Assessing trace-element mobility in Algeciras Bay (Spain) sediments by acid and complexing screening

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Abstract Acetic acid (HOAc) and diethylenetriaminepentaacetic acid (DTPA) single extraction agents were evaluated as screening methods to estimate the mobility of some trace elements in coastal sediments from Algeciras Bay. Sediments’ total metal concentrations of most heavy metals were found to be high around the areas impacted by anthropogenic activities such as sewage, atmospheric deposition and industrial activities, with notable values for As, Ni, Cr, Pb and Cd. The order of significant extraction efficiencies obtained with DTPA, were as follows: Pb (25.65%), Cu (19.78%), Cd (14.80%) and Zn (11.25%), while those obtained with HOAc were: Mn (33.00%), Tl (24.88%), Pb (18.99%), Cd (13.59%) and Co (11.78%). The comparison between the risk assessment codes (RAC) and the percent metal extractable fractions provided results of serious concern. Very high risk values of Cu, Zn, Cd and Pb extracts in DTPA were observed near the metallurgical industry, with Mn and Tl in HOAc extracts showing high risk values near the same industrial area and harbour activities. Sediments’ total metal concentrations were compared with the Low Alert-Level (LAL) sediment quality guidelines, where Co, Pb, Zn and Ni in both extractants and Cd and Cu in DTPA as well as Tl extracted in HOAc exceeded the LAL values respectively. The Spearman Rank test showed positive correlations between Co, Cu, Ni and Zn in DTPA extracts and their corresponding total metal concentrations, with Co, Cr, Fe, Ni, Ti and Zn in HOAc and total concentrations showing positive correlations. Furthermore, higher positive correlations were found between both extraction methods for Co (ρ = 0.797), Cu (ρ = 0.777), Ni (ρ = 0.789) and Zn (ρ = 0.942), indicating comparable potential extraction efficiencies between these extractants for these metals in the sediment studied.

1. Introduction

Contamination by trace elements, such as heavy metals and some metalloids has become an environmental problem because of their high toxicity and persistence in the environment (Morillo et al., 2002). Total metal determination in...
sediment gives valuable information about the overall levels, but it is insufficient to estimate their biological effects and potential toxicity (Lopez-Sanchez et al., 1996; Weisz et al., 2000; Kuang-Chung et al., 2001; Morillo et al., 2004, 2007). One important factor to evaluate the short and long-term impact of trace elements is their mobility, which is related to eco-toxicity and depends strongly on their specific chemical forms (Fuentes et al., 2004; González et al., 2009).

Methods based on the available/reactive fraction are usually used to determine the mobility and availability of metals to biota and their interaction with sediment (Sahuquillo et al., 2003; Arain et al., 2009). The methodology may consider sequential or single extractions. Sequential extractions allow the assessment of different metal fractions associated with all phases of the sediment, although they are labour-intensive. On the other hand, single extractions are simple, quick and cost-effective way to investigate the metal mobility in sediments by using weak acids or complexant solutions such as DTPA (Cappuny and Swennen, 2008; Hamdoun et al., in press; Peijnenburg et al., 2007; Meers et al., 2007; Luo et al., 2012).

Single extractions with weak acidic solutions are frequently used to evaluate availability in sediments as a percentage of trace elements in the exchangeable and carbonate fraction of the sediment. HOAc has been reported (Sahuquillo et al., 2003; Arain et al., 2008; Horváth et al., 2013) to have the capacity of remobilising trace elements that are weakly bound and sensitive to acidification processes (spill or acid rain), which are considered as the fraction readily and potentially bioavailable (Filgueiras et al., 2002). The HOAc extraction as recommended by the European Community Bureau of Reference (BCR) (Davidson et al., 1994, 1998) was applied in this study.

Single extractions with complexing agents are suitable to predict potentially active metal fraction (Ettler et al., 2007; Luo et al., 2012) associated with complexation processes, especially adsorbed and organic complexed metal. Chelating agents have the capability to form stable metal complexes over a wide pH range (Abumázar and Smith, 1999; Finzgar and Lestan, 2007; Peters, 1999; Sun et al., 2001). Their use offers a promising approach for the extraction of metals from contaminated sediments. Lindsay and Norvell (1978) proposed a DTPA based extraction solution, buffered at pH 7.3 to exclude effects involving carbonate dissolution.

