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POTENTIAL BIOAVAILABILITY ASSESSMENT AND DISTRIBUTION OF POTENTIALLY TOXIC
ELEMENTS IN CORES FROM PORTMAN BAY (SE, SPAIN)

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Abstract: A total of 120 sediments from 12 cores of Portman Bay (SE Spain) were studied to assess the degree of contamination and ecological risk related to potentially toxic elements (PTEs) by combining a geochemical and mineralogical characterisation with the assessment of the bioavailable forms of trace metals (As, Cd, Cu, Fe, Pb, Zn). With this purpose, sediment contamination was assessed by total and water-soluble content, and potential bioavailability by the simultaneously extracted metals and acid-volatile sulphides (SEM-AVS) approach, and by an oral bioaccessibility extraction procedure.

The sediments are essentially sandy (>80%). The most important minerals are: iron phases such as siderite, iron oxides and hydroxides and pyrite; clay minerals such as clinocllore, greenalite and

biotite; and quartz. Occasionally, jarosite and carbonates (calcite and dolomite) appear. The total PTEs content is high whereas the sediments generally have a very low soluble PTE content.

The SEM/AVS ratio is less than unity in most samples, indicating that there is enough sulphur so that if there was a release of metals, they could precipitate as sulphides. After the bioaccessibility extraction, the results showed that zinc and cadmium are more bioaccessible in the intestinal environment (alkaline) while the rest of the elements have greater availability in the stomach (acid).

Keywords: Sediment cores; Bioaccessibility; Potentially toxic elements; SEM; AVS; Portman Bay

Almost all mining processes cause adverse effects to the environment (Boonsrang *et al.* 2017). In ancient mining districts, with long histories of mining and metallurgical activity, mine wastes represent one of the main sources of pollution for soils, water, air and biota (Valente *et al.* 2011).

Mining and metallurgical activities generate considerable amounts of mine tailings. Most residual material has been left in tailing ponds or mine sites without treatment, generating an environmental risk (Falagan *et al.* 2017). Mine tailings contain many sulphide minerals, which could produce acid mine drainage (AMD). The release and dispersion of potentially toxic elements (PTEs) to the environment occurs through AMD, and the weathering and erosion of waste-rock dumps and tailings.

Acid mine drainage can severely contaminate soils, affect water quality and pollute ecological environments because of the low pH and high concentrations of heavy metals and other toxic elements.

Metal polluted sites represent a potentially hazardous risk for human health and the environment. Knowledge of the total PTE content in soils and sediments is not adequate to assess their potential ecological risk (Pignotti *et al.* 2018). Analysis of simultaneously extracted metals (SEM) coupled with the acid-volatile sulfide (AVS) content represents a useful approach to determine the potential bioavailability of trace metals (Chai *et al.* 2015). Generally, PTEs in anoxic sediments are considered non-toxic due to the formation of stable and insoluble metal sulphides, resulting in low PTE potential risk. However, sulphide in sediments, usually operationally defined as

AVS, is highly sensitive to oxidising conditions, and when it is oxidised and removed, simultaneously extracted metal (SEM) would possibly be released into the overlying water (De Jonge *et al.* 2012), and their bioavailability would be potentially increased (Simpson *et al.* 2012).

Exposure of the human population to the pollutants could take place through a wide variety of routes that include inhalation, oral ingestion, or skin absorption. One of the most important routes of exposure to a pollutant, after the diet, is the accidental ingestion of polluted soil (Luo *et al.* 2012). To simulate the PTE release processes in the gastrointestinal tract, several *in vitro* methods have been developed which are based on the use of extractant solutions to simulate digestion in the stomach and small intestine (Wragg & Cave 2003). These methods allow the determination of the bioaccessibility of a contaminant, and the main advantage is the speed of the analyses and the low cost compared to *in vivo* methods (Mendoza *et al.* 2017).

