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An anomalous metal-rich phosphogypsum: characterization and classification according to international regulations

Authors:

Francisco Macías[a*], Carlos R. Cánovas[a], Pablo Cruz–Hernández[a], Sergio Carrero[a], Maria P. Asta[b], José Miguel Nieto[a], Rafael Pérez–López[a]

[a] *Earth Science Department, University of Huelva, Campus "El Carmen", E-21071 Huelva, Spain.*

[b] *Environmental Microbiology Laboratory, École Polytechnique Fédérale de Lausanne, EPFL ENAC IIE EML, CE 1 543 (Centre Est), Station 6, CH-1015 Lausanne, Switzerland.*

*Corresponding author:

francisco.macias@dgeo.uhu.es

Tel.: +34-95-921-9834; fax: +34-95-921-9810

Abstract

Phosphogypsum is the main waste generated by the phosphate fertilizer industry. Despite the high level of pollutants found in phosphogypsum and the proximity of stacks to cities, there are no specific regulations for the management of this waste. This study addresses this issue by applying to phosphogypsum, from a fertilizer plant in Huelva (SW Spain), the leaching tests proposed by the current European and US environmental regulations for wastes management and classification. Two main conclusions were obtained: 1) the anomalous metal and metalloid concentrations (e.g. As, Fe, Pb, Sb, Mn, V and Cu) and higher mobility observed in the Huelva phosphogypsum compared to other stacks worldwide, and 2) the discrepancies observed between EU and US regulations dealing with hazardousness classification of these materials. This latter finding suggests the need to use complementary assessment protocols to obtain a better characterization and classification of these wastes. An evaluation of the potential risk to the aquatic life according to the US EPA regulation is proposed in this study. The results warn about the acute and chronic effects on the aquatic life of this waste and suggest the adoption of more strict measures for a safe disposal of phosphogypsum stacks.

Keywords:

leaching tests; hazardousness classification; aquatic life risk; arsenic anomaly.

1. Introduction

Phosphate fertilizer industry plays a key role to maintain the levels of farming production worldwide. This industry needs phosphoric acid for the fertilizer production, which is mainly obtained from the manufacturing process of phosphate rock by the "wet acid method" [1]. In this method, the previously washed phosphate rock is concentrated by flotation and digested with sulfuric acid to obtain phosphoric acid and an unwanted by-product known as phosphogypsum. For every ton of phosphoric acid manufactured, 5 tons of phosphogypsum are generated. Considering that the world phosphate rock production is increasing as well as the P_2O_5 consumption from fertilizers, then, the world phosphogypsum production is expected to reach values around 100-280 Mt per year [2].

The geochemical characteristics of phosphogypsum are strongly influenced by the ore phosphate rock composition and by the chemical behavior of impurities released during manufacturing process [3]. Thus, although phosphogypsum is mainly composed by gypsum ($CaSO_4 \cdot 2H_2O$), this waste also contains some impurities such as phosphate, sulfate and fluoride, mainly in form of residual acids, toxic trace elements (e.g. As, Cd, Cr, Cu or Zn) and radionuclides from uranium decay series. Then, the management, environmental policy and potential recycling of these wastes depend on the type and amount of impurities. From all the phosphogypsum generated in the world, only the 15% is recycled, mainly as building materials [1]. The remaining 85% is disposed of in large stacks, commonly in coastal areas, without any treatment and exposed to weathering processes. During operation, phosphogypsum is commonly stockpiled near the fertilizer plant over a composite liner to avoid infiltration. Upon closure, the stack is often capped with an impermeable layer to avoid leaching of contaminants.

Despite the high content of contaminants found in phosphogypsum and the proximity of stacks to cities, it is especially surprising that there are no specific regulations for the management of this waste. Furthermore, the phosphogypsum leaching capacity and the compliance of leachates to current regulations have not been properly addressed. There are several works dealing with the environmental impact of radionuclides contained in phosphogypsum, which suggest managing this by-product in radioactive waste landfills [e.g. 1, 4]. However, only few researches have been focused on the trace metals leachability during weathering processes or on the behavior of phosphogypsum stacks, based on leaching protocols, for management strategies according to international rules [5, 6]. In this sense, the high variability in phosphogypsum chemical composition associated to the different nature of phosphate rock, type of wet acid process performed and the release of contaminants during acid phosphoric manufacturing may cause significant differences on the leaching behavior among piles. Owing to this variability, the research on metal release from stacks worldwide under different weathering scenarios is of crucial importance.

Therefore, the present study addresses this issue by applying to phosphogypsum, from a fertilizer plant in Huelva (SW Spain), the leaching tests proposed by the current European and US environmental regulations for wastes management and classification (EN 12457-2 [7] and TCLP [8], respectively). In addition, owing to the intense interaction of Huelva phosphogypsum with seawater, leaching tests with this weathering agent have been also performed. The results of these tests have been compared with, to our knowledge, the only case reported worldwide applying these leaching protocols; the Mulberry stacks (Florida, US) [5]. Additionally, the potential risk to the aquatic life under different weathering scenarios has been studied by comparing the leachates composition to the so-called criterion continuous concentration and criterion maximum concentration from the National Recommended Water Quality Criteria of the US EPA [9]. The results obtained in this study will fill a gap in the knowledge of the potential pollutant release of these wastes under different weathering agents and help decision makers to determine the best cost-effective and environmentally safe disposal practices for these wastes.

2. Huelva phosphogypsum stack

The phosphoric acid production in the city of Huelva since 1967 to 2010 has caused the dumping of around 100Mt of phosphogypsum directly on 12 km^2 of salt-marshes of the Tinto River estuary, less than 100 m from the urban core (Fig. 1). The Huelva phosphogypsum is divided into four different zones within the stack (Fig. 1); zones 1 and 4 account for 65 Mt of phosphogypsum deposited over 680 ha, with heights ranging from 2 to 10 m. Both zones have been restored by conventional dry-covers to prevent weathering. Despite to this fact, highly-polluted acid leachates are directly discharged into the estuary [10]. Zones 2 and 3 are unrestored areas, accounting up to 40 Mt of phosphogypsum deposited over 440 ha, with average heights of 30 and 8 m, respectively. In both zones, the number and pollution grade of the acid discharges are far greater than those from the already-restored zones 1 and 4 [10].

