

**METALS FROM HUMAN ACTIVITIES IN A COASTAL LAGOON SALTMARSH  
- SEDIMENT TOXICITY AND PHYTOREMEDIATION BY *Sarcocornia fruticosa***

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**Abstract.** Anthropogenic pressure on coastal areas has been increasing in the last decades, threatening the saltmarshes and the ecosystem services they provide. *Sarcocornia fruticosa* can have an important role in sequestration of metals from human activities. This study evaluated the effect of metal toxicity in saltmarsh sediment (measured by Ecological Risk Index-ERI) on *S. fruticosa* ability to metal (Cd, Cr, Ni, Pb and Zn) remediation (Enrichment Factor and metal translocation). The impact of urbanization was studied through the metal loads on stormwaters during two main rainfall events, and the industrial impact was assessed through data analyses in a saltmarsh area influenced by a stream that receives industrial runoffs. The *S. fruticosa* response on metal remediation was affected by ERI. In more polluted locations, retained metals on roots and prevented the most toxic (Cd and Pb) from reaching the aerial organs, avoiding tissues death and metal remobilisation to the saltmarsh. Meanwhile, in rhizosediments with conditions to high metal bioavailability, *S. fruticosa* transported Cd and Pb to aerial organs, but used the Zn translocation to decrease their toxicity. This halophyte resilience is important to saltmarsh metal sequestration in high toxicity conditions, and allows the maintenance of other ecosystem services, contributing to the environmental protection and public health.

**Keywords:** trace metals, ecological risk index, halophyte, phytoremediation, Ria Formosa.

#### AIMS AND BACKGROUND

Despite the increasing human pressure, due to urbanization, agriculture, industry, and tourism, saltmarshes are amongst the biosphere's most productive ecosystems, storing more carbon

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than farms and rain forests and providing many different services<sup>1,4</sup>. Located in a transition zone between land and sea, saltmarshes act as deposits for pollutants such as metals<sup>1,3</sup>, which are of priority control, as they are persistent and bioaccumulative inducing serious toxic effects<sup>5,6</sup>. Metals that enter in saltmarshes are strongly related to human activities from surrounding land uses, and can be used to assess the ecological risk caused by different discharges<sup>6,7</sup>. The Ecological Risk Index (ERI) was proposed to evaluate the toxic effects of the overall heavy metal assemblage in sediments, considering the sum of the potential risk of individual heavy metal<sup>6-9</sup>. The urban impervious surfaces are increasing and precipitation events are promoters of toxic pollutants and metals wash-off. During this events, metals such as Cd, Cr, Pb, Ni and Zn are transported by the stormwaters to saltmarshes<sup>5,10</sup> and interact with sediments through numerous processes, that affect metal mobility and bioavailability for biota, depending on sediment characteristics, namely, mineral composition, pH, Eh, and organic matter content<sup>6,11</sup>. Vegetation also can sequester metals in the sediment surrounding its roots (rhizosediment), and/or accumulate them on belowground and above organs, depending on the metal and species<sup>2,12-14</sup>. *Sarcocornia fruticosa* is a perennial halophyte that grows in upper-middle saltmarshes, and has ability to stabilize metals, mainly in roots and rhizosediments<sup>2,12,14</sup>.

The paper aims to evaluate the response of *S. fruticosa* to remediate metals (Cd, Cr, Ni, Pb and Zn) from different anthropogenic activities, using the ERI as an indicator of metal toxicity in saltmarsh sediments.

## EXPERIMENTAL

This study was carried out in the SW Coast of Iberian Peninsula, in Faro – Portugal, with about 61 117 inhabitants and a Mediterranean climate. The urban perimeter catchment is about 4.7 km<sup>2</sup> and presents 96% of impervious surface. Faro lays on the margin of the Ria Formosa (RF), a shallow coastal lagoon where *S. fruticosa* appears as a dominant species. Aiming to complete a previous study<sup>15</sup>, two main rainfall events were monitored, in January and March 2015. The samples for metal quantification were collected every 15 min during the first h, and every 30 min until the end of each event. Two weeks after the March rainfall event, we selected two sampling stations in the upper saltmarsh: Station A (37°00'36" N; 7°55'30" W) next to a main conduct for stormwater drainage; and Station B (37°00'27" N; 7°55'32" W) in an area without drainage conducts, under the influence of the city diffuse pollution, and subject to tidal flooding. To analyse the impact of local industry, was selected Station C (37°1'54.83" N; 7°8'44.52" W) nearby the spot where flows a stream that receives