The single extractions results can be used to calculate alternative pollution indicators as the risk assessment code (RAC) (Passos et al., 2011; Zhao et al., 2012), better than those based on total metal content (Dung et al., 2013). RAC considers the percentage of available metals by defining, assessing and ranking the environmental risk degree of metal content in sediment, where classifications of risk levels are defined as follows: no risk: <1%; low risk (LR): 1% ≤ x ≤ 10%, medium risk (MR): 11% ≤ x ≤ 30%, high risk (HR): 31% ≤ x ≤ 50% and very high risk (VHR): >50%, depending on the percentage value (Perin et al., 1985).

This study reports the application of DTPA (Lindsay and Norvell, 1978) and HOAc as applied in the BCR sequential extraction scheme to estimate the mobility of sediment bound heavy metals in a bay from the south of Spain impacted by effluents from anthropogenic activities (urban sewage, pollution from atmospheric deposition, an important harbour and different industries). They offer the possibility of screening the mobilisable trace elements in sediments and environmental risk assessment. The extraction efficiencies of DTPA and HOAc were compared in sediments collected from different sampling sites. The studied elements, As, Ba, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Ti, V and Zn were selected on the basis of their origin, toxic effects as well as their ability to accumulate in sediments and biota. Some of them are considered essential to living organisms (Co, Cr(III), Cu, Fe, Mn, Ni, V and Zn) in traces amounts, however they may also be toxic if present in excess (Crichton, 2012a, 2012b). Some of them are related to metallurgical industrial effluents, such as Cr, Cu, Mn, Pb and Zn (Domènech and Peral, 2006) or municipal discharges (Zn) and, in a lesser extent, atmospheric depositions from metal smelting and coal burning (As or Pb) (Culicov et al., 2002; Zhao et al., 2012; Martin et al., 2014).

2. Materials and methods

2.1. Sample collection and pre-treatment

Algeciras Bay is a unique and important coastal ecosystem located in South-western Europe at the frontier between the Atlantic Ocean and the Mediterranean Sea, on the north-eastern end of the Strait of Gibraltar, South of Spain (Fig. 1), where the two-way exchange between the oceanic and sea waters occurs. The bay, with a surface area of about 73 km² and faces south-south eastward, is 8–10 km wide and 10–12 km long, and has a maximum depth of nearly 400 m, features by far the mildest surface currents of the strait. The mean circulation of Atlantic Water (AW) is characterised by an anticyclonic cell, while Mediterranean Water (MW) follows a preferred cyclonic pathway. The renewal of AW is largely modulated by tides, with meteorological forcing playing a secondary role. The opposite applies to the renewal of MW (Sánchez-Garrido et al., 2014).

The main rivers that drain into the bay are the Guadarranque and Palmones rivers. Five important cities are located around the bay (Algeciras, Los Berríos, San Roque, La Línea de la Concepción and Gibraltar), and are home to more than 250,000 inhabitants ('agglomeration' according to EU Directive 96/62/CE; Council Directive 96/62/EC, 1996).

The bay suffers from persistent anthropogenic pollution from the urban and industrial activities of the zone (e.g., stainless steel manufacturing plant, petrochemical and petroleum refineries, paper mills, thermal power plants, ironworks, shipyards, piers and breakwaters) and the maritime traffic using Algeciras Harbor (which is ranked among the most important ports of the world (AAPA, 2007), handling 43 million tons of goods in 2007 (APBA, 2008)). Large amounts of pollutants are discharged into the bay, especially direct wastewater discharges and atmospheric emissions (Carballo and Naranjo, 2002; Morillo et al., 2007; Tarazona et al., 1991).

