



Enrichment of marsh soils with heavy metals by effect of anthropic pollution

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ABSTRACT

The impact of waste disposal on marsh soils was assessed in topsoil samples collected at eight randomly selected points in the salt marsh in Ramallosa (Pontevedra, Spain) at 4-month intervals for 2 years. Polluted soil samples were characterized in physico-chemical terms and their heavy metal contents determined by comparison with control, unpolluted samples. The results revealed a marked effect of waste discharges on the soils in the area, which have low contents in heavy metals under normal environmental conditions. In fact, the studied soils were found to contain substantial amounts of total and DTPA-extractable Cd, Cu, Pb and Zn. Based on the relationship of the redox potential with the DTPA-extractable Cd, Cu, Pb, and Zn contents of the soils, strongly reductive conditions raised the total contents in these elements by effect of their remaining in the soils as precipitated sulphides. Such contents, however, decreased as oxidative conditions gradually prevailed. The contents in DTPA-extractable metals increased with increasing Eh through the release of the metals in ionic form to the soil solution under oxidative conditions. The contents in heavy metals concentrating in the polluted soils were several times higher than those in the control soils (*viz.* 2 vs. 6 for Cd, 4 vs. 6 for Cu, 4 vs. 20 for Pb, and 2 vs. 15 for Zn, all in mg kg^{-1}). This can be expected to influence the amounts of available heavy metals present in the soils, and hence the environmental quality of the area, in the near future. Based on its geoaccumulation index (Class ≥ 3 for Cd and Cu, and 1–4 for Pb and Zn), the Ramallosa marsh is highly polluted with Cd and moderately to highly polluted with Cu, Pb and Zn. The enrichment factors obtained confirm that the salt marsh is highly polluted (especially with Cd) as the primary result of anthropic activity.

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1. Introduction

Marshes, which constitute an important component of river, estuarine and coastal ecosystems, are extremely sensitive to pollution [1–5]. Agricultural and urban waste is often responsible for the origin of heavy metals entering the marine environment and reaching soils and sediments [1–5]. The oxidation status of soils and sediments affects the distribution of some trace metals between bound, unavailable forms and soluble, available forms [1,2,5]. A combination of anaerobic conditions and high matter contents makes a salt marsh the ideal medium for bacterial reduction of sulphate to sulphide [6]. In fact, sulphidization plays a prominent role in the development of marsh soils and the control of heavy metal solubility [1,2,5]. Salt marsh soils generally have low bulk densities (by effect of waterlogging), high contents in organic matter—which often comes from agricultural and urban waste in addition to marsh plant residues—and high sulphide contents [1,2,5,7]. The redox potential has a strong influence on the fate of heavy metals as it governs their distribution between available and insoluble fractions [7–9]. In fact, heavy metal contamination is

thought to strongly affect the structure and functioning of ecosystems [10]. Salt marshes exposed to polluted estuarine and coastal waters may be seriously threatened by ecotoxic effects and/or processes [11,12]. Soils and sediments in salt marshes generally reflect the nature of the materials brought in by rivers from adjacent land areas, derived from shoreline erosion, carried by marine currents from outer sources, produced *in situ* by organisms or resulting from human activities.

In Galicia, 40% of the population lives in or near rias; also, the major industrial areas are located in their vicinity, which has substantially raised their risk of contamination. The increasing levels of heavy metals detected in sediments in Galician rias in recent years have aroused growing interest [5,13–17].

The Ramallosa marsh is located in the southwest of the province of Pontevedra (NW Spain), in Ria de Vigo, which is the southernmost of the Rias Bajas (Fig. 1). The geology of the area is dominated by igneous and metamorphic rocks from the Precambrian–Paleozoic period. The only younger rocks present are Miocene–Quaternary continental sediments [16].

The Ramallosa salt marsh is very close to the village of Bayona (Pontevedra, Spain), a tourist area with a high population density (especially in summer). It is also a horticultural area, so its soils commonly receive fertilizer, manure and slurry inputs capable of polluting the local river (the Miñor). This river, which has