The singularity of the Huelva phosphogypsum stack relies on two outstanding circumstances: a) the waste was deposited over the marshland without any type of isolation, and b) the piles are located within the tidal prism of the estuary. As a consequence, the Huelva phosphogypsum is subject to three different weathering scenarios. Firstly, the wastes are subject to weathering by rainwater (at least zones 2 and 3), where in semiarid climates rainfall events are scarce but intense. Secondly, due to its location within the estuarine system, the stack is also affected by the weathering of seawater during tidal cycles. Finally, owing to the absence of composite liners in the bottom of the stack, the residue is in direct contact with the organic matter-rich marshland; for this reason, the upward flow of seawater and the downward flow of rainwater may interact with the stack, causing the weathering of the phosphogypsum under reducing conditions [6]. Detailed information about environmental setting of the Huelva stack and its pollution capacity can be found elsewhere [6, 10].

3. Materials and methods

3.1 Sampling and analysis of total composition of Huelva phosphogypsum

Phosphogypsum solid samples were collected in the zone 3 of the stack (Fig. 1) in November 2015, from a bore-hole at different depths (0.5, 1.6, 2.9, 3.5, 4.1, 5.6, 7 and 8.1 m). The two shallowest samples correspond to unsaturated zone (0.5 and 1.6 m samples), whereas the remaining samples correspond to saturated zone (from 2 to 8.1 m). The deepest sample represents the stack basement directly in contact with the estuarine marsh soils. Additionally, 6 surface phosphogypsum samples (Z3-1 to Z3-6) were collected in different locations of the zone 3 for seawater leaching experiments (Fig.1). After collection, samples were immediately frozen and lyophilized to preserve their characteristics.

The chemical composition of the samples was obtained by analyses after aqua-regia pseudo-total digestion. These data were compared to those obtained from different leaching protocols with the purpose of quantifying the proportion of pollutants released by each weathering process simulated. This chemical extraction has been traditionally used to determine the pseudo-total metal content in environmental samples, with good recovery percentages regarding the total content. Thus, 10 mL of aqua-regia (12 mol L^{-1} HCl and 15.8 mol L^{-1} HNO_3 in the ratio 3:1) were added to 1 g of phosphogypsum in Teflon reactors and reacted for 20 h in a fume cupboard, and then, simmered on a hot plate for 1 h at 100 ºC. The digestates were diluted with deionized water and stored refrigerated at 4ºC until analysis.

3.2 Leaching protocols for management and hazardousness assessment

Three different leaching tests were performed to assess the waste management and disposal according to its hazardousness. On the one hand, the phosphogypsum was subject to leaching protocols established by current regulations on waste disposal using both EU standard EN 12457-

2 [7] and US standard TCLP [8] leaching tests. On the other hand, the release of pollutants under seawater interaction was studied by leaching with seawater. All these leaching tests simulate the potential weathering agents that may currently release pollutants from the stacks, which will be briefly described below.

The EN 12457-2 leaching test is applied to assess the acceptance for disposal of a waste in European landfill sites, and has been widely used in mineral-processing wastes [e.g. 11-12]. The experimental concentrations obtained in the test must be normalized to the sample weight in order to be compared with the limit threshold values issued by the European Council Decision [13] as criterion for the acceptance of wastes in three types of landfill sites: landfills for inert wastes, non-hazardous wastes and hazardous wastes. The test was conducted by mixing phosphogypsum samples with deionized water at a liquid to solid ratio of 10:1, followed by stirring for 24 h, centrifugation and filtration of the supernatant and determination of dissolved elements. In addition, the use of deionized water in this test allows us to estimate the potential leaching of pollutants by phosphogypsum through contact with rainwater.

The TCLP leaching test [8] was originally designed to simulate co-disposal with municipal wastes, although its applicability has been extended for the hazardousness classification of mineral-processing wastes [14] regarding to the regulated limits of certain inorganic pollutants [e.g. 11, 15-16]. Additionally, metal concentrations in TCLP leachates can be also employed as limits to determine if a specific waste needs to be submitted to an universal treatment standard (UTS) to accomplish with Land Disposal Restrictions (LDR, EPA 530-R-01-007) [17]. The test was performed according to the method 1311 of the US EPA [8]. The samples were extracted for 18 h by stirring on a shaker with a liquid to solid ratio of 20:1. The extractant must be chosen as function of waste pH. For samples with pH < 5, such as the Huelva phosphogypsum, an acetic acid solution buffered to pH 4.9 was used as extractant. Following the extraction, samples were centrifuged, the supernatant filtered, acidified with HNO_3 and stored refrigerated at 4ºC until analysis. In this case, leaching of phosphogypsum with organic acids would simulate the leaching processes when the upward flow from the basement and/or the downward flow by meteoric water from the surface interacts with organic matter-rich environments from the salt-marshes.

Finally, the simulation of weathering by seawater was performed in 6 samples by mixing with seawater at a liquid to solid ratio of 10:1, followed by stirring for 24 h. Afterwards, filtration of the supernatant and determination of dissolved elements or pollutants were performed. Seawater used during this leaching test was obtained in the coast of Atlantic Ocean near to the city of Huelva.

3.3 Analytical methodology

Major element (Al, Fe, Mn and S) concentrations were obtained using Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES; Jobin Yvon Ultima 2) and trace element (As, Ba, Be, Cd, Co, Cr, Cu, Mo, Ni, Pb, Sb, Se, Sn, Tl, V and Zn) contents by Inductively Coupled Plasma-Mass Spectroscopy (ICP-MS; Agilent 7700). Detection limits were: 0.2 mg/L for S; 0.05 mg/L for Al and Fe; 0.02 mg/L for Mn; and 0.2 µg/L for trace elements. All analyses were performed in the laboratories of the University of Huelva. Three laboratory standards, prepared with concentrations within the range of the samples, were analyzed every 10 samples to check for accuracy. Furthermore, dilutions were performed to ensure that the concentration of the samples was within the concentration range of the standards. Blank solutions with the same matrix as the samples were also analyzed. The average measurement error was <5%.

3.4. Comparison with other phosphogypsum stacks worldwide

With the aim of checking remarkable differences of the waste by-products in various phosphoric industries, the total chemical composition of Huelva phosphogypsum has been compared with that reported for other phosphogypsum stacks around the world. Data were obtained from stacks located at Florida, Idaho and Louisiana reported by Mostary (2011) [5], Luther et al. (1993) [18] and Carbonell-Barrachina et al. (2002) [19], respectively; from Brazilian phosphogypsums published by Oliveira et al. (2012) [20], da Conceicao et al. (2006) [21] and Silva et al. (1999) [22]; from Canadian phosphogypsum reported by Rutherford et al. (1995) [23]; and from Tunisian and Jordanian stacks described by Choura et al. (2015) [24] and Abed et al. (2008) [25], respectively.