Seventeen sampling sites (Fig. 1) were located around the Bay in order to evaluate the effects of the effluents from the activities in and around its coast. Bulk sediments were collected using Van-Veen grab in 2007 at each site from which sub-samples of 400 g surface sediments were taken and stored at −20 °C within 6 h after sampling until analysis in order to limit biological and chemical activities. In addition, 400 g were taken for sediment characterisation.
Samples were oven-dried at 40 °C up to complete dryness and sieved in the laboratory using a Ro-Tap machine and seven sieves at 1 phi intervals, obtaining the statistical parameters described by Folk and Ward (1957), as follows: gravel (% > 2 mm); sand (2 > % > 0.063 mm); and silt + clay (% < 0.063 mm). The fine particle-size fractions (<0.063 mm), which were strongly associated with metal ions (Che et al., 2003; Tam and Wong, 2000) were used as analytical samples. The samples were packed in low-density polyethylene (LDPE) bottles and stored at room temperature until analysis. Each sample was processed in duplicate and analysed in three replicates (n = 3).

2.2. Reagents and apparatus

All reagents (reagent-matched multielement) and standard solutions (prepared by serial dilutions of 1000 mg/L commercial standard solutions) used in Inductively Coupled Plasma-Mass Spectrometer (ICP-MS) and Flame Atomic Absorption Spectrophotometer (FAAS) analysis were of Suprapur and proanalyse quality grades purchased from Merck (Darmstadt, Germany). Ultrapure water Milli-Q® Millipore system (18.00 MΩ cm resistivity TC) was always used for cleaning and for all dilutions throughout the work. Reagents and working standards were prepared under a clean laboratory environment in a class 100 laminar flow cabinet, with filtered atmosphere at 0.45 μm. Acids and other fuming reagents were prepared in the OR-ST 1500 fume chamber. The certified reference material BCR 701 was purchased from the European Community Bureau of Reference. The estuarine sediment Standard Reference Material (SRM) was purchased from National Institute of Standards and Technology (NIST). The DTPA and acetic acid extractions were carried out using an end-over-end shaker and a Sigma 4K10 centrifuge.

The analyses of total heavy metals in digested sediments and DTPA or acetic acid extracts were determined using ICP-MS for multi-element analyses and FAAS for Fe and Mn. Thus, a X-Series ICP-MS from Thermo Elemental, UK, equipped with Xi interface and a concentric nebuliser to deliver a sample at the rate of 1 mL/min with ASX-510 autosampler from CETAC and a Perkin-Elmer AAanalyst 800 FAAS with Perkin-Elmer multi-element (Cu–Fe–Mn–Zn) hollow cathode lamp coupled with a background correction (AA-BG) were used. Prior to sample analyses, X-Series ICP-MS was optimised using blanks spiked with In and U (Tune solution 20 μg/L). CeO/Ce and Ce²⁺/Ce solutions were used to reduce the risks of interferences due to oxides and doubly charged elements to the expected <2% and <3% respectively, whereas collision cell technology (CCT) was applied in order to minimise the risks of polyatomic interferences. The instrument was calibrated using ⁷¹Ga, ¹⁰³Rh and ²⁰⁹Bi as internal standards.

Figure 1  Map of Algeciras Bay showing the sampling points and the principal industrial activities of the area (reprinted from Journal of Hazardous Materials (Elsevier), vol. 190, Díaz-de Alba et al., 2011. Assessment of the metal pollution, potential toxicity and speciation of sediment from Algeciras Bay (South of Spain) using chemometric tools, 177–187 (11 pages); ©Copyright (2011), with permission from Elsevier).
standards in order to minimise interferences due to matrix effect and baseline drifts. The Perkin–Elmer AAAnalyst 800 FAAS was automatically calibrated.

