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## A preliminary zonation to support the remediation and the risk assessment of an area contaminated by potentially toxic elements in Murcia Region (SE, Spain)

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### Abstract

The objective of this work was to evaluate processes affecting soil samples in Portman Bay in order to establish a preliminary zonation of the affected area. For this aim, a complete physical, chemical and mineralogical characterization of sediments, both in surface and at depth was carried out.

Portman bay is situated close to the mining region of La Unión., located in the province of Murcia, south-eastern Spain. The entire area around the bay was subject to mining from the time of the Roman Empire to 1991. Since 1957, the wastes from mining operations were discharged directly into the sea in the inner part of the bay, while later on, they were also discharged to sea at a distance of the shore. These wastes mainly consisted in ore materials (galena, pyrite and sphalerite), phyllosilicates, in addition to siderite, iron oxides and sometimes alteration products such as jarosite, alunite, kaolinite and greenalite.

Mining activities have produced great amounts of wastes, characterized by high trace elements content, acidic pH and minerals from weathering processes.

The results of the applied characterization allowed a preliminary zoning of the risk in the area to be established, and this was the starting point to outline the remediation project.

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## 1. Introduction and study area

Mining is a major anthropogenic source of trace elements in soils and sediments, which often results in the transport and distribution of these elements into the surrounding environment<sup>1</sup>.

Portman bay is a singular point of mining impact in the Mediterranean area. The site is located in the province of Murcia, south-eastern Spain, and was completely inundated with more than 63 million tons of mining waste discharged through a huge washing plant. Wastes from mining activities mainly consisted of ore materials (galena, pyrite and sphalerite), phyllosilicates, in addition to siderite, iron oxides and sometimes alteration products such as jarosite, alunite, kaolinite and greenalite<sup>2</sup>. These materials were submitted to a concentration process by floatation with sea water and as a result of the discharge, the whole of the bay was filled up with wastes which also extended into the Mediterranean Sea. In the last years of activity, wastes were even poured alternatively in the sea or over the sediments filling the bay. These actions have produced a very high heterogeneity in the sediments. Although after the end of the discharges it has been possible to reach a certain degree of balance, the sediments, especially those closest to the sea, are subjected to marine dynamics and the effects of rainfall and runoffs.

The construction of the Roberto washer, situated along the beach of Portman Bay, began in 1952. It's started working in 1957, receiving 1000 tons of ore per day, getting to 6000 tons in 1968 and 7000 tons in 1972, until the year 1978 when it reached 8000 tons per day, with average grades between 1.5 and 2% Pb, and 2 and 3% Zn.

In 2007, a recuperation pilot project was developed and financed by the Spanish Government.

In the first step of this project, the complete physical, chemical and mineralogical characterization of sediments, both in surface and at depth was carried out.

Twenty surface samples were collected (<1 m) and twelve sediment cores were also collected at the same time (Figure 1).



Figure 1. Distribution of surficial and core samples in the study area

## 2. Methodology

To determine the total trace element content, zinc and iron levels were determined by flame atomic absorption spectrometry, while lead, cadmium and copper levels were determined by electrothermal atomization atomic

absorption spectrometry. The arsenic content was measured by atomic fluorescence spectrometry using an automated continuous flow hydride generation spectrometer. The reliability of the results was verified by analyzing standard reference materials. The mineralogical composition was determined using Cu-K radiation with an X-ray Diffractometer and appropriate software<sup>3</sup>.

**3. results**

Surface samples showed different textures depending on provenance: sediments with a fine-grained texture correspond to residues from Lavadero Roberto, with high trace element contents related to fine particles, which are the most reactive whereas others have a sandy texture because of grain sorting by sea currents (Figure 2). The surface sediments showed high spatial variability in pH values. The lowest pH corresponds to samples where sulfide weathering led to acidification and precipitation of jarosite and, and hydrolysis of silicates, forming clay minerals.

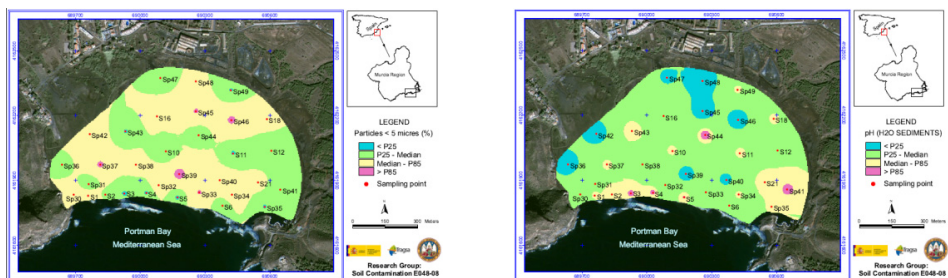


Figure 2. pH and percentage of particle < 5µm in collected samples

Sediment cores, collected near the shore, showed a neutral pH and sandy texture at depth. Trace element concentrations are lower than in surficial samples, and in the mineralogical composition a relative enrichment of minerals such as quartz or clay minerals was found while minerals such as jarosite, akaganeite or alunite are scarce. The highest contents of arsenic and lead were found at the surface (Figure 3).