Also for comparison purposes, data after applying the TCLP and EN standardized leaching tests in phosphogypsum from a giant stack located at Mulberry (Florida, US) [5] were used. Phosphate mining in Florida is one of the state's largest industries, and produces approximately 40 Mt of phosphogypsum per year [5], accounting between 14-40% of worldwide phosphogypsum production. In this US state, more than one billion tons of phosphogypsum are permanently stored in over 25 giant stacks, some of them with up to 60 m in height and 2 km^2 in extension [26]. For this reason, it seems reasonable to consider Mulberry phosphogypsum as a representative stack worldwide. These authors collected samples from four locations on the stack walls at different depths along the first 0.6 m. Then, samples collected from different depths for each location were thoroughly mixed to get a homogenous sample, obtaining finally a total of 8 samples. To our knowledge, this is the only case worldwide applying the EU standard EN 12457-2 and US standard TCLP leaching tests to phosphogypsum.

4. Results and Discussion

4.1 Chemical composition of Huelva phosphogypsum and comparison with other phosphogypsum stacks

The Huelva stack acts as an anthropogenic aquifer system, with clearly differentiated unsaturated (0-2 m) and saturated zones (from 2m depth to the bare marsh). This latter zone is subject to a strongly reducing environment, especially the phosphogypsum located at the bottom of the stack. This feature promotes chemical gradients along the profile, and therefore different responses to weathering may be expected.

As can be observed in Figure 2, most elements analyzed reached the highest concentrations in the bottom of the profile (with the exception of Se). This fact is due to sulfate-reducing processes occurring in the contact of phosphogypsum with bare marshland soils [27, 28] that promote precipitation and trapping of metals of the pore-waters into metallic sulfides. However, a slight enrichment is observed for Fe and other trace metals (i.e. Sn, Ba, Cr, Pb, Se and Mo) in the unsaturated zone (0-2 m) compared to the saturated zone (except to the bottom, in contact with the marshland; Fig. 2).

The chemical composition of the three zones identified in the Huelva stack, i.e. unsaturated, saturated and marshland contact zones, has been compared with that reported in others stacks around the world (Fig. 3). As can be observed, Huelva phosphogypsum exhibits the same range of concentrations for most elements as those reported worldwide, with the exception of the bottom material where enrichments in Fe, Pb, Sb, Mn, V, Cu, Co Ni and Cr are observed in relation to the rest of stacks (Fig. 3). However, the most striking feature is the anomalously high concentration of As observed along the whole profile, i.e. between 1 and 2 orders of magnitude higher than that found in the rest of reported stacks worldwide. The most probable origin of this anomalously high concentration of As in the Huelva phosphogypsum could be related with the quality of the sulfuric acid used during the industrial process. The sulfuric acid used during phosphoric acid manufacturing in Huelva was mainly obtained by pyrite roasting and SO_2 recovery [29]. The pyrite used came from the Tharsis Mines which contained up to 0.4% of As

[30], thus, the high level of As in the sulfuric acid may have been transferred to the phosphogypsum.

These results highlight the singularity of Huelva stack as an anomalous As and metal-rich phosphogypsum among the cases reported worldwide, especially in the bottom of the stack where Fe, Pb, Sb, Mn, V, Cu, Co, Ni and Cr are trapped as a consequence of the interaction between the phosphogypsum and the organic matter-rich marshland soils. As a difference of most phosphogypsum deposits worldwide, Huelva was not stockpiled over an impermeable liner but on bare marshland soils [10]. If these metal and metalloids, anomalously enriched in Huelva, were easily mobilized by weathering agents, the current state of the Huelva stack may pose a serious threat to the environment.

4.2 Management assessment and hazardousness classification based on international regulations

Owing to the anomalously high As concentration along the profile and high metal concentrations observed in the deepest zone of the Huelva stack, its hazardousness and the suitability for landfill disposal must be addressed. Table 1 shows the regulatory limits for waste acceptance at landfills in EU [13], and the results of the EN 12457-2 leaching test applied to the Huelva depth profile. For comparative purposes, the results reported in Mulberry [5] with the same test are also included.

According to these results, the unsaturated zone of the Huelva stack could be considered as a non-hazardous waste because sulfate and Cd exceed the limit of 6000 mg/kg and 0.04 mg/kg respectively, established for inert wastes landfills. On the other hand, the saturated zone may be considered as a hazardous material due to the high concentrations of As leached and, therefore, it must be deposited in landfills for this type of wastes. As well as the saturated zone, the phosphogypsum deposited in the bottom of the stack in contact with the marshland soils also exceeds the values of non-hazardous wastes for As and Cd. Thus, this zone of the stack must be also deposited in a hazardous waste landfill. The trend on metal and metalloids release in depth by EN 12457-2 leaching test is in agreement with the trend observed for total chemical composition (Fig. 2). In summary, the mobility of As and Cd confers the Huelva stacked material the classification of hazardous waste according to EU regulations. On the other hand, the Mulberry phosphogypsum should be considered as a non-hazardous waste according to the EU regulation by the release of Cu, Mo, Ni and Zn; only these metals exceed the threshold limits for inert waste landfills (Table 1). Unlike Huelva, As and Cd were below the detection limit for Mulberry (Table 1), elements which confer the hazardousness to the Huelva pile.

According to US EPA regulation [8, 14], the Huelva and Mulberry phosphogypsums can be considered as non-hazardous wastes due to the fact that the TCLP limits are not exceeded in any case (Table 2). The Mulberry phosphogypsum neither exceeds the UTS limits nor must therefore be treated before disposal to accomplish with Land Disposal Restrictions [17]. However, the waste stored in the bottom of the Huelva stack releases Cd at concentrations that exceed the UTS limit, so this zone of the stack must be treated before disposal. Most elements considered in the TCLP (mainly highly toxic, e.g. As, Cd, Pb, V) were below the detection limit in the extractants from Mulberry, unlike in the Huelva phosphogypsum where remarkable concentrations were reached. This pattern is in line with that of chemical composition and of deionized water leaching results obtained in Huelva and Mulberry, highlighting the anomalous metal and metalloid concentrations and higher mobility observed in the Huelva phosphogypsum.

The discrepancies between EU and US regulations dealing with hazardousness classifications of mineral processing wastes have been previously reported [11], which suggests the need to use complementary assessment protocols to obtain a better characterization and classification of these wastes. In case of discrepancies, a detailed investigation of the potential effects on the aquatic life should be performed in order to assure a safe waste disposal and a risk minimization to the environment.