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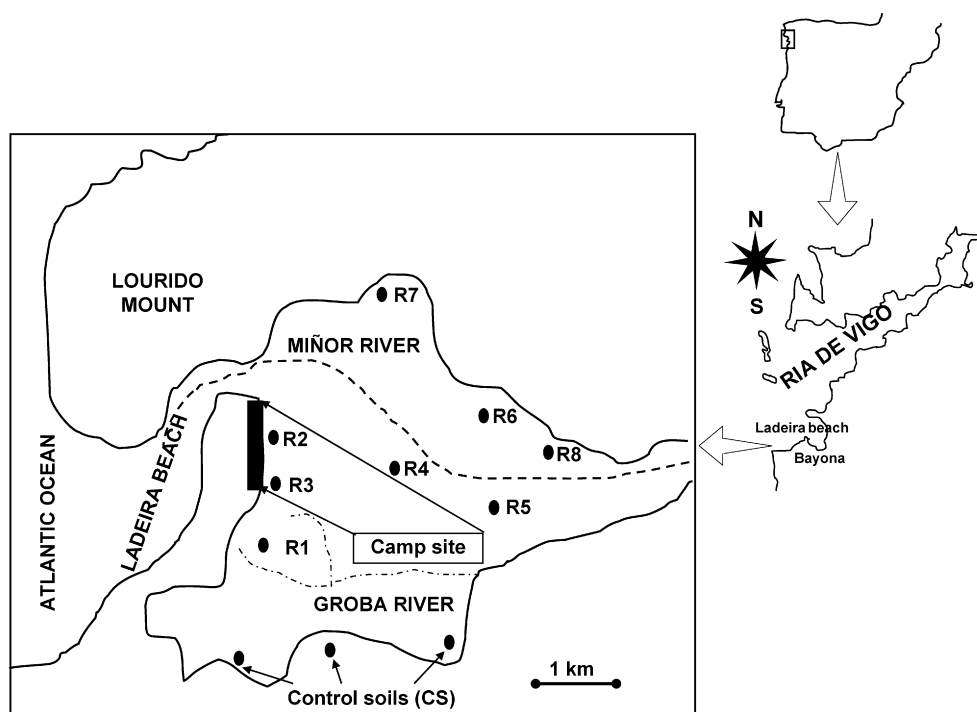


Fig. 1. Map of the study area.

formed the salt marsh, receives a number of discharges with the potential to contaminate the marsh soils. Also, a campsite with 203 bungalows—many of which are occupied throughout the year—and a number of plots for caravans and tents exists on the western edge of the marsh that is fully occupied from spring to autumn. Part of the campsite waste is dumped directly into the marsh. In addition, the southern part of the marsh receives the water from the Groba, a stream with a very short course and very little flow that rises in the nearby Sierra Groba. The Groba crosses a small forest, some agricultural areas and the village of Sabarís before flowing into the salt marsh near sampling point R1.

This paper examines the influence of agricultural and urban pollution on the heavy metal contents of soils in an estuarine environment. The main objective of the study was to assess the pollution status of soils in the Ramallosa salt marsh.

2. Materials and methods

The effects of waste disposal on neighbouring marsh soils were studied in topsoil samples collected at randomly selected sampling points (R) in the Ramallosa salt marsh at 4-month intervals for 2 years.

Polluted and unpolluted (control) zones were sampled 50 m from the lower water line. Soils from the polluted area were collected 5–75 m from the river Miñor channel and soils from the unpolluted area (control) approximately 200 m from it (Fig. 1). The polluted sampling sites were selected in such a way as to obtain a representative picture of pollution in the marsh. Some polluted and unpolluted zones were sampled 25 m from the lower water line. The polluted soils (R) were sampled 10–75 m from both sides of the river Miñor channel. Control soils (C) were sampled 150 m from the channel. All soils were Thionic Fluvisols as per the WRBSR classification [18].

A total of three soil samples were collected at each sampling point, using an Eijkkamp 04.20.SA sampler. The samples were placed in polyethylene bags prior to transfer at 4 °C in the dark to the laboratory for storage under identical conditions until analy-

sis. Once in the laboratory, the three samples from each zone were air-dried, passed through a 2-mm mesh sieve, pooled and homogenized in a vibratory homogenizer for solid samples (Fritsch Rotary Sampler Divider, Laborette 27). Three sub-samples per composite sample were selected for analysis.

The soil redox potential (Eh) was determined *in situ* at three different depths (1, 10 and 20 cm) at each sampling point by inserting polished platinum electrodes to the desired depth and allowing them to equilibrate for 15 min before measuring the voltage against a calomel electrode with a pH/mV-meter. Each Eh value reported represents the measured voltage plus 244 mV [19,20] and all measurements were made in triplicate.

The sub-2 mm soil fractions obtained as described above were used for potentiometric measurement of soil pH and also to determine organic matter according to Walkley and Black [21], total Kjeldahl-N according to Bremner and Mulvaney [22], extractable P using the modified Murphy–Riley ascorbic acid procedure and spectrophotometry [23], carbonate according to Horváth et al. [24] and particle size distribution with the Boyoucos hydrometer method as implemented by Day [25].

Cation exchange capacity (CEC) and exchangeable cation contents were determined according to Hendershot and Duquette [26]. The metals Al, Ca, K, Mg and Na were extracted with 0.1 M BaCl₂ and their concentrations determined by inductively coupled plasma spectrometry on a Perkin-Elmer Optima 4300 DV instrument. Exchangeable acidity was determined by using a 1 M KCl replacing solution and titration to a phenolphthalein end point.