industrial runoffs, in March 2007, at a time of great industrial activity<sup>16</sup>. Pure stands of *S. fruticosa* and non-vegetated areas were sampled at Stations A, B and C, during spring, in the growing season, and characterised the aboveground biomass in each sample station, clipping the plants at ground level. The 0-10 cm sediment layer was collected with the belowground biomass. Redox potential (Eh) and pH were determined *in situ* by electrometry, and at the laboratory, the plants and sediments were oven dried, weighed, ground with an agate mortar, and digested, for further metal analysis (Cd, Cr, Ni, Pb and Zn) by AAS. In sediments grain size, was considered gravel, sand, and silt, and clay particles, and the fraction < 2000 µm was performed by dry sieving. The organic matter (OM) contents were determined by loss on ignition (600°C, 2 h). To estimate the contribution of both runoff events on metal loads to the RF saltmarsh, were calculated Event Mean Concentrations<sup>17</sup> (EMC) =  $M/R$  (mg/l), where  $M$  is the total discharged mass of pollutant (mg) and  $R$  - total runoff volume (l). To evaluate the heavy metal toxicity in the sediments was quantified the ERI<sup>8,18</sup>. The  $ERI = \sum E_i$ , being  $E_i$  the potential ecological risk related to each metal.

$E_i = TFi \cdot C_i/C_0$  is the monomial potential ecological risk.

$TF_i$  is the toxicity factor of specific metal: Cd = 30; Cr = 2; Ni = 5; Pb = 5 and Zn = 1.

$C_i$  is the obtained concentration of specific metal (µg/g dw).

$C_0$  is the reference value of specific metal in surface sediment of Ria Formosa<sup>19</sup>: Cd= 0.06; Cr = 21.7; Ni = 14.6; Pb = 7.2; and Zn = 29.0

To evaluate the metal remediation was calculated the Enrichment Factor<sup>12</sup> (EF) =  $[Me]_{\text{root tissues}}/[Me]_{\text{rhizosediment}}$ , and quantified the metal distribution (%) among roots and aerial chlorophyllin and non-chlorophyllin organs. In the statistical analyses, the non-parametric Kruskal-Wallis and the Mann-Whitney tests were carried out using SPSS.

## RESULTS AND DISCUSSION

The January rainfall events lasted for 174 min (in January)<sup>15</sup> and 81 min (in March), having the maximum intensity peaks of 20.4 mm/h at 115 min (in January)<sup>15</sup> and of 0.3 mm/h at 34 min (in March), total accumulated rainfall of 12.7 mm (in January)<sup>15</sup> and of 9.3 mm (in March) being the accumulation periods of 30 days (in January)<sup>15</sup> and 34 days (in March). The EMC was higher at March event, for all metals except for Ni (Table 1), maybe due to the longer accumulation period in March event, and the seasonality of air and road traffic. In both precipitation events the TDM was, in decreasing order, Zn > Cr > Pb > Ni > Cd. These results are in accordance with the local anthropogenic pressure mainly caused by the airport location, road traffic, petroleum combustion, tires wastes, and urbanization<sup>20-23</sup>. To a lesser extent,

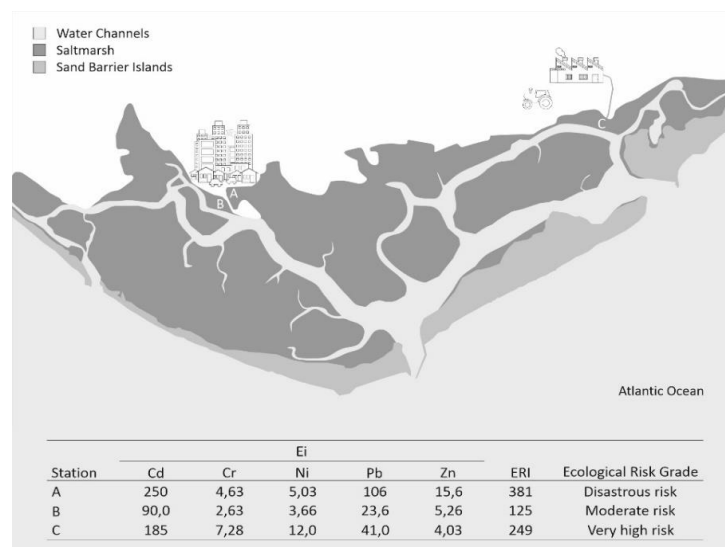
**Table 1.** Metal concentrations and loadings in Faro stormwaters