4.3 Environmental impact on aquatic life under different weathering scenarios

The impact of this anomalously metal-rich phosphogypsum on the aquatic life has been studied under different weathering scenarios: (1) weathering by rainwater (simulated by EN 12457-2 leaching test), which may occur in the unrestored zones of Huelva stack during rainfall events; (2) weathering under reducing conditions (simulated by TCLP leaching test), which may occur in the lower part of saturated zones and in the bottom of Huelva pile; and (3) weathering by seawater, which may occur during tidal cycles. The impact of these weathering scenarios on the aquatic life has been assessed by comparison with the criteria established by the US EPA. In this sense, the Criterion Continuous Concentration is the threshold value above which a certain element poses a significant risk to the majority of species in waters if chronic exposure is maintained. On the other hand, the Criterion Maximum Concentration represents the acute exposure to a metal, that is, the highest one-hour average concentration that should not result in unacceptable effects on aquatic organisms.

Tables 3 and 4 show the Criterion Continuous Concentration and Criterion Maximum Concentration limits, and the metal and metalloid release after EN 12457-2 and TCLP tests in the Huelva and Mulberry phosphogypsum stacks, respectively. As can be observed, only Al and, at a lesser extent, Zn exceed the limits in Mulberry, which pose a risk for aquatic life by both elements upon acute and chronic exposure. The metal exposure for aquatic life under rainfall weathering and reducing conditions of Huelva phosphogypsum is even more severe; Cd exceeds both limits along the whole profile while other pollutants (Al, As, Pb, Ni, Se and Zn) show exceedance of one of the two limits at different depths. Only Fe, Cu and Cr values remained below the threshold limits of the aquatic life criteria established by the US EPA along the whole profile. In addition to As and Cd, the release of other toxic metals (e.g. Pb, Se or Zn) under rainfall weathering and reducing conditions poses a risk to the aquatic life. The comparison with Mulberry highlights, once again, the hazardous nature of the Huelva stack and warns about the acute and chronic effects on the aquatic life during rainfall events and reducing conditions.

The interaction of seawater with Huelva stack also causes a significant release of toxic metals. Both limits for Cd were exceeded in all samples and for As in two cases (Table 5). The rest of the elements exceeded Criterion Continuous Concentration and/or Criterion Maximum Concentration limits in one or several samples (with the exception of Cu). Once more, both Cd and As appear to be the most mobile and harmful elements in Huelva phosphogypsum, which agree well with the anomalous total chemical composition and the release observed for these elements under previous weathering scenarios. Unfortunately, to our knowledge there is no data available to compare with these findings. There is only one work focused on the interaction between phosphogypsum and seawater [31], which only deals with the U release under this weathering agent. This is probably due to the lower values of metals contained in phosphogypsum worldwide compared to the anomalously high metal concentrations observed in Huelva. Thus, little attention has been paid to this issue up to now.

4.4. Potential release of metal and metalloids from different weathering agents; implication for remediation strategies.

As indicated in the previous section, the Criterion Continuous Concentration and Criterion Maximum Concentration limits are exceeded with different elements, then, a relative hazardousness order for weathering agents in Huelva stack could be established as: seawater > rainwater > reducing conditions. However, the potential release of metal and metalloids from each weathering agent interacting with the stack must be quantified as well as the factors controlling these processes. Table 6 shows the percentage of each pollutant released with respect to the total chemical composition for the phosphogypsum samples and for the weathering agents used. As it is shown, the rainwater weathering and the leaching under reducing conditions cause the release of high percentages of As, Cd, Cu, Ni and Zn in the saturated and bottom zones of the profile. Except for Cd, the remaining pollutants are leached in higher percentages in saturated zone than in the contact zone of phosphogypsum with marshland soils. These findings are supported by other studies [27, 28] which evidence the key role played by sulfate-reducing processes on the contaminant attenuation in phosphogypsum stacks.

On the other hand, the percentages released by seawater are exceptionally high for two of the six samples (Z3-2 and Z3-5). In these samples, the percentages of As, Cd, Cr, Cu, Ni, and Zn released under seawater leaching were twice or three times higher than those obtained with rainwater and reducing conditions, which is consistent with the hazardousness order established for the weathering agents from the US EPA water quality criteria limits. However, the metal and metalloid release potential in the remaining four samples with seawater was low, only Cd and Ni were released at significant rates in these samples (Table 6). The different release rates observed in samples subject to tidal influence within the stack may be related to chemical changes produced during the exposure to weathering agents. Phosphogypsum samples exposed to leaching by meteoric or estuarine waters may have lost most of residual acids and soluble trace elements originally present in comparison to other samples with a lesser contact with these agents. As can be seen in Table 6, the samples with lower potential to release metals and metalloids correspond to those with pH values close to neutrality. The alkalinity contained in seawater is high enough to neutralize the residual acid still contained in these samples, causing metal and metalloid depletion in the leaching solution; only the most mobile metals, such as, Cd and Zn remain in solution. This pH dependence of metal and metalloid release from the phosphogypsum samples has been previously pointed out by Pérez-López et al. (2010) [32], who reported a good correlation (R^2= 0.79) between pH and P, which is indicative of H_3PO_4 residual content.

These results have serious implications for restoration strategies and the environmental impact on the surrounding environment. Despite the high potential to release metals and metalloids shown by rainwater, the settlement of impermeable barriers, i.e. clay covers, to avoid water infiltration would mitigate the impact of this weathering agent on the metals and metalloids release to the environment. However, the absence of any isolation barrier in the base of the stack may cause the interaction of estuarine waters with phosphogypsum. Marshland soils act as a nearly impermeable barrier that withholds groundwater in depth and forces the water to flow laterally. When the groundwater reaches the edge of the stack, polluted water emerges forming superficial drainages, known as edge outflows, which release a high load of contaminants into the estuary [10]. According to this latter work, both As and Cd are the main contaminants reaching the estuary through edge outflow waters in highly remarkable percentages in relation to other pollution sources. These findings are in agreement with the results of the leaching tests performed in this study (Table 6) and may pose a great environmental concern. Both toxic pollutants, especially Cd, behave conservatively in estuarine waters [33], which not only poses a significant risk to the majority of species by chronic exposure but may also result in unacceptable effects on these organisms under acute exposure.

Therefore, despite the absence of specific regulations on the management and disposal of these by-products, the hazardousness evidenced by the present study justifies the exploration of alternative restoration measures to avoid the transference of pollutants from these wastes to the environment. Some discrepancies were observed according to the leaching protocols performed based on international regulations (i.e. EU and US). In this sense, these wastes must be deposited in properly conditioned landfills for hazardous wastes according to the EU regulations and in non-hazardous waste landfills after treatment (for Cd removal) according to the US regulation. However, other more cost-effective and environmentally-friendly such as reutilization of this waste or recycling of compounds contained should be also addressed. This later issue has been recently evaluated for Huelva phosphogypsum, suggesting that this waste is a potential source of critical raw materials [34] or Ca for mineral carbon sequestration [35].

