NATURAL ATTENUATION PROCESSES IN TWO WATER RESERVOIRS RECEIVING ACID MINE DRAINAGE

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Abstract

Characteristics of water profiles and sulphide formation processes in sediments were studied in two water reservoirs affected by acid mine drainage in order to investigate the mechanisms controlling the physical and chemical processes that, under favourable conditions, act to reduce the toxicity, mobility and concentration of metals and metalloids in the water column. Water columns and pore-waters from sediments were analysed for Fe species, trace elements (As, Cd, Co, Cu, Mn, Ni, Pb, Zn, Cr), sulphide, sulphate and bicarbonate. Inorganic reduced sulphur compounds (acid volatile sulphur, pyrite sulphur and elemental sulphur) and reactive Fe were determined in the sediments. A sequential extraction was also performed. Both reservoirs behave like holomictic and monomictic lakes, with a summer thermal stratification that disappears during winter. pH values between 4 and 7 can be observed along the water columns. Pore-water concentrations of up to 25 mg/l of Fe, 4 mg/l of Al, 1.3 mg/l of Zn, 170 µg/l of Pb, 11 µg/l of As, etc. have been found. The results suggest that toxic elements such as Cu, Zn, Co, Pb, Cr, As, etc. are mainly found in the bioavailable fraction which is the most hazardous for the environment. The calculated degree of sulphidization (DOS) and degree of pyritization (DOP) values indicates that removal of trace elements from anoxic pore-waters occurs by coprecipitation and/or adsorption on newly formed Fe sulphides (framboidal pyrite), attenuating the contamination. However oxidation of the sediments during turnover periods also occurs, which releases toxic elements back into the water column.

1. Introduction

Predicting the impact of an emission on the environment requires the evaluation of not only the short-term fate of the pollutants, but also of their medium- and long-term interaction within the ecosystem. The information obtained can be used to establish risk assessment criteria and to design remediation strategies. Dynamic studies are also required to predict changes over time in the fate of the pollutants in an area affected by contamination, and are based on quantifying the changes over time of the parameters that control soil-pollutant interaction (Martínez and McBride, 1999). Natural attenuation processes, such as increase of pH or metal diffusion to internal sorption sites in the soil phases by migration, adsorption, surface precipitation or redox processes, involve an increase in trace element fixation in the soil with time and a decrease in mobility. Sulphate reduction and metal sulphide precipitation have the potential to remediate acid mine drainage (Machemer and Wildeman, 1992).

The mining of massive-sulphide ore bodies can result in the exposure of high-sulphide waste in the form of mine tailings, waste rock and mine workings. The oxidation of sulphide minerals results in the development of decreased water quality characterized by high concentrations of Fe^{2+}, SO_4^{2-}, heavy metals and other constituents. The impact of mine drainage to surface waters and sediments has been well documented for lakes (Herlihy and Mills, 1985; Peine and Peiffer, 1998; Frommichen et al., 2004) and pit lakes (Shevenell et al., 1999; Ramstedt et al., 2003; Knoller et al., 2004; Denimal et al., 2005), however there are not almost works related to the impact to water reservoirs.

In dams, the sediment transported by a stream is deposited in the still waters of the reservoir. In this case, both bed load and suspended load are deposited, but the dissolved load eventually moves out with the water released from the reservoir. The presence of large amount of organic matter in these sediments typically results in oxygen depletion, which is followed by the production of sulphide by sulphate- reducing bacteria (Heijs and van Gemerden, 2000). The hydrogen sulphide produced by sulphate reduction may then chemically react with metals to form insoluble sulphides, such as FeS, FeS_2, ZnS, etc. (Rickard and Morse, 2005). These are accumulated in the sediment, thereby limiting the release of free sulphide (S^{2-}) into the overlying water. The formation and oxidation processes of monosulphides play an important role in the attenuation of the contamination of polluted anoxic solids.