	Event mean concentration (EMC) (mg/l)		Total discharged mass (TDM) (kg)	
	January	March	January	March
Cd	0.0008 <sup>15</sup>	0.0018	0.048 <sup>15</sup>	0.048
Cr	0.093	0.127	5	5
Pb	0.033 <sup>15</sup>	0.046	2 <sup>15</sup>	2
Ni	0.007 <sup>15</sup>	0.027	0.394 <sup>15</sup>	1.2
Zn	0.241	0.491	14	21

Cd, Cr, Ni, Pb are related with the application of inorganic fertilizers in urban green spaces and urban agriculture. The great abundance of Zn is due to its use against corrosion, thus directly related to construction materials and vehicles<sup>24,25</sup>.

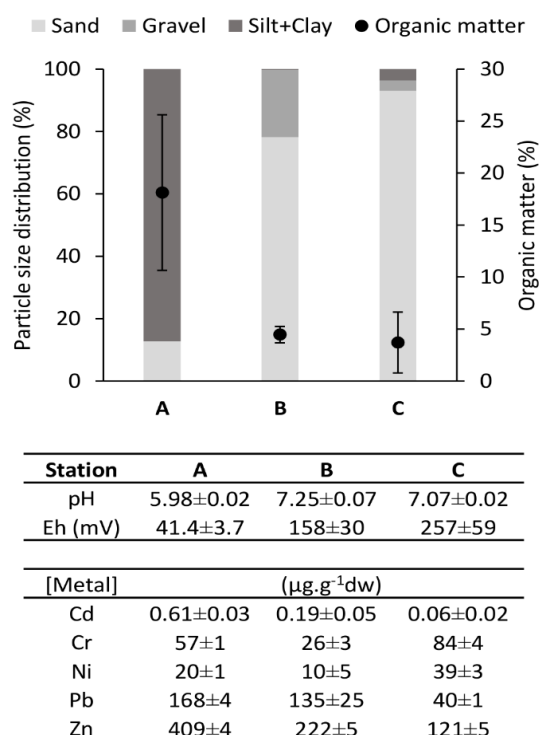
Particle size distribution of sediments showed significant differences ( $p < 0.05$ ) between sampling stations, station A was formed mainly of silt and clay (79.7%), while sediments from other stations presented mainly sand and gravel, respectively of 85.9 and 14.0% in station B, and of 95.7 and 1.29% in station C. The OM content was higher in sediment from station A ( $10.79 \pm 3.49\%$ ), and no differences were founded in OM of sediments from stations B and C, of  $3.78 \pm 0.65\%$  and  $4.45 \pm 1.50\%$ , respectively. Sediment from station A was acid, with a pH of  $6.48 \pm 0.20$ , while in stations B and C the pH values were higher, of  $7.25 \pm 0.17$  in station B and  $7.65 \pm 0.15$  in station C. Different values of Eh ( $p < 0.05$ ) were quantified in the three sampling stations. Sediments from stations A and B were oxidative, presenting positive Eh, of  $39.4 \pm 2.8$  mV and of  $27.7 \pm 2.6$  mV, respectively. Station C presented an anoxic sediment, however the Eh varied markedly, of  $-95 \pm 147$  mV. Metals mobility can be significantly affected by EH changes, as a result of redox-induced changes to the metal-binding capacity of humic materials, insoluble metal sulphide formation, and changes in Fe/Mn-oxyhydroxides, which are known to be effective in immobilizing some metals under oxidizing conditions<sup>11</sup>. Metal contents in sediments ( $\mu\text{g g}^{-1}$  dw) were significantly different ( $p < 0.05$ ) between sites, and observed in decreasing order (average  $\pm$  standard deviation) as follows: stations A and B, Zn (A=  $329 \pm 6$ ; B=  $111 \pm 7$ ) > Pb (A=  $152 \pm 9$ ; B=  $34 \pm 3$ ) > Cr (A=  $50.2 \pm 2.9$ ; B=  $28.5 \pm 6.8$ ) > Ni (A=  $14.7 \pm 0.3$ ; B=  $10.7 \pm 1.9$ ) > Cd (A=  $0.50 \pm 0.01$ ; B=  $0.18 \pm 0.05$ ); and station C, Zn ( $85 \pm 3$ ) > Cr ( $79 \pm 10$ ) > Pb ( $59 \pm 4$ ) > Ni ( $35 \pm 4$ ) > Cd ( $0.37 \pm 0.03$ ). All metal concentrations were higher in station A than in