5. Conclusions

Despite the high content of contaminants found in phosphogypsum and the proximity of stacks to cities, it is surprising the absence of specific regulations for the management of this waste and the lack of information of metal and metalloid release under different weathering scenarios. This study tries to fill this gap by applying different leaching protocols to the phosphogypsum generated in the Huelva fertilizer plant (SW Spain), assessing the compliance of leachates to current international regulations.

Compared to other stacks around the world, enrichment in Fe, Pb, Sb, Mn, V, Cu, Co Ni and Cr is observed in the Huelva phosphogypsum. However, the most remarkable finding is the anomalously high concentration of As observed along the whole profile, i.e. between 1 and 2 orders of magnitude higher than those observed in the rest of reported stacks worldwide. This is attributed to the quality of the sulfuric acid used in the manufacturing process (i.e. from As-rich pyrite roasting). The mobility of metals and metalloids under different weathering agents (i.e. rainfall, reducing conditions and seawater) acting simultaneously in Huelva stack was assessed and compared to that reported by, to our knowledge, the only case worldwide applying some of these protocols to phosphogypsum; the giant stack of Mulberry (Florida, US).

The mobility of As and Cd confers the Huelva stacked material the classification of hazardous waste according to EU regulations, while the Mulberry should be considered as a non-hazardous waste by the release of Cu, Mo, Ni and Zn. However, according to US EPA regulation both the Huelva and Mulberry can be considered as non-hazardous wastes due to TCLP limits were not exceeded in any case, although in the case of Huelva, the phosphogypsum must be treated before disposal because exceed the Cd UTS limit for the bottom zone. Two main conclusions can be raised from this comparison: 1) the anomalous metal and metalloid concentrations and higher mobility observed in Huelva compared to Mulberry and 2) the discrepancies observed between EU and US regulations dealing with hazardousness classification of these materials. This latter finding suggests the need to use complementary assessment protocols to obtain a better characterization and classification of these wastes. For this reason, the assessment of the potential effects on the aquatic life under different scenarios has been performed.

The exceedance of limits for Al and, at a lesser extent, Zn in Mulberry phosphogypsum may pose a risk for aquatic life upon acute and chronic exposure. The metal exposure for aquatic life under rainfall weathering and reducing conditions of Huelva is even more severe; Cd exceeds the US EPA water quality criteria limits along the whole profile while other pollutants (Al, As, Pb, Ni, Se and Zn) shows exceedance of these limits at different depths. Only Fe, Cu and Cr values remained below the threshold limits of the aquatic life criteria established by the US EPA along the whole profile. This highlights the higher environmental risk caused by the stockpiling of these wastes in comparison to that of Mulberry and justifies the disposal of these wastes in landfills for hazardous wastes.

The results of this study must be taken into account in the already-started restoration plan of the Huelva phosphogypsum, which only contemplates the use of conventional dry-covers; this situation will mitigate the weathering by rainwater, however, the stack would be subject to seawater weathering. The impact of this weathering agent strongly depends on the acidity balance between the estuarine waters and the acidic phosphogypsum pore-waters. The existence of acid and metal rich outflows from restored zones by dry-covers implies the need of alternative restoration measures to explore new routes for recycling and reuse of these by-products or, at least, to mitigate the metal and metalloid pollution by disposal in landfills for hazardous wastes.

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FIGURES

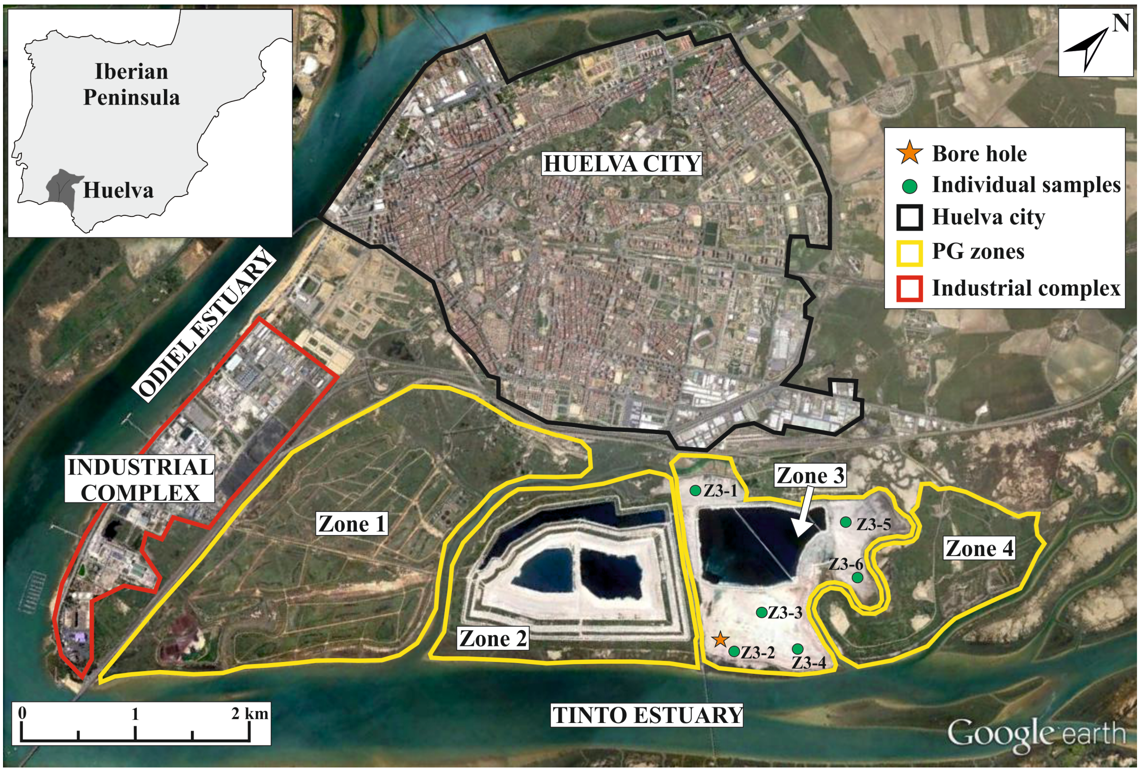

Figure 1. Location map of the Huelva phosphogypsum stack, with bore-hole and individual sampling points indicated. Image from Google Earth© software.