However, Fe monosulphides can also be a potential environmental hazard because they can rapidly oxidise and release metals and acidity into drainage waters (Smith, 2004). Variation of pH and oxygen are the most important factors that affect the mobility of trace metals (Wen and Allen, 1999). Disturbance and subsequent oxidation of the bottom sediments can occur during turnover periods and also by mobilisation and transport during large rainfall events and heavy flows.

The Odiel River basin (Fig. 1) is generally recognized as a fluvial system with a catastrophic ecological situation due to huge masses of mining wastes, where a serious danger originates from sulphide-rich tailings. The Odiel River drains the central part of the most famous sulphide mining regions in the world: The Iberian Pyrite Belt (SW Spain). This zone contains original reserves in the order of 1700 Mt divided up in more than 50 massive sulphide deposits. Pyrite, sphalerite, galena and chalcopyrite are the main mineral phases that make up these deposits, which also contain accessory amounts of As, Cd, Co, Ni, Cr, etc. As a consequence of the oxidative dissolution of the sulphides exposed in the surface associated to mining activities, acid mine drainage pollution is an important processes in the Odiel basin (Sanchez-España et al., 2005; Sarmiento et al., 2006; Sarmiento 2008). Near its mouth, the Odiel River has a very low pH and high concentrations of metals and metalloids (Cánovas et al., 2007; Olías et al., 2004; 2006; Sarmiento et al., 2004). Two water reservoirs were built up in the Odiel Basin: Olivargas and Sancho, which receive AMD discharges of several mines.

Two new dams are planned in the Odiel River within the National Hydrologic Plan, Alcolea (300 hm^3) and Coronada (800 hm^3) dams, whose uses will be mainly destined to the irrigation. Taking into account the important investment planned and the poor quality of the water from the Odiel river, a study of the effects which could be originated should be necessary to predict the sediment role in the fate of the contaminants. For this, we have used as example the hitherto unknown effect of AMD load in the Sancho and Olivargas reservoirs. Therefore, the main aims of this study are to identify the accumulation and release of metals associated with AMD processes in reservoirs, and to discuss the impacts these cycles will have on water and sediment quality.

2. Environmental setting

Olivargas reservoir has a capacity of 29 hm^3 and receives AMD streams that drain the mines of Valdelamusa, Aguas Teñidas and Cueva de la Mora (Fig. 1). In these streams the range of pH is between 2.6-3.5, 13-106 mg/l Al, 2-13 mg/l Cu, 12-338 mg/l Fe, 3-307 mg/l Zn, 448-3158 mg/l SO_4^{2-} and maximum concentration of 1095 μg/l of Co, 229 μg/l of As, 962 μg/l of Ni, 611 μg/l of Cd, 789 μg/l of Pb, etc., can be found (Sarmiento et al., 2006; Sarmiento, 2008).

Sancho reservoir has a capacity of 58 hm^3. The main recharged stream of this dam is the Meca River, which carries AMD from the Tharsis and El Carpio mines (Fig. 1). These mines give rise to the maximum levels of contamination by AMD in the whole Odiel basin. Values of pH around 2.6 and concentration about 1 g/L of Al, 2 g/L of Fe, 412 mg/l of Zn, 167 mg/l of Cu, 3.6 mg/l of As, 0.9 mg/l of Pb, 6.4 mg/l of Ni, etc. can be found in the streams draining these mines (Sarmiento et al., 2006; Sarmiento, 2008).

3. Methods

3.1. Physicochemical parameter profiles

Several surveys were carried out in both reservoirs: four in 2004 (March, June, September and October), and two in 2005 (May and October). The physicochemical parameters (pH, temperature, electrical conductivity, redox potential and dissolved oxygen) were measured in vertical profiles, using a specific probe SEBA HYDROMETRIE KLL-Q (accuracy: conductivity ± 0.5% of measure, pH ± 0.1, redox potential ± 2 mV and dissolved oxygen ± 0.5% of measure). Redox potential was corrected in order to obtain the Eh, referred to the hydrogen electrode (Nordstrom and Wilde, 1998). The profiles were performed along transect near the dam walls (Fig. 1) and the readings were measured every two meters, or 0.5 meters where the parameters were variable.