The objective of this study was the in-depth geochemical and mineralogical characterisation of waste materials from sulphide mining and metallurgy in Portmán Bay. The present work aims not only to characterise the concentrations of PTEs in these residues but also to evaluate the potential risk of target elements, both for human health and ecosystems. The potential risk of PTEs was assessed using the AVS and SEM methods together and the oral bioaccessibility, referred to the fraction that is soluble in the gastrointestinal environment.

Origin of the contamination in Portmán Bay: study area

Portmán Bay (Fig. 1) is located in the southeast of Spain, in an area influenced by the Sierra Minera de Cartagena-La Unión, and constitutes one of the major points of mineral-metallurgical contamination in the Mediterranean Sea (Martínez Sánchez *et al.* 2017). This man-made disaster represents a risk for people's health and can only be explained by its recent history.

Portmán, or Portus Magnus, was a refuge for such ancient peoples as the Iberians, Phoenicians, Carthaginians and Romans. The area has long been associated with mining activity, the deposits containing high levels of iron, lead, zinc and silver, all exploited (Peña *et al.* 2014) as far back as Roman times (III century BC). Mining activities originally (from the 7th century BC) focused on Ag and Pb. Following many centuries of intermittent activity, mining resumed in the 19th century, with a renewed interest in Zn and Fe. Open-air mining began in 1957, when the company Peñarroya España started to operate in "Roberto", a froth flotation plant, which initially treated 1000 tons/day

of mineral, which, with time, rose to 8000 tons/day. The extracted mineral was treated by separation techniques: separation by differential flotation of the mineral species, galena, sphalerite and pyrite. To carry out these operations of flotation, a great quantity of water was needed, and this was obtained directly from the sea.

Once the ores had been separated, the waste materials were discharged directly into the sea, originally in the inner part of the bay; later wastes were discharged farther offshore (Martínez-Sánchez *et al.* 2008). Indeed, 97.5% of all the rock treated in the flotation plant formed part of the tailings reaching the sea (Oyarzun *et al.* 2013), along with the residues of substances used in the differential flotation process. Although the dumping site was changed several times due to the predominant marine currents, the bay gradually filled up with mineral wastes. Once the bay had filled up, the wastes were simply poured onto the beach.

The effect of waves and currents on the dumped materials resulted in the washings spreading along the marine platform and inside the bay itself, totally blocking it, filling it up from the west. After 33 years of directly dumping into the sea, the bay was completely filled up with 60 million tons of non-inert wastes, pushing the coast line 500-600 metres further out to sea compared with the original situation. Although a degree of equilibrium has been reached since dumping stopped, the sediments are subject to marine dynamics, especially those nearer the sea line and the effects of rainfall, runoff and other tailings (Martínez-Sánchez *et al.* 2014).

When dumping stopped in 1991, the need for solutions to the potentially contaminated site was evident, and a regeneration project was developed, being divided into three stages. From 1994 to 2006, The Ministry of the Environment carried out several studies through Centre for Public Works Studies and Experimentation (CEDEX) with proposals based on the removal of the dumped wastes. The studies involved an analytical characterisation of the sediments, which revealed the high total contents of arsenic and PTEs, although no risks assessment was made.

In 2006 a competition brought to light ideas for the bay's recovery with recreational use of the park and beach. The winning proposal '*in situ*' was the seed of the environmental recovery project being carried out at present. A pilot project was carried out over four years, adjusting the treatment technologies to the bay's situation, the construction of rehabilitated plots and a centre of investigation, where the experiments of control, analysis and stabilisation were carried out, and ecotoxicological methods assayed. All these experiments provided results that satisfied the need for the mandatory evaluation of the environmental impact of the project (Martínez-Sánchez *et al.* 2017).