Available contents in heavy metals (Cd, Cu, Pb and Zn) were quantified by extraction with DTPA [27], and total contents by extraction with a 1:3:3 (v/v/v) mixture of nitric, hydrochloric and hydrofluoric acids in a Teflon pump that was heated in a microwave oven [28]. Extractions were not sequential, each extract being obtained directly from a soil sample stored at 4 °C in the dark. The Cd, Cu, Pb and Zn contents of each extract were determined by ICP-OES. The ICP technique has the advantage that it affords the simultaneous determination of all metals at low detection levels in a single sample. The detection limits for the studied trace elements were 0.1 µg ml⁻¹ for Pb, 0.025 µg ml⁻¹ for Zn, 0.02 µg ml⁻¹

for Cd and $0.05 \mu\text{g ml}^{-1}$ for Cu. Analytical blanks were analysed identically with the samples and metal concentrations determined by using standard solutions prepared in the same acid matrix. The suspensions were analysed in triplicate and the results, in $\mu\text{g g}^{-1}$ dry soil, averaged.

The overall accuracy and precision of the analytical procedure for total heavy metal contents—extraction included—were checked according to Marcet et al. [28], using the marine sediment reference material MESS-3 from the Marine Analytical Chemistry Standards Program of the Canadian National Research Council. MESS-3 is an estuarine sediment with low-to-medium metal concentrations, which makes it suitable for control analyses of Galician salt marsh soils (Table 1). Based on the results, consistency between the certified and found contents was quite good, and recovery of the analytes nearly quantitative.

Pollution in the salt marsh soils was assessed via enrichment factors and geoaccumulation indices [29]. Assessing metal contamination in estuarine sediments and salt marsh soils is quite difficult, but geoaccumulation indices (Igeo) and enrichment factors (EF) relative to pre-industrial sediments or soils from the same environment provide an effective choice. However, useful data for pre-industrial sediments in a given area are not always available. Both Igeo and EF depend on the particular background data used. Metal contents in sediments and salt marsh soils can be obtained from average metal concentrations of texturally and mineralogically equivalent sediments or soils, whether measured in or reported for a known pristine region [30]. The world average shale and world average soil are among the materials typically used to establish background metal levels. Such levels, however, tend to be very general and, as pointed out by Gibbs [31], who recommends using regional background values instead, may be misleading for specific coastal areas. In fact, the estimated pollution status of a given zone can be more strongly dependent on the particular background used than on the specific index chosen.

The geoaccumulation index (Igeo), which was originally defined by Müller [32] for metal concentrations in the <2 mm fraction and subsequently developed for the global standard shale values, is expressed as follows:

$$I_{\text{geo}} = \log_2 \left(\frac{C_n}{1.5B_n} \right)$$

where C_n is the measured concentration of metal n in the soil, B_n the background value for the same metal, and 1.5 a multiplying factor intended to offset potential oscillations in background data resulting from lithological variations. We calculated Igeo from the background values reported by Rubio et al. [16] for metals in the area of Ria de Vigo (Table 1); by exception, the background concentration of Cd, which was not determined by the previous authors, was taken from Turekian and Wedepohl [33].

The geoaccumulation index encompasses seven grades or classes, with Igeo = 6 indicating an enrichment factor of almost 100 times above the background value [32] (Table 2). Some authors [34] have criticized the use of Igeo to assess the pollution status of soils and proposed the use of normalized values instead. There are several normalization methods ranging from the use of simple

Table 2
Geoaccumulation indices [32].

Igeo	Class	Pollution intensity
>5	6	Very strong
4–5	5	Strong to very strong
3–4	4	Strong
2–3	3	Moderate to strong
1–2	2	Moderate
0–1	1	Zero to moderate
0	0	Zero

metal/normalizer ratios to more complex methods based on regression analysis [35]. Following Rubio et al. [16], we chose to normalize metal concentrations as ratios to aluminium content. Thus, we calculated enrichment factors (EF) from background values, using the expression [16]:

$$EF = \frac{(\text{metal}/\text{Al})_{\text{soil}}}{(\text{metal}/\text{Al})_{\text{background}}}$$

Data was statistically processed and the least significant differences (LSD) or Dunnett's T3 at the 5% level used to separate means. Heavy metal contents and enrichment factors were related to soil properties via correlation, regression and principal component analyses (PCA) [36].