3.2. Water sampling and analysis

In the studies of September 2004 and May 2005, water samples at different depths were taken using a Van Dorn bottle point sampler (2 l).

All the samples were collected in pre-cleaned polypropylene bottles, which were rinsed thoroughly with HNO_3 solution (10%) and deionizeddistilled water before use for cations and only deionizeddistilled water for anions. Water samples were filtered immediately through 0.22µm Millipore filters fitted on Sartorius polycarbonate filter holders. Samples for major cations and metal analysis were acidified in the field to pH<2 with HNO_3 (2%) suprapur. Then, they were stored in the dark at 4ºC in polyethylene bottles until analysis. Samples collected for alkalinity and anion determinations were filtered but not acidified.

Concentration of dissolved Al, As, Ca, Mg, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Sb, total S, Sn, Se, Hg y Zn were determined by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES Yobin-Ybon Ultima2). Multielements standards solutions prepared from single certified standards supplied by SCP SCIENCE were used for calibration. They were run at the beginning and at the end of each analytical serie. Certified Reference Material SRM-1640 NIST fresh-water-type and inter-laboratory standard IRMM-N3 wastewater test material, European Commission Institute for Reference Materials and Measurements, were also analysed. Detection limits were calculated by average and standard deviations from ten blanks. Detection limits for major cations were less than 200 µg/l for Al, Fe, Mn, Mg and Ca. For trace elements were 50 µg/l for Zn, 5 µg/l for Cu, 2 µg/l for As and 1 µg/l for the rest of elements. SO_4^{2-} was determined by Ion Chromatography using a Dionex DX-120 machine fitted with an AS 9-HC of 4 x 250 mm column and a 4 mm ASRS-ULTRA suppressing membrane. Detection limit was 0.5 mg/l. Alkalinity was determined by the titration method (Standard Methods 2320 for the Examination of Water and Wastewater) with standardized HCl and bromcresol green indicator.

3.3. Sediment sampling and analysis

In the sampling of May 2005, bottom sediments were collected near the dam walls using a Ponar Dredge sampler. The samples were stored in polyethylene bottles and frozen immediately. At the laboratory, the sediment samples were defrosted at room temperature within a nitrogen filled glove box, and the pore-water was extracted by centrifugation. The centrifuged sediments were then freeze-dried.

Aliquots of pore-water sample were taken for Fe(II)/Fe(III), anions, cations, hydrogen sulphide, alkalinity, pH and redox potencial analysis. Aliquot for determination of cations were acidified with nitric acid and the hydrogen sulphide samples were added to an equivalent volume of 5% zinc acetate, which acted as a preservative. The pH and Eh were measured using a pH microelectrode (from BDH) and the alkalinity by Alkalinity Test Kit (HACH). The Fe(II)/Fe(III) speciation were determined using the ferrozine method as outlined by Viollier et al. (2000). Concentration of dissolved cations and total sulphur were determined by Inductively Coupled Plasma Atomic Emission Spectrometry, and anions were determined by Ion Chromatography, alike above mentioned.

The reactive Fe (Fe_r) was partitioned from the sediments by ascorbate extraction as outline in Kostka and Luther (1994). Sulphur was speciated into acid volatile sulphur (AVS, including amorphous Fe monosulphides (FeS), mackinawite, greigite as well as other HCl-soluble sulphides), pyrite-sulphur (py-S) and elemental sulphur (S^0) by a three step sequential digestion and their concentration determined within the sediments using a method described by Duan el al. (1997). The sequential extraction was performed using the three steps BCR procedure outlined by Rauret et al. (1999), and adding *aqua regia* extraction as a fourth step. The extractants were analysed by ICP-AES alike above. AVS-Fe and py-Fe were determined stoichiometrically from reduced inorganic sulphur results.

Pyrite grain morphology was observed under a scanning electron microscope (SEM; JEOL JSM-5410) coupled to Microanalysis Link-Oxford. Samples were prepared by sprinkling dry sediment over a stub pretreated with a mixture of carbon and glue and coating them with a thin film of carbon using the evaporation technique.