station B, and comparing all stations, the highest concentrations of Zn, Pb and Cd were reported in sediment from station A, which is under the direct influence of urban stormwater discharge. As reported before, sediment characteristics affected the metal retention<sup>6</sup>, and higher content of OM in the sediment from station A, contributed to increase metal concentrations, due to the bonding of metallic cations to the negatively charged cells surfaces. Furthermore, in station A sediment is richer in clay particles, with large surface area and negative charge, having more capacity to retain metals<sup>11,12</sup>. However, Ni and Cr concentrations were higher in sediments from station C, an area under the influence of industrial and agricultural pressure. Among the studied metals, Cd followed by Pb showed higher toxicity (Ei) at the three sampling sites (Fig. 1), due to their high toxicity factors. Zinc exhibited higher toxicity in stations A and B, where it was quantified in higher concentrations, but in station C, Ni and Cr have higher toxicity than Zn. The ERI was used to access the toxicity posed by metals together, considering the ecological risk grade in coastal sediments<sup>6</sup> as follows: - Low risk  $Ei < 30$ ; - Moderate risk  $30 < Ei < 50$ ; - Considerable risk  $50 < Ei < 100$ ;  $150 < ERI < 200$ ; - Very high risk:  $100 < Ei < 150$ ;  $200 < ERI < 300$ ; - Disastrous risk:  $Ei > 150$ ;  $ERI > 300$ . The ERI of studied metals in the surface sediments at stations A, B and C in RF saltmarsh (Fig. 1), recorded a Disastrous risk, Moderate risk and Very High risk, respectively. The presence of *S. fruticosa* changed the characteristics of sediment surrounding roots, i.e. the rhizosediment (Fig. 2), and significant differences ( $p < 0.05$ ) were founded in metal concentrations. Particle size distribution changed, as well as, OM contents (except for station C). Root systems contributed to oxidise the rhizosediments, causing shifts in the Eh



**Fig. 1.** Monomial potential ecological risk (Ei), ecological risk index (ERI) and ecological risk grade of surface sediments