Material and methods

Field surveys and measurements

The sediments filling the bay are affected by mining activities but have undergone different evolution:

(1) the direct discharge of steriles from the mineral flotation plant, and soluble and particulate materials from Sierra Minera, also affected by mining activities. These materials from primary contamination sources are characterised by an acidic pH;

(2) sediments affected by mining activities, which underwent a grain selection process through the action of coastal dynamics; and

(3) materials of mining origin, which have been subjected to natural attenuation by mixing with carbonate materials and which were transported by watercourses to the beach (García-Lorenzo *et al.* 2012). Among these materials, the most representative are those originated by the froth flotation plant. To characterise this area in order to develop a recovery project, a sampling design was carried out with cores of 10 m depth (Pérez Sirvent *et al.* 2017). A total of 12 cores were taken, aligned in three rows with respect to the coastline (Fig. 1). A sample was obtained for each metre of the profile, thus providing data of texture, and chemical and mineralogical composition.

Physical, chemical and mineralogical analyses

Sediment samples were air-dried and sieved through a 2-mm screen for general analytical determinations. The pH was determined in a 1:5 (m/V) suspension of soil in pure, deionised water (Milli-Q; resistivity $\geq 18 \text{ M}\Omega \text{ cm}$).

The mineralogy was studied by X-ray diffraction (XRD). Samples were ground in an agate mortar and sieved through a 53- μm mesh. Mineral phases were identified by powder XRD using a Philipps Analytical PW 3040 Cu K α radiation power diffractometer, fitted with graphite monochromator radiation K α_1 = 1,5406 Å. Diffractograms were recorded continuously at 2 θ angles from 2 to 68°, with 0.02 stepping intervals and 1 s per step.

The semiquantitative mineralogical analysis was carried out according to the Chung method (1975), using Xpowder software. The Chung method is based on the determination of the Reference

Intensity Ratios (RIR) of the existing phases, which allows the intensity calculations to be normalized on the sum of all phases in the sample is equal to 100%.

The particle size distribution was evaluated by static light scattering (LS) equipped with a microliquid module (Coulter LS 13320, Beckman Coulter, Inc., Fullerton, CA, USA). The Coulter LS 13320 software uses Mie theory to produce an optimal analysis of the light energy distribution and to obtain the size distribution of the particles.

Total and water-soluble elemental analysis

To determine the total PTE content, the sediment samples were first ground to a fine powder using a zirconium ball mill. Aliquots (0.1 g) of sediments were placed in Teflon vessels, and a mixture of 5 ml concentrated HF (37 %), 200 µl concentrated HNO₃ (65 %) and 5 ml water was added.

An ETHOS laboratory microwave system (Milestone, Sorisole (BG), Italy) equipped with temperature and pressure feedback controls, magnetic stirring capability and 10 high pressure vessels of 100-ml inner volume, operating at a maximum exit power of 1500 W, was employed for the digestion process. When digestion in the microwave system was complete, the samples were transferred to a volumetric flask and brought to 50 ml before measurement. Teflon or other suitable plasticware was used for handling these liquids. All the experiments were conducted in triplicate.

In addition to total contents, sediment samples were subjected to leaching tests according to standards UNE-EN-12457 (AENOR 2003) (a soil : water ratio of 1:1 during 24 h) in order to assess the natural mobility of PTEs.

Potential risk assessment

A method for the determination of AVS and SEM in sediments, using a common elemental analyser with thermal conductivity detector, was used with the purpose of determining the potential mobilisation. A mixture of Sn and V₂O₅ for pyrolysis and combustion to determine total sulphur (TS), and non-volatile sulphur (NVS) was used after acid attack with 2 M HCl. AVS was calculated as the difference between TS and NVS. The SEM/AVS ratio is an index recommended by the US EPA for the assessment of potential risk related to PTEs in anoxic sediments. Sediments are suggested to be

potentially toxic if the SEM/AVS ratio is greater than 1, and not toxic when the SEM/AVS ratio is less than 1 (Wang *et al.* 2016).