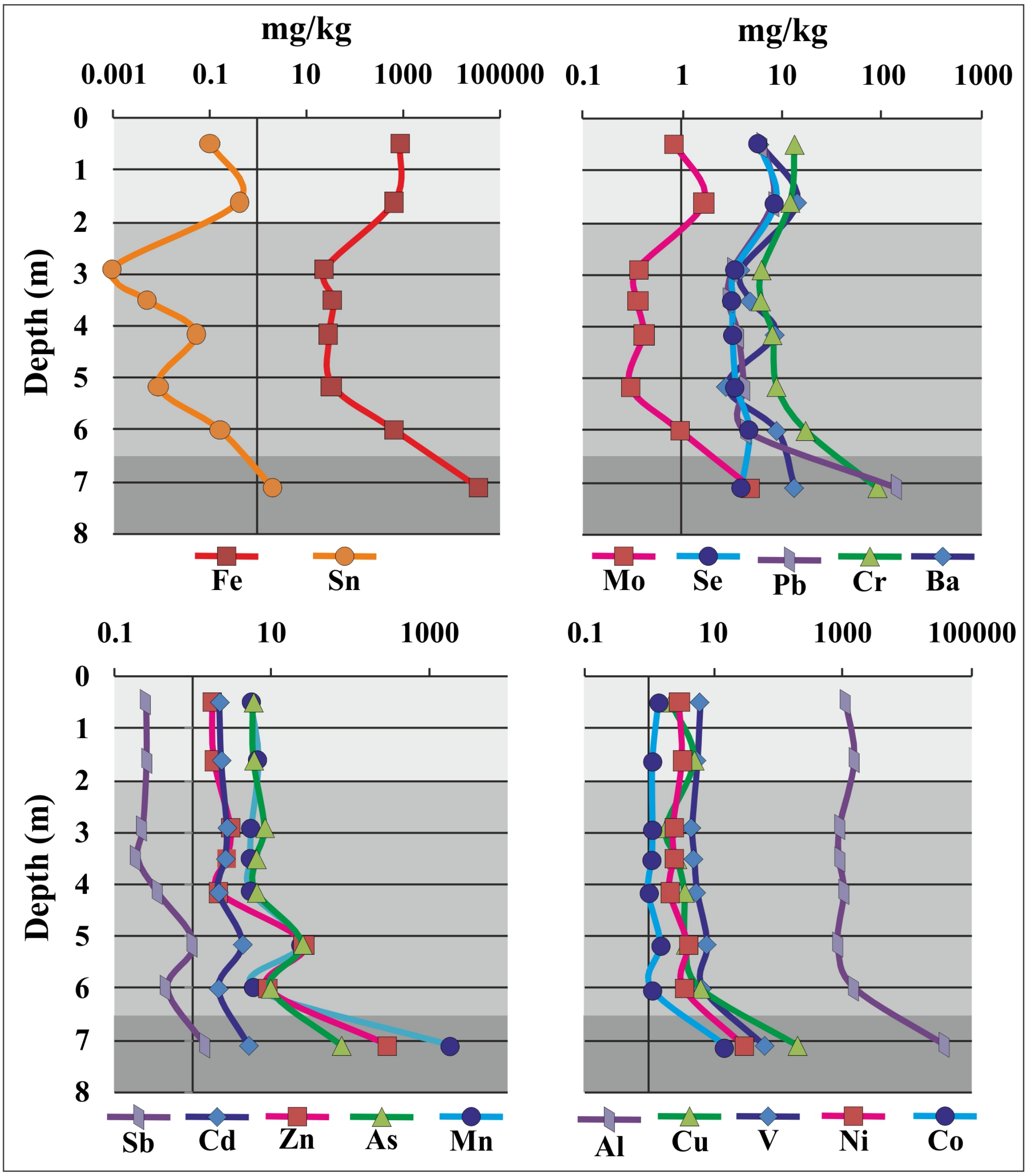

Figure 2. Metal content of the Huelva phosphogypsum at different depths (see text for explanation).

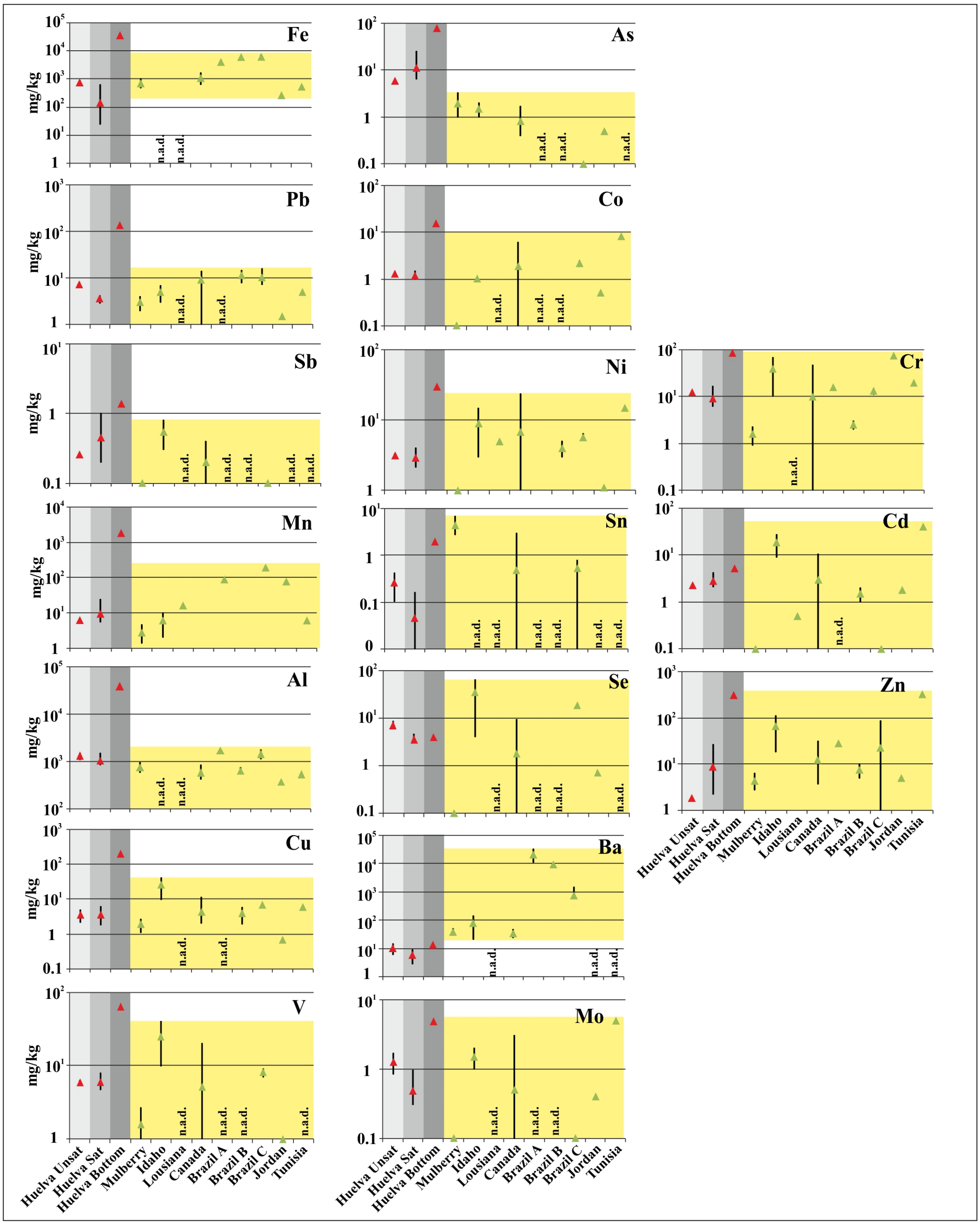

Figure 3. Content in metal and metalloids of Huelva phosphogypsum profile and comparison with other phosphogypsum stacks worldwide. Max, min and mean values are plotted. n.a.d. (no available data).