3. Results and discussion

As can be seen from Table 3, there were some differences in general properties and heavy metal contents between the polluted and control soils. Thus, the organic matter content and cation exchange capacity of the polluted soils were differed significantly from those of the control, unpolluted soils. Also, the redox potential of the control soils was significantly different from those of most polluted soils—R3 and R7 excepted—as they were among the most distant from the course of the Miñor and the lower water line—and hence subject to similar waterlogging—drying cycles. Soil R1, with a low Eh, was distant from the Miñor but near the mouth of the Groba, so it was almost permanently waterlogged.

The heavy metal concentrations of the polluted soils (Table 4) exceed the average concentrations in other unpolluted Galician coastal sediments [2,13,28,37,38] and those in the parent materials [39]. Also, the Cd, Pb, and Zn total contents are higher than the maximum limits established in some reference guides [40,41]; by exception, soils R1, R4, R6, and R7 had Pb and Zn contents slightly lower than the NHMPPE [41] intervention limit.

Contamination can be evaluated via geoaccumulation indices and enrichment factors. Both Igeo and EF depend on the particular background data used. Based on the background values for Cu, Pb, and Zn for the Ria de Vigo area reported by some authors [16], that of Turekian and Wedepohl [33] for Cd, and the geoaccumulation indices and pollution classes of Table 2, the Ramallosa marsh soils are highly to very highly polluted by all detected heavy metals (Table 5). Also, all soils except the control exceed Class 1. Based on these index values, the Ramallosa marsh is, overall, highly polluted with all the studied metals.

Enrichment factors (EFs) were calculated from the background values for the Ria de Vigo reported by Rubio et al. [16]; metal concentrations were normalized as ratios to aluminium content. The factors obtained were similarly informative to Igeo except for Cd. Although the soils were enriched with all heavy metals, the Cd levels were extremely high except in the control soils (Table 4). Since the background values employed to calculate Igeo were all identical, the differences can be ascribed to the use of normalized concentration values.

The soils from R2, which were those collected closest to the campsite, exhibited the highest EFs for Cd, Cu, Pb and Zn, followed

Table 1
Measured and certified concentrations of heavy metals in reference material MESS-3 (means \pm standard deviations; $n = 10$) and background concentrations.

Metal (mg kg^{-1})	Certified value (mg kg^{-1})	Measured value (mg kg^{-1})	Source	Background level (mg kg^{-1})
Cd	0.24 ± 0.01	0.35 ± 0.17	[33]	0.13
Cu	33.9 ± 1.6	31 ± 5	[16]	29.41
Pb	21.1 ± 0.7	23.6 ± 2.5	[16]	51.29
Zn	159 ± 8	161 ± 5	[16]	105.34
Al	$85,900 \pm 2300$	$86,185 \pm 2895$	[16]	6480

Table 3
Average topsoil properties.

Soil	pH	Eh (mV)	OM (%)	CECe cmol ₍₊₎ kg ⁻¹	Sand (%)	Silt (%)	Clay (%)
R1 ^a	5.76c	-41.07e	19.92b	6.96b	85.12b	11.65e	3.23f
R2 ^a	5.94c	29.83d	23.16b	7.16b	78.41de	13.96c	7.63cd
R3 ^a	7.42abc	92.00ab	3.03d	5.71c	79.30d	12.72d	7.98c
R4 ^a	7.71ab	69.75bc	2.85d	4.49d	87.42a	9.83f	2.75fg
R5 ^a	7.01abc	54.33c	6.92cd	5.26cd	87.96a	9.65f	2.39g
R6 ^a	4.71b	77.37b	8.93cd	5.62c	64.76g	16.76b	18.48a
R7 ^a	7.74a	87.17ab	3.87d	3.39e	81.00c	11.90e	7.10d
R8 ^a	7.04abc	13.17d	7.09cd	4.61d	74.36f	19.55a	6.09e
Control ^b	6.97b	106.33 ^a	89.52a	8.35a	77.57e	11.82e	10.62b

Values followed by different letters in each column were significantly different at $p < 0.05$.

^a Means of 54 analyses (three samples and three replicate measurements at each of six sampling times).

^b Mean of 162 analyses (nine samples and three replicate measurements at each of six sampling times).

Table 4
Mean topsoil metal contents, geoaccumulation indices, pollution classes and enrichment factors.