Contaminant bioaccessibility, rather than total content, is used as a key indicator of the potential risk that contaminants pose to the environment and human health. Oral bioaccessibility refers to the fraction that is soluble in the gastrointestinal environment and is available for absorption by blood. To assess the bioaccessible fraction, the gastric solution was prepared according to the standard operating procedure (SOP) developed by the Solubility/Bioavailability Research Consortium (SBRC) (Ruby *et al.* 1999; Kelly *et al.* 2002).

Zinc and Fe contents were determined by flame atomic absorption spectrometry (FAAS) using a Perkin-Elmer 800 atomic absorption spectrophotometer. Lead, Cd and Cu were determined by electrothermal atomization atomic absorption spectrometry (ETAAS) using the same instrument. Arsenic was quantified by atomic fluorescence spectrometry using an automated continuous flow hydride generation spectrometer (PSA Millenium Merlin 10055). The reliability of the results was verified by means of certified reference materials (NIST SRM 2711 Montana Soil, NIST SRM 2709 San Joaquin Soil, NCS DC 73319, NCS DC 73320, NCS DC 73321, NCS DC 73323, NCS DC 73324, NCS DC 73325, NRC BCSS-1, NRC PACS-1).

Results and discussion

Physical characteristics of sediment cores

The studied materials mostly have a sandy texture (Fig. 2a). However, the great influence of the direct discharge to the bay can be seen in samples collected in S16 core (Fig. 2b), located in the internal area in front of the froth flotation plant, where the texture is finer, sandy loam to loamy sand. The finest texture has been quantified in the first metre. A similar behaviour can be observed in samples collected in S1 and S2, located in the west of the bay, closer to the area of direct discharge into the sea. These samples showed a slightly finer texture in the first surface meter, particularly a loam texture in the first meter of S1 and sandy loam in the first meter of S2 (Fig. 2b).

The content of clay particles ($<2\ \mu\text{m}$) is very low, with a median value of 0.14 %. More than 75% of the samples presented a clay percentage lower than 1%. Samples from S1, S2, S16, S18 and S21 are above the background value, established as the median, and the maximum (18%) is present

in the first metre of S1, where the direct discharge from the flotation plant took place. The rest of the cores showed a very low clay percentage and colloidal properties do not appear developed.

The background value for particle content < 50 µm was 7%, and 75 % of the samples showed a percentage lower than 20 %. Samples from S1, S2, S16, S18 and S21 surveys showed values above the background, and the maximum, 51%, was determined in the deepest part of the S1 core.

Depending on the particle size, a zonation could be established in the bay: areas whose particles showed a thicker texture, and therefore with less specific surface and less reactivity, are located in the central zone and extended to the sea, at increasing depth. Other areas, in the east and west of the bay, where the particle size decreases, the specific surface and reactivity increase.

Chemical characteristics of sediment cores

Materials at depth show neutral to slightly basic pH values; the background value, established as the median, was 8. The minimum value is 6.2 and was determined in the first metre of S16. In the surface samples of S6 and S12, values lower than 7 have also been determined, at 6.3 and 6.7, respectively. Taking into account that the dissolution processes of PTEs are very influenced by pH, it is expected that at these pH values the soluble mobilisation at depth is minimal.

Total and water-soluble elements

The total PTE content is very high, corresponding to materials affected by mining activities, in the following order, Zn>Pb>As>Cu>Cd.

All samples showed high Fe content, with a background value of 31.1 %. The highest values were found in S1, S2, followed by S3, S4, S5 and S6, all of them located close to the coast line, and where a grain selection process, carried out by marine currents, has produced an enrichment in magnetite and other iron phases. On the other hand, the finer fraction was mobilised by these currents.

In S1, Fe values oscillate between 36.3% and 53.8%, in all cases, contents above the established background value of 31.1%. In S2, S3, S4, S5 and S6 cores, the highest value was determined in the most surficial sample, in some cores, S2 and S5, with values higher than the 95th

percentile (p95), established as 52.1% (Fig. 3a). In the rest of the cores, located farther from the coastline, the grain selection process has not taken place and the Fe enrichment did not occur.