TABLES

Landfills for:	**As**	**Ba**	**Cd**	**Cr**	**Cu**	**Mo**	**Ni**	**Pb**	**Sb**	**Se**	**Zn**	**$SO4^{2-}$**
Inert wastes	0.5	20	0.04	0.5	2	0.5	0.4	0.5	0.06	0.1	4	6000
Non-hazardous wastes	2	100	1	10	50	10	10	10	0.7	0.5	50	20000
Hazardous wastes	25	300	5	70	100	30	40	50	5	7	200	50000
Huelva PG depth profile (m):												
0.5	0.03	0.19	0.12	b.d.l	0.03	0.04	0.09	b.d.l	b.d.l	0.06	0.31	13758.63
1.6	0.09	0.2	0.11	b.d.l	0.04	0.05	0.1	0.02	b.d.l	0.07	0.32	14067.45
2.9	4.24	0.29	0.35	0.22	0.78	0.02	0.43	0.13	0.03	0.02	2.63	15045.97
3.5	3.72	0.29	0.34	0.33	0.74	0.02	0.41	0.14	0.04	0.02	2.57	14799.06
4.1	3.47	0.35	0.38	0.39	1.52	0.02	0.48	0.17	0.05	0.02	2.57	16168.68
5.1	3.22	0.28	0.35	0.34	1.26	0.03	0.38	0.11	0.06	0.03	6.73	18082.20
6	6.71	0.3	0.42	0.26	0.7	0.02	0.46	0.1	0.04	0.03	9.16	16739.63
7.1	6.76	0.23	1.78	0.03	1.78	0.18	1.06	0.01	0.05	0.1	24.71	18028.75
Mulberry PG (n=8)												
Max	b.d.l	1.20	b.d.l	b.d.l	3.40	2.00	0.80	b.d.l	b.d.l	b.d.l	5.80	n.a.d
Min	b.d.l	0.40	b.d.l	b.d.l	1.80	0.40	0.20	b.d.l	b.d.l	b.d.l	2.00	n.a.d
Mean	b.d.l	0.80	b.d.l	b.d.l	2.40	1.00	0.40	b.d.l	b.d.l	b.d.l	3.60	n.a.d

b.d.l (below detection limit), n.a.d (no available data).

Table 1. Results of the EN 12457-2 leaching test applied to the Huelva depth profile and Mulberry phosphogypsum stack, and comparison with the regulatory limits for waste acceptance at landfills in EU. Data in mg/kg.

Limits:	**As**	**Ba**	**Cd**	**Cr**	**Ni**	**Pb**	**V**	**Zn**	**Se**	**Sb**	**Be**	**Tl**
TCLP	5	100	1	5	n.r.l	5	n.r.l	n.r.l	1	n.r.l	n.r.l	n.r.l
UTS	5	21	0.11	0.6	11	0.75	1.6	4.3	5.7	1.15	1.22	0.2
Huelva PG depth profile (m):												
0.5	0.002	0.027	0.010	b.d.l	0.011	0.002	b.d.l	0.026	b.d.l	b.d.l	b.d.l	b.d.l
1.6	0.006	0.026	0.008	b.d.l	0.012	0.005	b.d.l	0.021	0.004	b.d.l	b.d.l	b.d.l
2.9	0.213	0.036	0.019	0.005	0.026	0.008	0.015	0.124	b.d.l	0.002	b.d.l	b.d.l
3.5	0.185	0.034	0.020	0.008	0.027	0.009	0.033	0.126	b.d.l	0.003	b.d.l	b.d.l
4.1	0.177	0.041	0.022	0.005	0.029	0.004	0.028	0.121	b.d.l	0.003	b.d.l	b.d.l
5.1	0.345	0.032	0.024	0.005	0.027	0.001	0.019	0.419	b.d.l	0.002	b.d.l	b.d.l
6	0.156	0.028	0.020	0.007	0.024	0.001	0.018	0.304	b.d.l	0.002	b.d.l	b.d.l
7.1	0.400	0.030	0.127	0.008	0.068	0.008	0.075	1.591	0.004	0.004	b.d.l	0.001
Mulberry PG (n=8)												
Max	b.d.l	0.16	b.d.l	0.04	0.07	b.d.l	b.d.l	0.29	b.d.l	b.d.l	n.a.d	n.a.d
Min	b.d.l	0.07	b.d.l	0.02	0.01	b.d.l	b.d.l	0.05	b.d.l	b.d.l	n.a.d	n.a.d
Mean	b.d.l	0.11	b.d.l	0.03	0.03	b.d.l	b.d.l	0.14	b.d.l	b.d.l	n.a.d	n.a.d

n.r.l (no referenced limit), b.d.l (below detection limit), n.a.d (no available data).