	R1 ^a	R2 ^a	R3 ^a	R4 ^a	R5 ^a	R6 ^a	R7 ^a	R8 ^a	Control soils ^b
DTPA-extractable (mg kg ⁻¹)									
Cd	9.11h	39.84f	64.26a	43.86ef	51.34b	42.64ef	47.06be	31.19g	0.03i
Cu	19.94d	22.75bc	23.70ab	24.67a	23.21a	26.10a	26.55a	21.94cd	1.71e
Pb	3.04d	6.08c	8.87b	9.99b	6.95c	12.79a	12.02a	5.96c	1.02e
Zn	22.55f	69.55e	94.05d	120.22c	79.05de	162.40a	143.97b	63.08e	3.68g
Total content (mg kg ⁻¹)									
Cd	68.93c	97.77b	134.60a	62.60c	90.93b	53.60c	55.27c	125.83a	0.30d
Cu	163.73c	189.38b	207.03a	141.23d	168.01c	132.58d	145.76d	190.31b	31.10e
Pb	447.33d	798.50b	1,076.50a	259.00e	635.50c	274.83e	235.67e	775.33b	55.62f
Zn	655.67c	1,229.00b	1,689.00a	512.33cd	1,047.33b	300.67cd	446.50c	1,341.67ab	114.05d
Al	12,400b	11,100b	23,200a	11,700b	13,000b	11,500b	20,300a	21,700a	4200c
Cd									
Igeo ^c	8.47d	8.97bc	9.43a	8.33de	8.87c	8.04e	8.08e	9.29ab	0.68f
Pollut. class	6	6	6	6	6	6	6	6	1
EF ^d	2460.62d	4457.28a	2,909.02bc	2,697.81cd	3,504.65abc	2348.86d	1,371.88e	2,873.57bc	3.79f
Cu									
Igeo ^c	2.28c	2.49b	2.62a	2.07de	2.32c	1.97e	2.11d	2.50b	0f
Pollut. class	3	3	3	3	3	2	3	3	0
EF ^d	38.49b	49.86a	25.83c	35.17b	37.37b	33.78b	20.80d	25.26cd	2.01e
Pb									
Igeo ^c	2.02c	2.86b	3.29a	1.24de	2.53b	1.32d	0.89e	2.82b	0f
Pollut. class	3	3	4	2	3	2	1	3	0
EF ^d	32.15b	64.27a	41.17b	19.96d	43.39b	21.78d	10.29e	31.64c	1.08e
Zn									
Igeo ^c	1.67c	2.60ab	3.07a	1.24cd	2.38b	0.26e	1.07d	2.72ab	0f
Pollut. class	2	3	4	2	3	1	2	3	0
EF ^d	25.65d	54.29a	35.60bc	22.56d	39.29b	12.69e	10.93e	30.05cd	1.19f

Values followed by different letters in each row were significantly different at $p < 0.05$.

^a Means of 54 analyses (three samples and three replicate measurements at each of six sampling times).

^b Mean of 162 analyses (nine samples and three replicate measurements at each of six sampling times).

^c Geoaccumulation index.

^d Enrichment factor.

Table 5
Pearson coefficients for the linear correlation between soil properties, extractable metal contents and enrichment factors.

	Eh	MO	CEC
DTPA-extractable			
Cd	0.881 ^{**}	-0.536 ^{**}	-0.303 [*]
Cu	0.794 ^{**}	-0.491 ^{**}	-0.509 ^{**}
Pb	0.825 ^{**}	-0.571 ^{**}	-0.522 ^{**}
Zn	0.789 ^{**}	-0.496 ^{**}	-0.459 ^{**}
Enrichment factor			
Cd		0.332 [*]	0.429 ^{**}
Cu		0.616 ^{**}	0.614 ^{**}
Pb		0.507 ^{**}	0.642 ^{**}
Zn		0.381 ^{**}	0.463 ^{**}

^{**} Significant at the 0.01 level.

^{*} Significant at the 0.05 level.

by R5 and R8. The latter two were collected closest to the course of the Miñor. This suggests that metal contamination in the studied area is largely due to discharges into the river and waste deposits from the campsite.

Based on the foregoing, the Ramallosa marsh is highly polluted with Cu, Pb, Zn, and, especially, Cd, as a consequence of anthropic activity—mainly the discharge of paint and urban wastewater from the tourist area in the vicinity of the river Miñor. Continuous monitoring and further studies of the area will be required in order to identify potential long-term effects.

High total contents in trace metals constitute a serious environmental hazard; also, although a high proportion of metals is bound to the residual fraction—where metals are more strongly and permanently retained—, changes in the environmental conditions (e.g. a reduction in organic matter content, competition with other metals for sorption sites, discharges increasing soil acidity) may

Table 6
Pearson coefficients for the linear correlation between metal contents, enrichment factors and geoaccumulation indices.