The Zn content, with a background value of 8134 mg kg^{-1} , has a variable distribution with depth (Fig. 3b). In S1, the values are below the 50th percentile (p50) in the first 6 m while at depth anomalous values ($> p95$) have been determined between 7 and 9 m. In S2, the Zn content ranges from p50 to p95, except at 3 to 5 m, where the values exceed this percentile with concentrations of 11952 and 12224 mg kg^{-1} , respectively. In the deepest sample, the Zn content is below the median, at 6700 mg kg^{-1} . In S3, mobilization of this element took place, showing, in most samples of the first 6 m, Zn contents below the p50. At greater depth, Zn values are between p50 and p95. No anomalous values ($>p95$) for this element were found in this core. On the other hand, in S4 the highest Zn concentrations are found in the most surficial samples, with a value of 22124 mg kg^{-1} between 1 and 2 m. In this case, the migration of the element seems to have been diminished, and below 4 m, the Zn values are below the background level. This same behaviour is observed in S5 and S6, where the highest concentrations occur in the first 3 m depth.

In cores collected in the second line, S10, S11, S12 and S21, no values higher than p95 for Zn have been determined at any depth. Finally, in S16 and S18, taken at the furthest part of the coastline, there are diverse values: in S16, an anomalous concentration, greater than p95 (11948 mg kg^{-1}), was determined at 1 m depth, with a value of 12536 mg kg^{-1} , and in the surficial sample, a minimum of 6803 mg kg^{-1} was quantified for this element, suggesting the washing of this element with depth. The rest of the values ranged between 50th and 95th percentiles. On the other hand, in S18, anomalous values have not been evident, and the concentrations show slight variations with depth.

Lead has a background value (median) of 1219 mg kg^{-1} , and the maximum values were found in S1, S2, S16 and S18 (Fig. 3c). As commented above, these cores show the highest clay percentage, suggesting a higher content in fine, reactive particles. The maximum Pb value, 3701 mg kg^{-1} , was determined in the first m of S1, coinciding with a direct discharge point from the froth flotation plant. In addition, in S5 and S6 the most elevated Pb content was determined in the first m (Fig. 3c). On the other hand, S16 and S18, even located further away of this discharge point, are not influenced by sea currents and washing of PTEs did not take place. In the last step of mining exploitation, wastes were discharged directly in this part of the bay.

The As content has a background value of 274 mg kg^{-1} in the bay, and its content is lower in cores located in the coastline, increasing away from the shore. The highest concentrations of each

core are given by the surface sample, 471, 248, 451, 451, 421, and 556 mg kg⁻¹ in S1, S2, S3, S4, S5, and S6 cores, respectively (Fig. 3d). The As content in these cores decreases at depths greater than 1 m, maintaining a regular concentration up to 10 m. In the case of S10, an anomalous surface value was observed, at 914 mg kg⁻¹, decreasing as increasing depth to 248 mg kg⁻¹ at 10 m. A similar behaviour was found in S12, with a surficial maximum value of 763 mg kg⁻¹ that decreases with depth, although values above the 50th percentile were found in all samples. Values for As measured in S21 are below the background value, except for the surface sample and at depths greater than 5 m.

The total Cu content has a background value of 50 mg kg⁻¹, with anomalous values of this element being observed at intermediate depths (5-8 m) in S5 and S6, and on the surface of S10. It is important to highlight that cores collected close to the coastline generally have low Cu values, in many cases below the 50th percentile, while those collected in the central zone of the bay have values between the 50th and 95th percentiles, and in some cases even above p95, established as 91 mg kg⁻¹ (Fig. 3e).

For Cd (Fig. 3f), values greater than p95 (26 mg kg⁻¹) have been quantified only in S18 and S21, in the first case between 5 and 6 m depth, while in S21 values above of the 95th percentile were found from this depth to 10 m. In the other samples, the total Cd values are not high, in many cases below the median, established at 12 mg kg⁻¹.