3.4. Geochemical modelling

Water chemistry was interpreted with the assistance of the equilibrium chemical-speciation/masstransfer model PHREEQC (Parkhurst and Appelo, 1999) using the thermodynamic database WATEQ4F (Ball and Nordstrom, 1991). WATEQ4F was used to calculate the saturation indices for discrete minerals that may be controlling the concentrations of dissolved species in the pore-water of the sediments. Solubility constants from literature were used for other minerals such as schwertmannite.

4. Results and discussion

4.1. Water column characteristics

4.1.1. Physicochemical profiles

The seasonally variable stratification of Olivargas and Sancho dams are illustrated by vertical temperature profiles at six different times (Fig. 2a).

Olivargas dam: In aestival season (June and September 2004) the epilimnion has temperature of 25 ºC and extends down to 5 m. The metalimnion extends between 5 and 10 m. The temperature in the hypolimnion remains constant. In the turnover stage of the dams, represented by the profiles obtained in March 2004, almost no vertical temperature differentiation is observed.

Electrical conductivity (CE) shows differences between 2004 and 2005 (Fig. 2a), probably due to the rainfalls in 2005 were around 25% lesser than in 2004. In the epilimnion the electrical conductivities have similar depth-patterns than temperature, showing maximum values in the thermal stratification periods. The epilimnion displays an average conductivity of 200 µS/cm. The electrical conductivity decreases in the metalimnion and shows the maximum values in deepest zone of the hipolimniom.

The pH values oscillate between 6.5-8 in the epilimniom, increasing in the aestival season and decreasing after turnover. In the hypolimnion the pH increases in the deepest layers.

Anoxic conditions prevail after summer (September and October 2004 and October 2005) below 15 m. The water column remains oxic in March and June 2004 and May 2005. Dissolved O_2 concentrations (DO) range from 7-9 mg/l, in the epilimnion and indicate conditions close to equilibrium with atmosphere near the surface (O_2 solubility is 7.7 mg/l, Benson and Krause, 1984). The vertical dissolved oxygen concentration profile shows a clinograde distribution, however the concentration increases up to 12 mg/l in the metalimnion in June and September 2004 and May 2005 in both reservoirs. The Eh values tend to be strongly decreased in the deepest layers.

Sancho dam: As in Olivargas, the profiles performed also show stratification (Fig. 2b). In summer the epilimnion could be observed extending from the surface to 10-15 m, with average temperature centred on 24 ºC. In the metalimnion, the temperature decreases between 15 and 20 m. The hypolimnion has an average temperature of 11-14 ºC. During winter surveys, profiles are centred on 15 ºC, thermal stratification disappears.

The electrical conductivity values are higher than in the Olivargas dam, reaching 400 µS/cm in the epilimniom (in October 2005). The metalimnion shows a decrease of conductivity and the hypolimnion generally has the lowest values. The conductivity variation between the surface and the bottom was constant or slightly higher in the turnover stage after winter.

The pH values remain around 4.2 along the water column for every survey, except in the hypolimnion where it increases above 5 especially after summer.

As in Olivargas dam, the vertical dissolved oxygen concentration profile shows a clinograde distribution. Anoxic conditions or very low oxygen concentrations prevail after summer (September and October 2004 and October 2005) below 20 m. The water column remains oxic in winter and spring. Eh values are also are higher (600-750 mV) than in the Olivargas dam. They decrease below 20 m when conditions are anoxic.

Olivargas and Sancho dams behave like holomictic and monomictic lakes, which have a summer thermal stratification which is removed by winter turnover. The anoxic bottom layer is lesser and less marked in the Sancho dam.

In the maximum stratification periods, the strong decreased of the redox potential in the deepest layers of both reservoirs is related to the absence of oxygen and the increase of the pH. However, the electrical conductivity increases in the Olivargas and decreases in the Sancho dam. This can be connected with the anaerobic reduction of sulphates in the bottom of the reservoirs, including alkalinity production. In the Olivargas dam, the increase of alkalinity involves an increase of the electrical conductivity, while in the Sancho dam it is not observed, probably due to the alkalinity is released like CO_2 caused by the low pH (below 5).