2.3. Quality Assurance and Control (QA/QC)

All laboratory glassware and plastic ware (LDPE) sample and reagent containers were soaked in a detergent solution and rinsed with ultrapure water from Milli Q® Millipore system (15.0 MΩ cm resistivity TC), before soaking again in 2% ultrapure HNO3 bath overnight. The vessels were then rinsed thoroughly with ultra pure water and air dried in a laminar flow hood, and sealed in polyethylene bags if not for immediate use. Reagent containers were filled with 2% ultrapure HNO3 and stored. The standards were prepared in similar matrices to those of the samples to avoid compromising the accuracy of the results. Reagent and procedural blank determinations for total and mobilised metals in DTPA or acetic acid extracts were carried out in the same manner as the samples using the same acid concentrations and solutions and run between each 10 sets of samples. The standards were also run in replicates of three (n = 3), between each 10 sets of samples to check the precision of the methods. The average values of relative standard deviations (% RSD) obtained from the three replicates of standards and samples were generally <10% for each metal analysed and were therefore considered to be satisfactory for environmental analysis (Morillo et al., 2004, 2007), except As and Cd, which had wide spreads (up to 25% and 52% RSD, respectively). Limits of detection (LOD) and quantification (LOQ) were defined as (3 × s)/m and (10 × s)/m of the blank, respectively, where s is the standard deviation of 10 blank measurements and m is the slope of the calibration graph (Araín et al., 2009). In order to assess the accuracy and repeatability of the analytical process and make comparative analysis, Standard Reference Material for estuarine sediment (SRM)® 1646a and Certified Reference Material (CRM)® 701 were analysed in the same manner as samples (Díaz-de Alba et al., 2011). Because of reference material for the DTPA extracts was not available, the suitability of the methods used to analyse the metals in DTPA extracts was checked by three replicate analysis of a blank sample spiked with a multielement standard of As, Ba, Cd, Co, Cr, Cu, Ni, Pb, Ti, V and Zn for ICP-MS multielement analysis and Fe and Mn for FAAS analysis: Fe, Mn, Ni, Pb, Ti, V and Zn, in a final concentration of 10 μg/L of As, Cd, Co, Cu, Ni and V; 40 μg/L of Zn and Cr; 50 μg/L of Mn, 100 μg/L of Ba and 125 μg/L of Fe.

2.4. Procedure for the determination of total metal contents and DTPA and HOAc extractable metals in sediments

The total digestion of the sediments was carried out as follows: 5 mL of 48% HF was added to 0.2 g of the dried fine fraction of sediment and heated using Infrared (IR) radiation until dryness. The same procedure was done a second time. After the HF steps, 5 mL of 65% HNO3 was added onto the residue and treated in the same manner for the HF steps. The residues from HNO3 were dissolved in 20 mL of 3.85 mol/L HCl and heated with stirring for one hour at 85 ± 5°C to extract the digested metals. Then the extract was filtered and stored at 4°C until analysis. The DTPA extractions were performed according to the original procedure (Lindsay and Norvell, 1978), in which 15 mL of the extractant (0.005 mol/L DTPA + 0.01 mol/L CaCl2 + 0.1 mol/L triethanolamine) was added to 3 g of dried fine sediment and mechanically shaken on an end-over-end shaker for 2 h at a speed of 120 rpm at room temperature. The extract was filtered and acidified with Suprapur HNO3 to prevent adsorption to the storage polyethylene containers’ walls and growth of bacteria. The acidified extractant was stored at 4°C until analysis. The acetic acid extraction was done according to the first step of BCR sequential extraction, where 40 mL of 0.11 mol/L acetic acid was added to duplicates of 1 g of dried fine sediment in 100 mL polypropylene centrifuge tubes. The mixture was shaken mechanically at a speed of 150 rpm for 16 h on an end-over-end shaker, avoiding delay between the addition of extractant solution and the beginning of shaking. After shaking for 16 h, the extract was separated from the solid phase by centrifugation at 4000 rpm for 30 min at 4°C using a Sigma 4K10 centrifuge and the supernatant was collected into a polyethylene bottle. The bottle was tightly closed and stored in a refrigerator at about 4°C until analysis.

2.5. Data analysis

Statistical analysis was performed using STATISTICA 7 Software package (STATSOFT 2004, Inc., USA). Data distribution did not show normal distribution and homogeneity of variance, therefore non-parametric tests were performed. Spearman’s rank correlation coefficient was used as nonparametric test in order to determine the correlation among the data.