Mineralogical characteristics

The mineralogical composition of cores close to the coastline is similar to those collected in the inner part of the bay but slight differences have been found. In cores S1 to S6, samples show a characteristic mineralogical composition of materials that have undergone a grain selection process, the most abundant being quartz, iron minerals (siderite) and phyllosilicates. Pyrite (FeS₂) and magnetite (Fe₃O₄) show a regular distribution in all samples. Anomalous percentages of these minerals have been found in the most surficial part of S4 and S6 for pyrite and for magnetite at intermediate depth of S1 and S6 (Fig. 4).

The inherited phases from the material that once constituted the waste discharged into the sea are represented by phyllosilicates, quartz and magnetite, representing the gangue, while pyrite is a residual mineral of the beneficiated ore. Hematite (Fe₂O₃) and siderite (FeCO₃) are partly inherited and partly neoformed as a result of alteration processes. In S11, a high hematite content has been found, with percentages greater than 20 % in almost all samples.

Jarosite ($(K, NH_4, Na)Fe_3(SO_4)_2(OH)_6$) has its origin in the oxidation process of pyrite and other sulphides, which has been partially carried out on surface in supergene conditions. The influence of sea is clear since natrojarosite ($NaFe_3(SO_4)_2(OH)_6$) is the most representative phase. Then, the marine influence is highlighted with the contribution of sodium to the alteration processes. These results suggest that the study area acted as a salt marsh when the discharges took place and the bay was not completely closed. Natrojarosite is present in the surficial samples with variable proportions, showing an anomalous high percentage in the first m of S1 (15 %). Only in the surficial horizons has akaganeite (β -FeOOH) been quantified, related to the current processes of alteration in oxidising conditions.

The grain selection process becomes clear by comparing the samples metre by metre, with clear differences between the first metre and the rest.

Natural mobility of PTEs

The collected materials generally have a very low soluble PTE content (Table 1). For Pb, all samples are below the detection limit, established as $10 \mu\text{g kg}^{-1}$. The most mobile element was Zn, with an average value of 0.6 mg kg^{-1} and a maximum of 26 mg kg^{-1} in S2, from 1 to 2 m depth. In S1, S2 and S16, the maximum soluble concentration of Zn has been quantified at this depth. The highest values of Cd, Cu and As are also evident from 1 to 2 m in S1 and S2. Elevated soluble Cd content has been determined both in S5 to S6 from 4 to 5 m, with values of 165 and $132 \mu\text{g kg}^{-1}$, respectively. For As, S10 shows the highest soluble concentrations in the first 4 m, with values ranging from 19 to $12 \mu\text{g kg}^{-1}$. Similar behaviour has been observed in S11 but with lower soluble As content. Finally, soluble Fe concentration was very low in all samples. The low Fe mobility in water agrees with the low solubility of the Fe minerals present in the samples, such as iron carbonates, oxides and oxyhydroxides.

Potential risk assessment

The results of AVS and SEM analysis are summarized in Table 1. Acid-volatile sulphides in the samples fall in the range between 72 and $4367 \mu\text{mol/g}$. The samples show a variable sulphide

presence, both pyrite and other sulphides of Zn, Cd, Cu and As in undetermined quantities, together with volatile sulphides. The samples are characterised by a homogeneous pyrite percentage. In addition, there are acid volatile sulphides that include amorphous sulphides, the surveys closest to the beach presenting the lowest values of AVS.

The SEM/AVS ratio is less than unity except for S1 from 1 to 2 m depth. This low ratio would indicate that there is enough sulphur so that if there was a release of metals, they could precipitate as sulphides.

In surficial samples, the level of volatile sulphur is higher than at depth, as is the SEM/AVS ratio.

Bioaccessibility of metals

The results of the bioaccessibility extraction show that the most bioaccessible element is Zn, followed by Pb and Cu (Fig. 5). Cadmium and As have very low values. If both conditions, gastric and intestinal are compared, it is observed that Zn and Cd are more bioaccessible in the intestinal environment (alkaline) while the rest of the elements have greater availability in the stomach (acid).