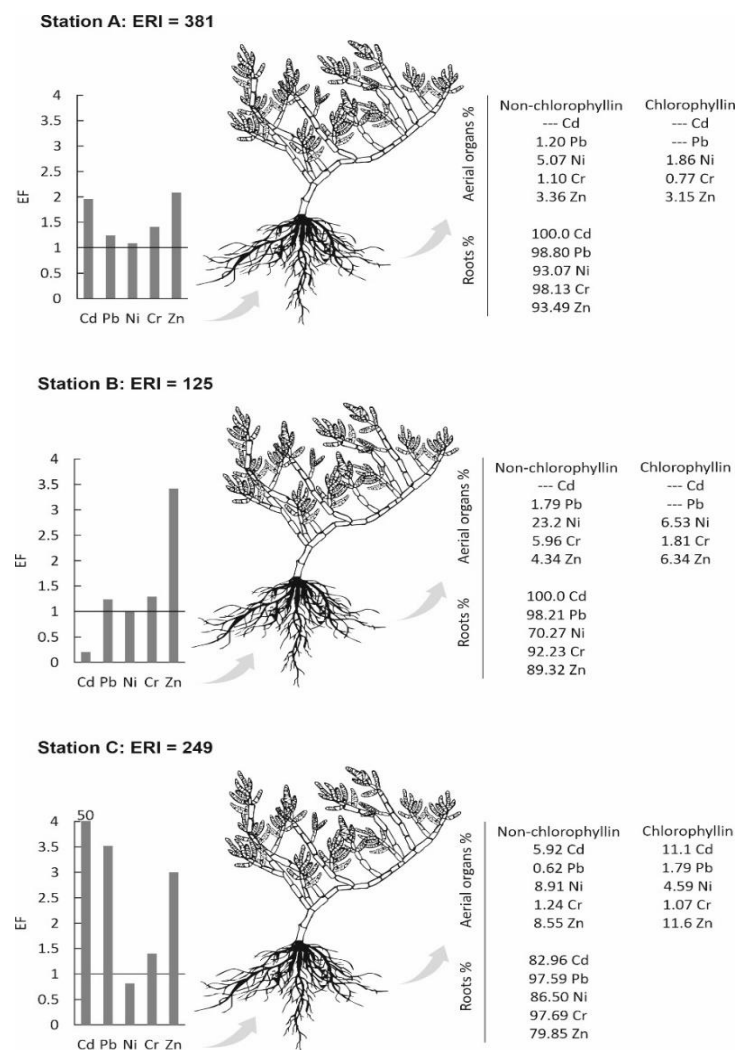
and thus potentially affecting metal availability. Metal concentrations in rhizosediments from stations A and B were higher for all studied metals (except for Cr in station B), than in non-vegetated sediments, confirming previous studies in RF, Guadiana, Tagus and Lima estuaries<sup>12,14,24</sup>. The station A presented the highest metal concentrations in sediments, a positive Eh, and the lowest pH ( $5.98\pm 0.02$ ), suggesting higher metals bioavailability. At station C *S. fruticosa* had a marked effect on the rhizosediment oxidation, promoting the Cd and Pb mobility. No differences were reported ( $p>0.05$ ) for Ni and Cr concentrations, and for Zn the concentration



**Fig. 2.** Rhizosediments characteristics and metal concentrations

in rhizosediment was higher than in non-vegetated sediment. For Pb, Cr and Zn the EF were higher than 1 in all sampling stations (Fig. 3) showing the *S. fruticosa* capacity to remediate these metals, despite the different rhizosediments characteristics<sup>12,14</sup>. The highest EF reported was for Zn (except in station C, where EF for Cd and Pb were higher), perhaps because Zn is an essential element for enzymatic activity and protein production<sup>6</sup>. Despite this, Zn can produce toxic effects above tolerable concentrations by plants<sup>14</sup>. Station A (the most polluted) presented a higher Ei for Zn (15.6) and a lower EF (2.10), than other sites. Zinc seems to have a protective effect against the toxicity of Cd and Pb<sup>6</sup>, and, in fact, station C presented

simultaneously high EF for Zn (EF=3.01), Cd (EF=50) and Pb (EF=3.53). Cadmium is a highly toxic element without any known physiological function in plants, inducing toxicity even in low concentrations<sup>14</sup> and among the studied metals, Cd presented the highest Ei at the three sampling sites (Fig. 1). At station B, with the lower ERI (125), the roots of *S. fruticosa* didn't remove Cd from rhizosediment (EF<1), maybe because the higher pH of rhizosediment (7.25±0.07) decreased Cd bioavailability. Station A, with the highest ERI (381), presented lower EF for all metals, except for Cd (EF= 1.97) and Ni (EF=1.10), maybe because the positive Eh and acid rhizosediment (pH= 5.98±0.02), that increased the metal bioavailability. In this study the reported EF of *S. fruticosa* seemed to be influenced by the sediment toxicity posed by metals (ERI), and by rhizosediment characteristics, namely by Eh and pH, depending on metal. However, the bioavailability of trace metals from sediments, also can be affected by other factors such as the presence of sulphides and organic acids, which can produce insoluble metal complexes. Roots acted as the main pool of metals in *S. fruticosa* in



**Fig. 3.** Ecological Risk Index (ERI) and metal remediation (EF and Translocation)

all studied sites, as reported in previous works<sup>12,14</sup>. Furthermore, in stations A and B, under urbanistic pressure, roots functioned as a barrier for translocation of toxic metals, as Cd and Pb, preventing physiological damages in plant, i.e. the aerial chlorophyllin tissues did not receive Cd and Pb from roots, and non-chlorophyllin organs didn't receive Cd. In station C, Zn, Pb and Cd concentrations in rhizosediments were lower and EF for these metals were higher, here *S. fruticosa* translocated more metals to aerial organs, including the more toxic (Cd and Pb).