	DTPA-extractable content				Total content				EF ^a				Igeo ^b			
	Cd	Cu	Pb	Zn	Cd	Cu	Pb	Zn	Cd	Cu	Pb	Zn	Cd	Cu	Pb	Zn
DTPA-extractable content																
Cd	1	0.584**	0.577**	0.549**	0.236	0.150	0.264	0.255	0.064	-0.243	0.050	0.057	0.213	0.132	0.128	0.126
Cu	0.584**	1	0.895**	0.914**	-0.342*	-0.418**	-0.405**	-0.363*	-0.341*	-0.336*	-0.462**	-0.412**	-0.420**	-0.453**	-0.528**	-0.444**
Pb	0.577**	0.895**	1	0.945**	-0.368*	-0.447**	-0.419**	-0.426**	-0.404*	-0.364*	-0.520**	-0.538**	-0.451**	-0.482**	-0.532**	-0.538**
Zn	0.549**	0.914**	0.945**	1	-0.383**	-0.474**	-0.455**	-0.429**	-0.394*	-0.339*	-0.525**	-0.501**	-0.464**	-0.513**	-0.567**	-0.520**
Total content																
Cd	0.236	-0.342*	-0.368*	-0.383**	1	0.901**	0.863**	0.884**	0.543**	-0.041	0.513**	0.540**	0.961**	0.884**	0.803**	0.759**
Cu	0.150	-0.418**	-0.447**	-0.474**	0.901**	1	0.904**	0.903**	0.463**	0.105	0.643**	0.647**	0.874**	0.996**	0.850**	0.828**
Pb	0.264	-0.405**	-0.419**	-0.455**	0.863**	0.904**	1	0.902**	0.499**	0.088	0.738**	0.646**	0.850**	0.901**	0.948**	0.796**
Zn	0.255	-0.363*	-0.426**	-0.429**	0.884**	0.903**	0.902**	1	0.462**	0.029	0.607**	0.754**	0.866**	0.902**	0.849**	0.938**
EF^a																
Cd	0.064	-0.341*	-0.404**	-0.394**	0.543**	0.463**	0.499**	0.462**	1	0.683**	0.784**	0.725**	0.617**	0.470**	0.555**	0.430**
Cu	-0.243	-0.336*	-0.364*	-0.339*	-0.041	0.105	0.088	0.029	0.683**	1	0.694**	0.603**	0.046	0.125	0.211	0.096
Pb	0.050	-0.462**	-0.520**	-0.525**	0.513**	0.643**	0.738**	0.607**	0.784**	0.694**	1	0.840**	0.574**	0.660**	0.785**	0.596**
Zn	0.057	-0.412**	-0.538**	-0.501**	0.540**	0.647**	0.646**	0.754**	0.725**	0.603**	0.840**	1	0.598**	0.668**	0.691**	0.800**
Igeo^b																
Cd	0.213	-0.420**	-0.451**	-0.464**	0.961**	0.874**	0.850**	0.866**	0.617**	0.046	0.574**	0.598**	1	0.879**	0.829**	0.785**
Cu	0.132	-0.453**	-0.482**	-0.513**	0.884**	0.996**	0.901**	0.902**	0.470**	0.125	0.660**	0.668**	0.879**	1	0.862**	0.849**
Pb	0.128	-0.528**	-0.532**	-0.567**	0.803**	0.850**	0.948**	0.849**	0.555**	0.211	0.785**	0.691**	0.829**	0.862**	1	0.777**
Zn	0.126	-0.444**	-0.538**	-0.520**	0.759**	0.828**	0.796**	0.938**	0.430**	0.096	0.596**	0.800**	0.785**	0.849**	0.777**	1

^a Enrichment factor.

^b Geoaccumulation index.

** Significant at the 0.01 level.

* Significant at the 0.05 level.

Table 7
Principal component analysis of available and total heavy metal contents.

	Communalities					
	Initial	Extraction				
DTPA-extractable						
Cd	1.000	0.828				
Cu	1.000	0.871				
Pb	1.000	0.963				
Zn	1.000	0.958				
Total content						
Cd	1.000	0.936				
Cu	1.000	0.920				
Pb	1.000	0.932				
Zn	1.000	0.931				
Extraction method: principal component analysis						
Total variance explained						
Component	Initial eigenvalues			Extraction sums of squared loadings		
	Total	% of variance	Cumulative %	Total	Percent variance	Cumulative %
1	4.803	60.038	60.038	4.803	60.038	60.038
2	2.536	31.701	91.739	2.536	31.701	91.739
3	0.337	4.216	95.955			
4	0.118	1.478	97.433			
5	0.080	1.002	98.435			
6	0.072	0.904	99.339			
7	0.034	0.424	99.763			
8	0.019	0.237	100.000			
Extraction method: principal component analysis						
	Component matrix ^a					
	Component 1	Component 2				
DTPA-extractable						
Cd	0.849	0.328				
Cu	0.839	0.408				
Pb	0.571	0.798				
Zn	0.534	0.820				
Total content						
Cd	0.864	-0.436				
Cu	0.924	-0.256				
Pb	0.768	-0.586				
Zn	0.760	-0.595				
Extraction method: principal component analysis						

^a Two components extracted.

facilitate their mobilization and increase their bioavailability as a result.