In general, As is the least mobile element in all the studied media, followed by Pb and Cu. The most mobile elements are Zn and Cd. In terms of depth, the bioavailability of all elements is higher in the surficial samples than at depth (Fig. 5).

Conclusions

The results obtained have been the basis for the decision making needed by the environmental recovery project of Portman Bay. The high total PTE content in the collected sediments would not justify an action of environmental recovery. The PTE mobility in Portman Bay is closely related to the mineralogical composition and the granulometry, and is a consequence of the grain selection process produced in the discharge to the sea. The sediments of coarser texture have a high pH, low PTE mobility and a mineralogical composition that is usually associated with high contents of siderite and iron oxides and hydroxides, such as goethite, magnetite, hematite and akageneite.

Fine-textured sediments have not suffered grain selection, either because they were directly discharged on the beach or because the coastal dynamics did not allow their dispersion. They correspond to materials with lower pH, presence of jarosite in some cases, and abundance of phyllosilicates and iron oxides and oxyhydroxides.

Pyrite is the main mineral responsible, in the studied area, for the future reactivity of these sediments under supergene conditions, together with the production of AMD, and is present in almost all the studied samples, but not in the same granulometric fraction. The values obtained for AVS and SEM allow for the estimation of the sediment alteration capacity that will depend on the mineral concentration, the size and degree of crystallization, as well as changing environmental conditions, including the possibility of exposing of these materials to supergene conditions.

Finally, bioaccessibility values show that only Zn (intestinal bioaccessible fraction) and Pb (bioaccessible stomach fraction) can reach high values in certain samples.

With this work, the necessary tools were used for a correct risk assessment procedure both in the current scenario and in the future, allowing the selection of the best technology for the environmental recovery of Portman Bay.

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Table 1 Statistical parameters from the natural mobility results (see AENOR 2003 for leaching details) (n=120)

	Pb $\mu\text{g kg}^{-1}$	Zn mg kg^{-1}	Cd $\mu\text{g kg}^{-1}$	Cu $\mu\text{g kg}^{-1}$	As $\mu\text{g kg}^{-1}$	Fe mg kg^{-1}
Min	6.32	0.10	1.00	2.34	0.01	0.02
Max	7.16	26.60	165.12	894.00	50.00	4.63
Mean	6.74	0.63	15.84	39.65	6.14	0.53
SD	2.89	27.26	104.83	5.86	0.57	8.33
25 th	6.54	0.08	4.03	10.00	3.52	0.25
50 th	6.74	0.16	9.63	15.00	4.70	0.47
75 th	7.06	0.35	15.01	36.86	7.02	0.59

Table 2 Statistical parameters calculated for the SEM/AVS results (n=120)

	AVS $\mu\text{mol/g}$	Fe -SEM %	Pb-SEM mg/kg	Zn-SEM mg/kg	Cd-SEM mg/kg	Cu-SEM mg/kg	$\Sigma\text{SEM } \mu\text{mol/g}$	$\Sigma\text{SEM/AVS}$
Min	71.7	9.7	92.0	1883	7.0	10.9	36.87	0.02
Max	4367	26.3	5491	12536	33.0	65.9	204	1.5
Mean	823	19.5	1457	6552	14.1	25.9	108	0.2
SD	664	2.8	820	1979	5.0	11.1	30.8	0.2
25 th	439	17.9	952	5167	11.0	18.0	85.4	0.1
50 th	679	19.4	1319	6540	13.0	22.9	107	0.2
75 th	973	21.5	1896	7899	16.0	29.2	128	0.2

Figure 1 Main environmental elements and changes in the Portman Bay sector and sample location