## CONCLUSIONS

Urban stormwaters were a main source of toxic metal for RF saltmarsh, the presence of *S. fruticosa* was important and the plant seemed to present different behaviours, depending on the sediment toxicity posed by metals (ERI), coming from different human activities. Although, in all studied conditions *S. fruticosa* retained metals mainly in rhizosphere (roots and rhizosediment), in the more polluted site, this halophyte prevented most toxic metals from reaching the aerial organs, avoiding metabolic damage, vegetal tissues death and metal remobilization to the saltmarsh. In locations with higher Cd and Pb bioavailability, *S. fruticosa* translocated these metals to aerial organs, but the Zn translocation seemed to decrease their toxicity. Apart from the ability of *S. fruticosa* to metal phytoremediation, its resilience in more polluted sites, allows the maintenance of other saltmarsh services and contributes to the environmental health.

The references must be presented according to Journal titles abbreviations and the first 10 examples!

## REFERENCES

1. K. I. JINKS, M. A. RASHEED, C. J. BROWN et al.: Saltmarsh Grass Supports Fishery Food Webs in Subtropical Australian Estuaries. *Estuar Coast Shelf Sci*, **238**, 106719 (2020).
2. O. BEN SAID, M. MOREIRA DA SILVA, F. HANNIER, H. BEYREM, L. CHÍCHARO: Using *Sarcocornia fruticosa* and *Saccharomyces cerevisiae* to Remediate Metal Contaminated Sediments of the Ria Formosa Lagoon (SE Portugal). *Ecohydrol Hydrobiol*, **19** (4), 588 (2019).
3. A. I. SOUSA, A. I. LILLEBØ, M. A. PARDAL, I. CAÇADOR: Productivity and Nutrient Cycling in Salt Marshes: Contribution to Ecosystem Health. *Estuar Coast Shelf Sci*, **87** (4), 640 (2010<sup>a</sup>).

4. A. I. SOUSA, A. I. LILLEBØ, M. A. PARDAL, I. CAÇADOR: The Influence of *Spartina maritima* on Carbon Retention Capacity in Salt Marshes from Warm-temperate Estuaries. *Mar Pollut Bull*, **61** (4–6), 215 (2010<sup>b</sup>).
5. B. HE, Z. J. YUN, J. B. SHI, G. JIANG: Research Progress of Heavy Metal Pollution in China: Sources, Analytical Methods, Status, and Toxicity. *Chin Sci Bull*, **58** (2), 134 (2013).
6. D. M. SALEM, A. KHALED, A. EI NEMR, A. EI-SIKAILY: Comprehensive Risk Assessment of Heavy Metals in Surface Sediments along the Egyptian Red Sea Coast. *Egypt J Aquat Res*, **40** (4), 349 (2014).
7. Y. YI, Z. YANG, S. ZHANG: Ecological Risk Assessment of Heavy Metals in Sediment and Human Health Risk Assessment of Heavy Metals in Fishes in the Middle and Lower Reaches of the Yangtze River Basin. *Environ Pollut*, **159**, 2575 (2011).
8. L. HAKANSON: An Ecology Risk Index for Aquatic Pollution Control: a Sedimentological Approach. *Water Res*, **14**, 975 (1980).
9. B. LIU, J. WANG, M. XU, L. ZHAO, Z. WANG: Spatial Distribution, Source Apportionment and Ecological Risk Assessment of Heavy Metals in the Sediments of Haizhou Bay National Ocean Park, China. *Mar Pollut Bull*, **149**, 110651 (2019).
10. S. WANG, Q. HE, H. AI, Z. WANG, Q. ZHANG: Pollutant Concentrations and Pollution Loads in Stormwater Runoff from Different Land Uses in Chongqing. *Journal of Environmental Sciences (China)*, **25** (3), 502 (2013).
11. G. DU LAING, J. RINKLEBE, B. VANDECASTEELE, E. MEERS, F.M. TACK: Trace metal behaviour in estuarine and riverine floodplain soils and sediments: A review. *Sci Total Environ*, **407** (13), 3972 (2009).
12. M. CAETANO, C. VALE, R. CESÁRIO, N. FONSECA: Evidence for preferential depths of metal retention in roots of salt marsh plants. *Sci Total Environ*, **390** (2–3), 466 (2019).
13. P. N CARVALHO, M.C. BASTO, M.M. SILVA, A. MACHADO, A. BORDALO, M.T. VASCONCELOS: Ability of salt marsh plants for TBT remediation in sediments. *Environ. Sci. Pollut. Res*, **17** 1279 (2010).
14. B. DUARTE, M. CAETANO, P.R. ALMEIDA, C. VALE, I. CAÇADOR: Accumulation and biological cycling of heavy metal in four salt marsh species, from Tagus estuary (Portugal). *Environ. Pollut*, **158** (5), 1661 (2010).
15. N. VELOSO, P. CRUZ, H. CARVALHO, M. MOREIRA DA SILVA: Monitoring Urban Storm Water - Facing Climate Changes in a Coastal Mediterranean City. *The Sustainable City X*, **9**, 93 (2015).