Discharges can therefore cause a geochemical change towards oxidative conditions or a reduction in pH in salt marsh soils. Such changes can lead to the release of heavy metals to the close environment, thereby increasing their bioavailability.

Soil properties, DTPA-extractable metal contents and calculated EF values were subjected to bivariate correlation analysis (Tables 5 and 6) and linear regression analysis (Fig. 2). DTPA-extractable heavy metal contents exhibited significant positive correlation with the redox potential, and significant negative correlation with the organic matter content and cation exchange capacity. The prevalence of insoluble forms can be ascribed to the low Eh values of the soils. The highest levels in DTPA-extractable forms were found under oxidative conditions. This is consistent with previous results for various polluted salt marshes [2] and also with those of Gambrell et al. [8], who, similarly to us, found soluble heavy metals to be scarcely affected by the redox potential. Also, the higher was the cation exchange capacity—which depends on the organic matter content, among other factors—, the lower were the DTPA-extractable contents and availability of the studied metals.

The assumption that the heavy metals originated from the polluting discharges was confirmed by the significant mutual correlation between the total Cd, Cu, Pb and Zn levels (Table 6).

Pearson's correlation coefficients between the total contents for the different metals were high; this suggests an anthropic origin for the body of heavy metals which is further supported by the correlation between their EF and Igeo values, and the mutual correlation between Igeo and EF values.

In order to facilitate the identification of patterns in the heavy metal contents of the studied soils, control and polluted soil samples taken to be points in the six-dimensional space defined by their DTPA-extractable and total heavy metal contents, and the data subjected to principal components analysis [42]. The first two components, PC1 and PC2, accounted for 60% and 31.7%, respectively, of the total variance, with high eigenvalues (4.8 and 2.5, respectively). Based on the loadings of the metals on these components (Fig. 3), PC1 provided an indication of increased DTPA-extractable and total contents, and PC2 afforded discrimination between DTPA-extractable contents on the one hand and total contents on the other. Accordingly, soils R4, R6 and R7 fell, with positive values, in the second quadrant near the PC2 axis in the PC1–PC2 plane; on the other hand, all others—control soils included—had negative