Table 2. Results of the TCLP leaching test (method 1311 of US EPA) applied to the Huelva depth profile and Mulberry phosphogypsum stack, and comparison with the regulatory limits established by the Land Disposal Restrictions (LDR, EPA 530-R-01-007). Data in mg/L.

		pH	Al	As	Cd	Cr	Cu	Fe	Pb	Ni	Se	Zn
Total depth profile (mg/Kg)	Unsaturated	n.a	1301.7	5.9	2.3	12.5	3.6	791.3	7.3	3.2	7.2	1.8
	Saturated	2.12	1029.3	11.1	2.8	9.2	3.6	158.2	3.6	2.9	3.6	8.7
	Bottom	2.15	38303.7	77.7	5.2	87.9	197.8	36121.3	136.8	30.0	3.9	301.8
Rainwater (%)	Unsaturated		4.1	1.0	4.9	0.0	1.1	0.0	0.1	2.9	0.9	16.9
	Saturated		1.4	49.2	14.2	3.9	31.2	7.1	3.7	15.8	0.7	84.5
	Bottom		0.2	8.7	34.3	0.0	0.9	0.0	0.0	3.5	2.6	8.2
Reducing conditions (%)	Unsaturated		3	1.3	8.2	0.0	2.0	0.0	0.9	7.1	0.4	25.8
	Saturated		1.1	45.0	15.9	1.5	27.9	0.0	2.8	19.3	0.0	76.4
	Bottom		0.3	10.3	48.9	0.2	4.9	0.0	0.1	4.5	2.2	10.5
Total individual samples (mg/kg)	Z3-1	6.66	1923.4	b.d.l	2.1	3.6	b.d.l	300.3	4.4	1.4	b.d.l	4.2
	Z3-2	2.49	1627.4	6.4	2.8	16.7	3.3	208.6	10.8	2.7	b.d.l	13.1
	Z3-3	6.35	1314.4	b.d.l	1.6	9.9	b.d.l	299.6	3.6	0.9	b.d.l	1.9
	Z3-4	6.41	1275.8	b.d.l	1.4	20.3	b.d.l	287.0	2.8	0.9	1.2	2.3
	Z3-5	3.04	1244.4	11.6	2.3	11.2	2.2	216.6	3.2	1.9	b.d.l	9.9
	Z3-6	6.35	1001.0	b.d.l	1.4	3.6	b.d.l	120.4	2.0	1.1	b.d.l	2.4
Seawater (%)	Z3-1		0.6	0.0	8.8	0.0	0.0	0.0	0.0	5.9	0.0	0.0
	Z3-2		1.5	86.1	49.8	21.4	100.0	7.2	0.0	66.7	0.0	90.6
	Z3-3		0.9	0.0	7.5	0.0	0.0	0.0	0.0	11.4	0.0	0.0
	Z3-4		0.6	0.0	8.6	0.0	0.0	0.0	0.0	17.2	0.0	4.4
	Z3-5		1.3	71.7	38.5	2.7	100.0	1.0	9.4	45.5	0.0	63.5
	Z3-6		0.4	0.0	17.91	0.0	0.0	0.0	0.0	24.0	0.0	13.2

Table 3. Results of the leaching experiments with deionized water and comparison with the Mulberry results and the Criterion Continuous Concentration and Criterion Maximum Concentration limits established in the aquatic life criteria by the US EPA (see text for explanation). Data in mg/L.

US EPA Water Quality Criteria limits:	Al	As	Cd	Cr	Cu	Fe	Pb	Ni	Se	Zn
Criterion Continous Concentration	0.087	0.15	0.00025	0.085	1.3	1	0.0025	0.052	0.005	0.12
Criterion Maximun Concentration	0.75	0.34	0.002	0.586	n.r.l	n.r.l	0.065	0.47	n.r.l	0.12
Huelva depth profile (m):										
0.5	5.279*	0.003	0.012*	b.d.l	0.003	0.005	b.d.l	0.009	0.006**	0.032
1.6	5.450*	0.009	0.011*	b.d.l	0.004	b.d.l	0.002	0.010	0.007**	0.032
2.9	1.692*	0.428*	0.035*	0.022	0.078	0.083	0.013**	0.043	0.002	0.265*
3.5	1.590*	0.384*	0.035*	0.034	0.076	0.180	0.014**	0.042	0.002	0.265*
4.1	1.434*	0.350*	0.038*	0.039	0.153	0.470	0.017**	0.048	0.002	0.260*
5.6	1.152*	0.335**	0.036*	0.036	0.131	0.400	0.011**	0.040	0.003	0.699*
7	1.111*	0.697*	0.044*	0.027	0.073	0.801	0.011**	0.048	0.003	0.951*
8.1	6.371*	0.729*	0.192*	0.003	0.193	0.051	0.002	0.114**	0.011**	2.668*
Mulberry (n=8):										
Max	2.210*	b.d.l	b.d.l	b.d.l	0.170	b.d.l	b.d.l	0.040	b.d.l	0.290*
Min	1.200*	b.d.l	b.d.l	b.d.l	0.090	b.d.l	b.d.l	0.010	b.d.l	0.100
Mean	1.630*	b.d.l	b.d.l	b.d.l	0.120	b.d.l	b.d.l	0.020	b.d.l	0.180*

* (Both US EPA Water Quality Criteria limits has been exceeded), ** (only Criterion Continuous Concentration has been exceeded). n.r.l (no referenced limit), b.d.l (below detection limit).

Table 4. Results of the leaching experiments with organic acid and comparison with the Mulberry results and the Criterion Continuous Concentration and Criterion Maximum Concentration limits established in the aquatic life criteria by the US EPA (see text for explanation). Data in mg/L.

Table 5. Results of the leaching experiments with seawater and comparison with the Criterion Continuous Concentration and Criterion Maximum Concentration limits established in the aquatic life criteria by the US EPA (see text for explanation). Data in mg/L.

US EPA Water Quality Criteria limits:	**Al**	**As**	**Cd**	**Cr**	**Cu**	**Fe**	**Pb**	**Ni**	**Se**	**Zn**
Criterion Continous Concentration	0.087	0.15	0.00025	0.085	1.3	1	0.0025	0.052	0.005	0.12
Criterion Maximun Concentration	0.75	0.34	0.002	0.586	n.r.l	n.r.l	0.065	0.47	n.r.l	0.12
Huelva individual samples:										
Z3-1	0.300**	b.d.l	0.018*	b.d.l	b.d.l	b.d.l	b.d.l	0.008	b.d.l	b.d.l
Z3-2	0.600**	0.550*	0.141*	0.360**	0.434	1.490*	b.d.l	0.178**	0.020**	1.190*
Z3-3	0.300**	b.d.l	0.012*	b.d.l	b.d.l	b.d.l	b.d.l	0.010	b.d.l	b.d.l
Z3-4	0.200**	b.d.l	0.012*	b.d.l	0.004	b.d.l	b.d.l	0.015	b.d.l	0.010
Z3-5	0.400**	0.830*	0.089*	0.030	0.409	0.220	0.030**	0.087**	b.d.l	0.629*
Z3-6	0.100**	0.050	0.025*	b.d.l	0.008	b.d.l	b.d.l	0.025	b.d.l	0.031

* (Both US EPA Water Quality Criteria limits has been exceeded), ** (only Criterion Continuous Concentration has been exceeded). n.r.l (no referenced limit), b.d.l (below detection limit).

Table 5. Results of the leaching experiments with seawater and comparison with the Criterion Continuous Concentration and Criterion Maximum Concentration limits established in the aquatic life criteria by the US EPA (see text for explanation). Data in mg/L.