lagoon saltmarshes (sites M5B and BARB).*

To evaluate metal accumulation in the plants, the Enrichment Factors (**EF = [metal]roots/[metal]rhizo-sediment**) were calculated (**Tab. 3**). In both saltmarshes, the halophyte vegetation showed accumulation (EF>1) of As and Cd, but not of Ni. *S .fruticosa* showed the greater bioaccumulation while M5B seemed to be a more favorable site for such processes, probably due to redox conditions in the sediment that enhance metal mobility. The translocation of metals from the halophytes' roots to their shoots and leaves was evident at both saltmarshes. Notably, at BARB, Cr in the shoot of *S. fruticosa* was particularly high (181 mg kg^{-1}) compared to its content in the roots (69 mg kg^{-1}) and rhizosediment (86 mg kg^{-1}). In *L. vulgare*, the Zn content in the leaves was almost double of that in the shoots and about a half of that in the roots. Zn is an essential element for plant physiology, playing a key role as enzymatic co-factor and, thus, its presence in the leaves is not surprising. No translocation was observed for Cd and Hg, and they appeared to be immobilized in the halophytes' roots.

Final remarks

The present study is the first attempt to investigate heavy metal content in the sediments and vegetation of the Marano and Grado Lagoon saltmarshes. The results showed that these areas can be considered as a sink (and a possible source) for several heavy metals. Halophytes showed the ability to absorb metals from the saltmarsh sediment and to accumulate them in the roots and/or translocate them to the aboveground biomass. Bioaccumulation varied with the species and the different environmental conditions, showing the highest efficiencies in *S. fruticosa* and in the industrially-impacted Marano basin.

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