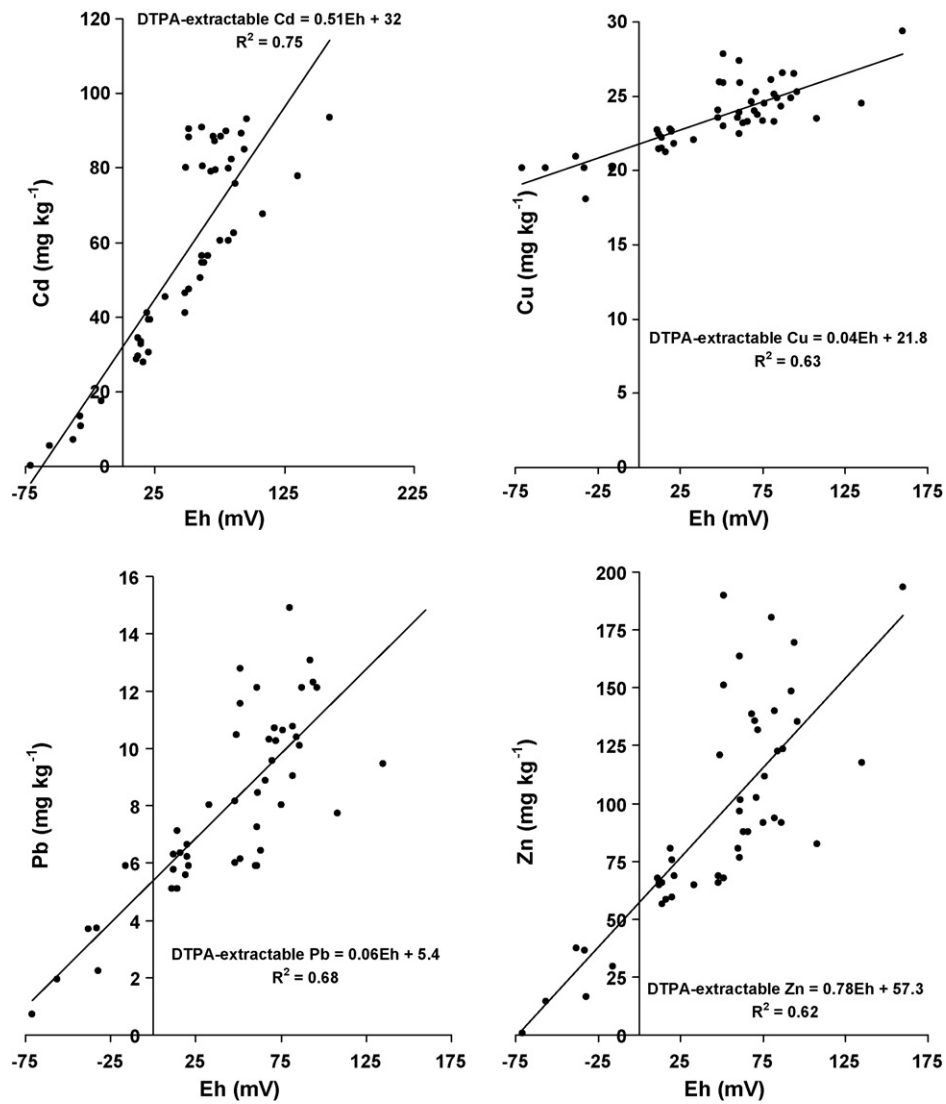


Fig. 2. Variation of the DTPA-extractable Cd, Cu, Pb and Zn contents with Eh.

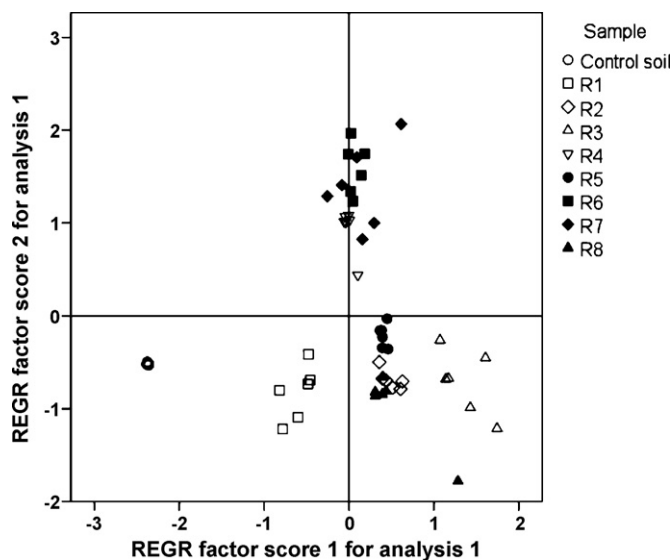


Fig. 3. Principal component analysis of the results.

values in PC2. Based on the results, R4, R6 and R7 had high DTPA-extractable Pb and Zn contents (Table 7). These soils had the lowest contents in organic matter and were among those exhibiting the lowest CEC values, which is consistent with the negative correlation of this component with the OM content (Pearson correlation value = -0.485) and CEC (Pearson correlation value = -0.285), and also with its positive correlation with Eh ($r^2 = 0.467$).

Based on its loading on PC1, the control soil had the lowest DTPA-extractable and total contents in the studied metals, followed by R1, which was the most distant from the course of the river Miñor. The other soils (R2, R3, R5 and R8) had positive loadings on PC1 and negative loadings on PC2; these were the soils closest to either the river course (R5 and R8) or the main anthropic source of these metals (R3 and R2).

The PC2 results were subjected to multiple linear regression in conjunction with those soil properties which, based on the foregoing, had the strongest effects on the contents and availability of the studied heavy metals (*viz.* pH, Eh, CEC and OM). The choice of this component was dictated by its ability to discriminate between DTPA-extractable (available) and total metal contents. The ensuing equation was

$$PC2 = -0.39pH + 0.55Eh - 0.07OM - 0.52CEC (r^2 = 0.549)$$

Therefore, DTPA-extractable contents increased with increasing redox potential, which is consistent with the fact that oxidation results in increased availability. Also, total contents increased with increasing organic matter content and CEC, which, as stated above, facilitate binding of the studied metals.

4. Conclusions

The cadmium, copper, lead and zinc concentrations in the studied polluted soils exceeded the average concentrations in other, unpolluted Galician coastal sediments and those in the parent materials; also, they were higher than the maximum limits established in some reference guides.

Based on its geoaccumulation index and enrichment factors, the Ramallosa marsh is highly polluted with Cu, Pb, Zn and, especially, Cd, as a consequence of anthropic activity.

The results of the correlation and principal component analyses reveal that the redox potential is the single factor most strongly influencing bioavailability in the studied metals, and that the organic matter content and cation exchange capacity are the individual soil properties most markedly facilitating their retention.

The contents in heavy metals concentrating in the polluted soils were several times greater than those in the control soils. This is bound to affect the contents in available heavy metals, and hence the environmental quality of the study area, in the near future. Therefore, the local fauna and flora may be jeopardized if the acid conditions currently prevalent cause part of the metals to be solubilized.

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