3. Results and discussions

3.1. Quality Control (QC)

The Limit of Detection (LODs) and the Limit of Quantifications (LOQs) for total concentrations of heavy metals and DTPA-HOAc extracts are given in Table 1. The satisfactory results obtained from the analysis of the SRM® 1646a and CRM® 701 sediment samples demonstrated the validation of the total trace elements analysis and the adequacy of the procedure for the metal extractions. Tables 2 and 3 show the comparison of the certified values and the recoveries obtained in this study. The measurement efficiencies of ICP-MS and FAAS for DTPA extracts tested using spiked blank samples provided satisfactory recoveries of between 85 ± 4% and 105 ± 11% for ICP-MS multielement analysis and 86 ± 2% and 101 ± 8% for FAAS analysis, respectively. In addition, the 9s (r² = 0.999) rule for the determination coefficients was confirmed in each case (Table 4), signifying that the linear model expresses a high amount of the variability observed in the experimental standards.

3.2. Sediment characterisation

The geographical coordinates, water depth and characterisation of sediments from each sampling site are shown in the Supplementary Material (Table SM.1). The samples called
The concentrations of sediments' total heavy metals are given in the Supplementary Material (Table SM.2). The results were obtained from duplicate samples from which three replicate samples were analysed. Higher sediments' total concentrations of the most heavy metals were found around sites 3.1, 3.2, 4.1, 4.2, 5.1, 5.2, 6.1, 6.2, 7.1, 7.2 and 8.1 probably due to their proximity to the industrial zones in Palmones and Guadarranque, where the Acerinox stainless steel manufacturing industry, thermal power plant, petrochemical refinery and paper mills are situated. On the other hand, highest concentrations of As were recorded near the impacted by maritime activities at the Algeciras harbour. Highest concentration of Mn was recorded at site 10.1, probably due to atmospheric deposition from the industrial zones and the sewage overflow from the urban-based industrial processes. The sediments from this bay are still considered to be pristine with respect to metal pollution except for As, Cd, Cr, Ni, and Pb compared to the pollution indicators for the sediments' total metals (Díaz-de Alba et al., 2011). This can be attributed to the strong currents and the physical conditions of the bay, which disperse the pollutants and considerably diminish their effects, even though there is a significant number of anthropogenic activities along the bay.

3.3. Single extractions of metals

The efficiencies of the single extractions studied using DTPA and HOAc compared with the RAC pollution indicators are shown in Fig. 2. In addition, the metal contents in mg/kg of the extracts in sediment from each sampling sites are given in Fig. 3. Most metals showed the highest percentages of extractable mobile fractions around the sites impacted by industrial effluents, except Ba and V, which recorded high percentage of extractable mobile fractions in the areas impacted by maritime activities.

The ranges of environmental availabilities varied widely among the sediments and between the two single extracts. The mean values of percent extractable mobile metal fractions in the whole ecosystem for DTPA extracts were as follows: As: 0.64%, Ba: 0.10%, Cd: 14.80%, Co: 4.50%, Cr: 0.031%, Cu: 19.78%, Fe: 0.50%, Mn: 2.40%, Ni: 1.31%, Pb: 25.65%, Ti: 0.54%, V: 0.34%, Zn: 11.25%, while for HOAc extracts were: As: 0.34%, Ba: n.d., Cd: 13.59%, Co: 11.78%, Cr: 0.10%, Cu: 1.37%, Fe: 0.37%, Mn: 33.00%, Ni: 3.15%, Pb: 18.99%, Ti: 24.88%, V: 0.37%, Zn: 9.43%. The values showed different environmental availabilities for different metals. The mean...
values for extraction efficiencies were recorded in ascending order as follows: DTPA extracts – Ba < Cr < V < Fe < Tl < As < Ni < Mn < Co < Cd < Cu < Pb, while with HOAc the order was – Ba < Cr < As < V < Fe < Cu < Ni < Zn < Co < Cd < Pb < Tl < Mn. It was observed that the two extractants showed some similarities as well as differences in their extraction efficiencies. DTPA proved to be more efficient in extracting Pb, Cu and Cd, while HOAc was more efficient in extracting Mn, Tl and Pb. On the other hand, DTPA showed the poorest extraction efficiency for Ba, 

Table 4  Recoveries of spiked DTPA samples (% Recovery ± % RSD).