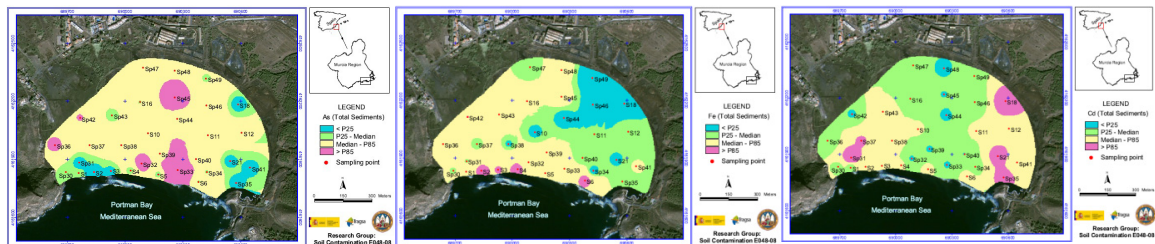


Figure 3. Total Fe, Cd and As content (mg/kg) in samples

In contrast, zinc and cadmium showed higher concentrations at depth. Iron content was higher in surficial samples, except for S1 and S2 where iron content increased with depth, consistent with mineralogical results. Minerals discharged from Lavadero Roberto included phyllosilicates, quartz and magnetite (gangue) and pyrite as a residual ore mineral. Hematite and siderite are both components of the original wastes and also newly formed minerals produced by weathering. Sulfide weathering took place in the uppermost layer, with jarosite being the main weathering product -particularly natrojarosite- indicative of the influence of seawater in this process. At depth, phases such as jarosite, akaganeite and gypsum disappear. The presence of Fe<sup>2+</sup> minerals, such as pyrite, siderite and magnetite, suggests reducing conditions at depth.

The data allowed a preliminary zoning of the risk in the area to be established, and this was the starting point to outline the remediation project (Figure 4). The risk assessment was carried out both for the human health and the ecosystems, and based in four main points: (i) the hazard identification; (ii) the toxicological assessment; (iii) the exposure assessment and; (iv) the risk characterization. After the current risk was assessed for the selected receptors in the selected routes (ingestion, dermal, inhalation, water and wind dispersion), the proposed soil uses after the remediation project (park use and beach use) were also evaluated in the same way.

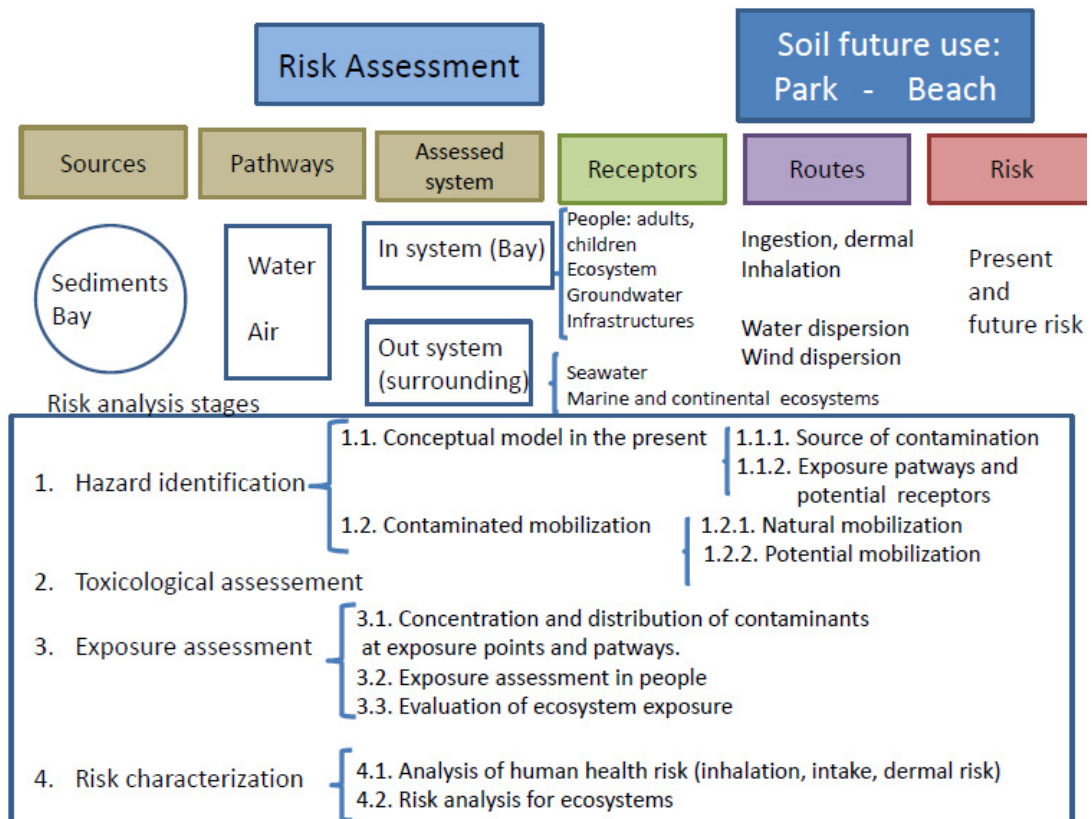


Figure 4: Risk assessment proposed methodology

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