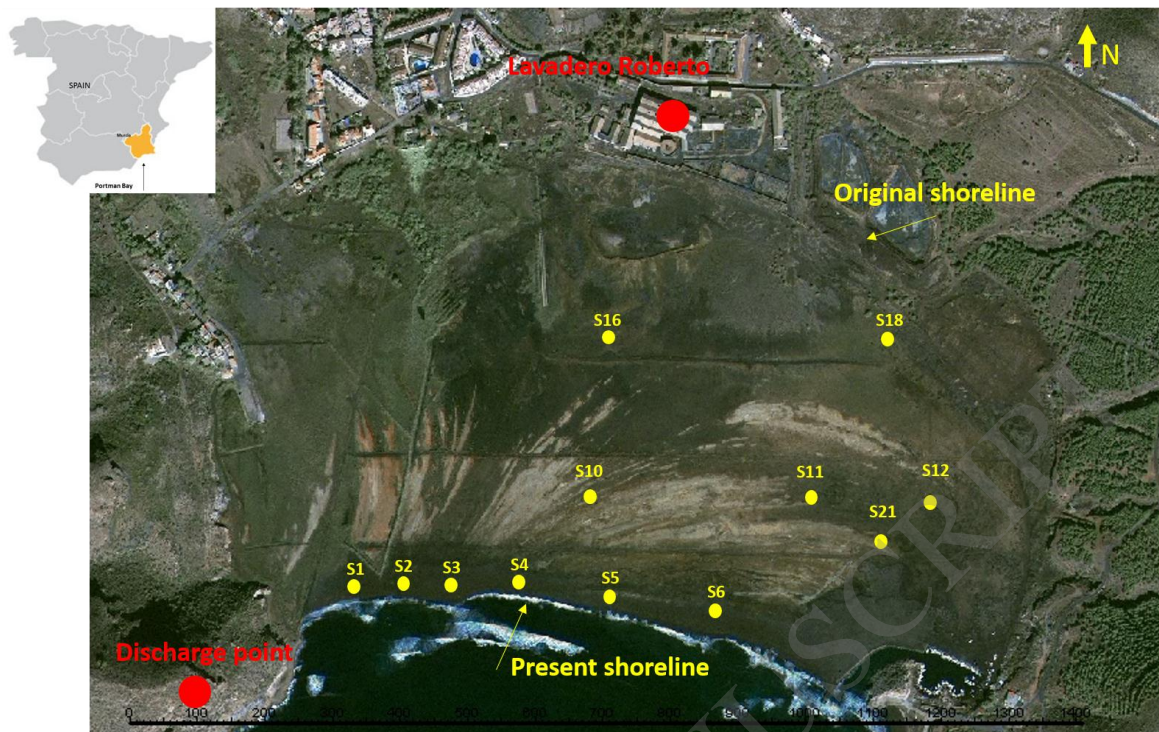
Figure 2 Ternary diagram of sediment sample textures

Figure 3 Box plots of statistical total PTE content in sediment surveys

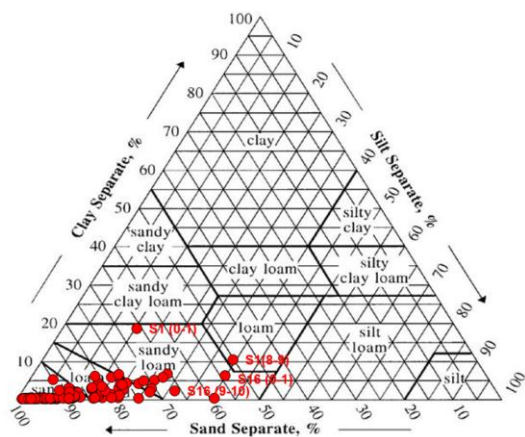
Figure 4 Box plot of statistical mineralogical composition

(Qtz: quartz; Py: pyrite; Mg: magnetite; Hem: hematite; Sd: siderite; Aka: akaganeite; Gt: goethite; Alu: alunite; Gp: gypsum; Na-Jar: natrojarosite; Phy: phyllosilicate)

Figure 5 Statistical results of bioaccessible PTEs



a)



b)