<table>
<thead>
<tr>
<th>Metal</th>
<th>As</th>
<th>Ba</th>
<th>Cd</th>
<th>Co</th>
<th>Cr</th>
<th>Cu</th>
<th>Fe</th>
<th>Mn</th>
<th>Ni</th>
<th>Pb</th>
<th>Tl</th>
<th>V</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>% Recovery (±% RSD)</td>
<td>85 ± 4</td>
<td>88 ± 3</td>
<td>105 ± 11</td>
<td>103 ± 6</td>
<td>91 ± 3</td>
<td>89 ± 2</td>
<td>101 ± 8</td>
<td>86 ± 2</td>
<td>101 ± 5</td>
<td>94 ± 5</td>
<td>92 ± 6</td>
<td>89 ± 5</td>
<td>87 ± 7</td>
</tr>
</tbody>
</table>

Note: All determination coefficients ($R^2$) were $\geq 0.999$. 

Figure 2  Risk assessment codes (RAC) for As, Ba, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Tl, V and Zn extracted by acetic acid and DTPA in sediments from Algeciras Bay (note: Y-axis also corresponds to percentage of metals (%) extracted by DTPA and acetic acid).
Figure 3  Concentration of extractable As, Ba, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Ti, V, and Zn by acetic acid and DTPA (mg/kg) and the comparison with Low Alert Level (LAL) sediment quality guidelines.
Cr and V, while HOAc showed poorest efficiency in Ba, Cr and As. However, both extractants seemed to have efficiently extracted Pb, Cd and Zn, fairly Fe, Ni and Co, and poorly Ba, Cr, and V. The order of extraction efficiencies for the two extractants as well as the mean percent extractable values for Cu, Ni, Pb and Zn showed similar trends as those reported by Luo et al. (2012) in Hong Kong Island, and Poggio et al. (2009) in Grugliasco (Italy). However, the results of percent DTPA extractable Pb and Zn in this study were higher than those reported by Massas et al. (2009) in Syros Island (Greece), whereas Cr and Fe were lower. From the results of this study and those done in other parts of the World, it can be observed that the metal availabilities in different sites are highly variable probably due to the different environmental conditions to which the ecosystems may have been exposed.

Pb and Cu were efficiently extracted by DTPA, with highest percent extractable fractions being 64.09% and 71.08% respectively, at the sites impacted by industrial activities. HOAc efficiently extracted Mn and Tl with the highest percent extractable fraction of 58.36% and 53.05% respectively, also at the sites impacted by industrial activities. The high percent extractable Pb in DTPA observed, may have been due to the presence of the divalent lead (Pb$^{2+}$), which has been reported by other studies (Harada and Tsunogai, 1988) to be the most stable valence state in anoxic marine sediments such as those impacted by industrial and domestic sources, with high organic matter loadings from the city of Algeciras through Palmones River (Tarazona et al., 1991). Cu was highly sensitive to complexing process, implying that DTPA had the ability to mobilise Cu from the potentially active fractions (Gupta et al.,
1996), particularly from the oxidisable fraction, which associates with organic and sulphur compounds and easily form complexes with organic matter due to the high stability constant of organic Cu compounds as suggested by Morillo et al. (2004). The ability of DTPA to extract metals complexed by organic matter was reported by Piccolo (1989), Ure (1996) and McGrath (1996). This was evident in this study due to the fact the greatest percentage relative extraction of Cu in DTPA was found near the mouth of river Palmones and the Palmones industrial zones from which large amounts of organic matter enter the Bay (Díaz-de Alba et al., 2011; Tarazona et al., 1991). DTPA was also responsible for the extracting of Cd with extractable value up to 64.09% mainly in the sediments from the area affected by industrial activities, likely from the Acerinox steel manufacturing and thermal power plant.