16. M. MOREIRA DA SILVA, J. ANÍBAL, D. DUARTE, L. CHÍCHARO: *Sarcocornia fruticosa* and *spartina maritima* as heavy metals remediators in Southwestern European Salt Marsh (Ria Formosa, Portugal). *J. Environ. Prot. Ecol*, **16** (4), 1468 (2015).
17. M.C. MANQUIZ, J.Y. CHOI, S.Y. LEE, H.J. CHO, L.H. KIM: Appropriate Methods in Determining the Event Mean Concentration and Pollutant Removal Efficiency of a Best Management Practice. *Environ. Eng. Res*, **15** (4), 215 (2010).
18. H. EFFENDI, M. KAWAROE, MURSALIN, D.F. LESTARI: Ecological Risk Assessment of Heavy Metal Pollution in Surface Sediment of Mahakam Delta, East Kalimantan. *Procedia Environ. Sci*, **33**, 574 (2016).
19. C.A. SOUSA, J. DELGADO, D. SZALAJ, T. BOSKI: Holocene background concentrations and actual enrichment factors of metals in sediments from Ria Formosa, Portugal. *Mar. Pollut. Bull*, **149**, 110533 (2019).
20. R.K. SHARMA, M. AGRAWAL: Biological effects on heavy metals: An overview. *J. Environ. Biol*, **26**, 301 (2005).
21. X. CHEN, X. XIA, Y. ZHAO, P. ZHANG: Heavy metal concentrations in roadside soils and correlation with urban traffic in Beijing, China. *J. Hazard. Mater*, **181**, (1–3), 640 (2010).
22. S. COSTA-BÖDDEKER, L.X. THUYÊN, P. HOELZMANN, H.C. DE STIGTER, P. VAN GAEVER, H.D. HUY, A. SCHWALB: The hidden threat of heavy metal pollution in high sedimentation and highly dynamic environment: Assessment of metal accumulation rates in the Thi Vai Estuary, Southern Vietnam. *Environ. Pollut*, **242**, 348 (2018).
23. M.T. SHAJIB, H.C. HANSEN, T. LIANG, P.E. HOLM: Metal in surface specific urban runoff in Beijing. *Environ. Pollut*, **248**, 584 (2019).
24. K.H.VARDHAN, P.S. KUMAR, R.C. PANDA: A review on heavy metal pollution, toxicity and remedial measures: Current trends and future perspectives. *J. Mol. Liqu*, **290**, 111197 (2019).
25. M. DACI-AJVAZI, B. THACI, N. DACI, S. GASHI: Evaluation of packed adsorption column for lead, cadmium and zinc removal using different biosorbents. *J. Environ. Prot. Ecol*, **19**, (3) 997 (2018).

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