The higher percent extractable fraction of Mn found in HOAc was probably due to its known close association with the carbonate, which are acid-soluble fractions (Morillo et al., 2004). Ti was also highly extracted when using HOAc; this behaviour is mainly pH-driven and can be attributed to acid ion exchange and/or acid leaching, as the formation of Ti-LMWOA (low molecular weight organic acid) complexes is negligible (Váněk et al., 2012). HOAc was responsible for the extraction of up to 29.96% of Cd in the sites mostly impacted by maritime activities, such as the sites around the port of Algeciras.

These results generally showed that Co, Mn, Ni and Ti were mostly found in the exchangeable fraction, considering that they were satisfactorily extracted in HOAc, whereas Cu was predominantly extracted in DTPA, suggesting that this metal may have been associated with other sediment fractions apart from the exchangeable one, preferably the oxidisable fraction, which is associated with organic matter. However, Cd, Pb and Zn were found to be adequately extracted in both media, indicating that they may have been associated with the exchangeable or other fractions such as the reducible or oxidisable ones.

The comparison among the risk assessment codes and the percent extractable metals provided interesting results with respect to risk assessment, where VHR values for Cu, Zn, Cd and Pb were found in DTPA extracts at site 6.1. In addition, VHR for Mn was found in HOAc extracts at sites 4.2 and 5.2 and Ti at sites 6.1 and 6.2. HR values for Pb were obtained in DTPA extracts at sites 4.2 and 6.1; HR values for Mn were found in HOAc extracts at sites 1.2, 3.1, 4.1, 5.1, 6.1, 6.2, 7.2, 9.2 and 10.1; Ti at sites 4.1, 4.2, 5.1 and 5.2; and Pb at 9.2 and 10.1. MR values for Pb were observed in the rest of sampling sites in both reagents. In addition, MR values for Cu, Zn, and Cd in DTPA extracts and Co and Zn in HOAc were detected from sites 4 to 7, respectively; Cd showed MR values in HOAc at sites 1, 2, 3, 8, 9 and 10. As, Ba, Cr, Fe, Ni and V showed low or non-risk RAC codes values. The potential mobilisation of the elements studied was significant for some ones compared to the RAC indices, especially for metals which had high sediments’ total concentrations such as Pb or Cd and those with high extractable concentration values exceeding quality guidelines. Therefore, the mean concentrations of efficiently extracted metals (Cd, Co, Cu, Ni, Pb, and Zn) in the two extractants within the whole ecosystem were compared with the Low Alert-Level (LAL) sediment quality guidelines (Manheim and Commeau, 1981), defined for the total contents, as shown in Fig. 3. Co, Pb, Zn and Ni extracted in both extractants as well as Cd and Cu extracted in DTPA exceeded the LAL respectively, while Ti extracted in acetic acid also exceeded the LAL. The results helped to predict the potential bioavailability of these metals, implying that if water conditions were weakly acidic, then Co, Ni, Pb, Ti and Zn would be potentially available metals for uptake by marine organisms, whereas complexing conditions could promote the potential availability of Cd, Co, Cu, Ni, Pb and Zn for uptake.

3.4. Statistical correlations

Table SM.3 in the Supplementary Material is the matrix of Spearman’s rank correlation coefficients (ρ) for the sediments’ total concentrations of heavy metals studied. The results did not show any evidence of dependence between the metal concentrations and the water column depth. Significant positive correlation was observed for As, except at sites 2.1, 2.2 and 3.2, where anthropogenic inputs produced higher concentrations than those provided by regression; thus, sites 2.1 and 3.2 can be identified as Arsenic (As) pollution hotspots due to the fact that the concentrations exceeded the Lower Trigger value (20 mg/kg) assigned by the National Interim Sediment Quality Guideline Value (ISQG). Granulometry analysis showed that percentage silt + clay content correlated positively with Ba, Cr, Fe, Ni, Ti and Zn, demonstrating the capability of the sediment fraction to retain these metals; however, As showed negative correlation, hence indicating a different behaviour from the other metals within the bay. The positive correlations between organic matter and all metals except As and Mn showed the influence of the organic matter over metallic contents in sediments from this ecosystem. Similarly, there were positive correlations among all metals studied except As and Mn, indicating that the metals may be originating from a common source. As and Mn seem to have had a commonality in the sense that their highest concentrations were found in the extreme sites towards the open ocean, whereas the negative correlation observed between As and Cr was probably due to their different origins and behaviours.

Spearman correlations (ρ < 0.05) analysis between organic matter, extractable metal fraction and the sediments’ total metal content (mg/kg) were also obtained as shown in Table SM.4. Positive correlations were found between organic matter and Co and Zn in both DTPA and HOAc likely indicating the presence of labile organic complexes; Cu and Pb in DTPA likely shown a less selective extractability by organic ligands; and Cr and Fe in HOAc extracts meaning the presence of these metals in the exchangeable fraction (Manouchehri et al., 2014). The DTPA extracts correlated positively with sediments’ total concentrations of Co, Cu, Ni and Zn, with HOAc extracts correlating with total concentrations of Co, Cr, Fe, Ni, Ti and Zn. Some observations were outstanding, particularly the positive correlations found between the total concentration of Cr and Cu-DTPA (ρ = 0.826) and Zn-HOAc (ρ = 0.863) and the total content of Ni with Zn-HOAc (ρ = 0.871); as well as the high negative correlation between V-HOAc and different total metals as Cr, Cu, Fe, Ni, Ti and Zn. Because of their less specific nature, multidentate ligands (as DTPA) extract cations bound to several components of solid phase (exchangeable, surface adsorbing site, carbonate, organic matter and amorphous Fe and Mn oxides) (Manouchehri et al., 2014). Thus, metal only correlated with DTPA can be associated with different phases of the sediment.
Figure 4  Relationship between the percentage of metal extracted by DTPA and acetic acid.
Similarly, higher positive correlations between both extractants for Co ($\rho = 0.797$), Cu ($\rho = 0.777$), Ni ($\rho = 0.789$) and Zn ($\rho = 0.942$) were observed, indicating that the two extractants had comparable potential extraction capability for these metals as shown in Fig. 4. Some sets of behaviours were found to be associated with the metals and sampling sites. For instance, a set of metals with comparable effects in both extractants, such as Co, Cu and Zn, in which site 6.1 seemed to be an outlier, with 7.2 being an outlier for only Co. Another set was between As and Cd, which showed comparable effects only when extreme areas such as 1.2, 2.1, 2.2, 3.1, 3.2, 8.1, 9.1, 9.2 and 10.1 were taken into account. On the other hand, Fe showed an opposite behaviour; where the regression equation was obtained by only taking into account the values from intermediate sites (area 4.1, 4.2, 5.1, 5.2, 6.1, 6.2, 7.1 and 7.2). No significant regression was obtained for Cr, Mn, Pb, Ti and V but the sampling sites could be grouped into extreme and intermediate sites except for V.

The results showed that the two extractants had the capacity to mobilise and release metals in sites with high sediments’ total metal concentrations, such as the ones with proximity to industrial zones and the city of Algeciras, respectively. It was noted that the results could as well depend not only on the extractant used but also on the sediment characteristics and the extracted metals.

4. Conclusions

The screening of the mobility of trace elements by single extractions using DTPA and acetic acid provided useful information on the effect of complexation and acidification processes on extractability of metals from sediments impacted by effluents from urban sewage, atmospheric deposition, shipping and industrial activities. Comparable potential extraction capabilities were found for Co, Cu, Ni and Zn. It was noted that sediment characteristics and metal properties may have affected the extraction efficiencies for other metals. The most important metals extracted in both extraction conditions were Cd, Pb and Zn. Mn and Ti were found to be sensitive to acid dissolution, whereas Pb and Cu were found to be sensitive to complexation processes. These results helped to predict the potential bioavailability of the studied metals. The screening methods used showed that the complexing and acidification processes in the bay could be a serious concern if not managed due to their potential capability to release the exchangeable and mobilisable fractions of the sediment-bound heavy metals, which may in turn be available for uptake by marine organisms.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.arabjc.2015.06.041.

References