4.1.2. Hydrochemistry

Water samplings at different depths were carried out in September 2004 and May 2005 (Fig. 3). The waters type in the Olivargas dam is SO_4-HCO_3-Ca-Na-Mg, whereas in the Sancho is SO_4- Ca-Na-Mg, which are constant over the period of analyses.

In September 2004 (maximum thermal stratification), the value of most parameters were different along the water profiles in both reservoirs. In the Olivargas dam, the pH decreases from 7.3 at 5 m depth to 6.2 (below 20 m depth). Electrical conductivity (from 211 to 170 µS/cm) and sulphate concentrations (from 54 to 33 mg/l) also decrease along the profile (Fig. 3a). On the contrary, Fe, Mn and bicarbonate concentrations increase to the bottom (Fig. 3a). This variation was also found in the Sancho dam in this period, decreasing the electrical conductivity (from 369 to 362 µS/cm) and sulphate concentration (123 to 110 mg/l), while the Fe concentration increases (up to 1.4 mg/l). In this reservoir, variations of some trace elements can also be observed (Fig. 3b), decreasing the concentration of Ni (from 40 to 29 µg/l), Sb (from 10 to 6 µg/l), Co (from 70 to 61 µg/l) and Pb (from 12 to 7.5 µg/l) as the depth.

In May 2005 most of the parameters remained constant along the profiles in both reservoirs (Fig. 3c, 3d) due to the turnover-mixing effect; however the concentrations are lower than in September owing to the dilution processes arising from the rains of the wet season.

In spite of most of the metals analysed in September decreased along the profile, Fe and Mn showed higher concentration (Fig. 3a). Fe contents and their variability can be explained because, under oxidizing conditions and at neutral pH, Fe precipitates as Fe oxyhydroxides and is then, in theory, extracted from the dissolved fraction. On the other hand, although Mn^{2+} is stable over a wider range of Eh and pH, it can be adsorbed or co-precipitated in Fe oxides (Stumm and Morgan, 1996). In May 2005 when dissolved oxygen profiles showed the existence of an oxic layer at depth, the Fe concentration was below detection limit. On the contrary, in September 2004 dissolved oxygen profiles showed the existence of an anoxic layer at depth, as a result, the Fe and Mn concentrations increase in this zone. Besides, in September 2004 the bicarbonate concentration also increases in the depth (Fig. 3a), pointing out possible sulphate reduction processes as will be discussed below.

4.2. The bottom sediments

4.2.1. Interstitial waters

Table 1 shows the physicochemical parameters and chemical composition of the pore-water sediments and the overlain water. The values oscillate considerably: in the Olivargas the water temperature increased from 9 ºC in the bottom of the water column, to 15 ºC in the sediment, and in the Sancho from 12 to 17 ºC. The pH also increased in the Sancho pore-water (from 4.4 to 6.6), while in the Olivargas remained around 7. The electrical conductivity decreased in both reservoirs with relation to the water in touch with the sediments. The dissolved oxygen is absent in the pore-waters and the conditions are more reducing than the water columns.

The sudden increase in pH (especially in Sancho) and bicarbonate concentration as well as the disappearance of sulphate at the sediment-water interface (Table 1), point out the formation of monosulphides, indicating that sulphate reduction and sulphide immobilization are responsible for most of the H^+ consumption (Huerta-Diaz et al., 1998).

Pore-water in the Olivargas sediments has concentrations of toxic elements higher than the Sancho, especially As, Pb and Zn (Table 1). Pore-water $\Sigma S(-II)_{(aq)}$ concentrations were low in both sediments (0.25 and 2.1 mg/l in Sancho and Olivargas, respectively).

Pore-water Fe(III) was 17.4 in Sancho and 21.7 mg/l in Olivargas, whilst Fe(II) was 6.11 and 3.11 mg/l, respectively. The very low, but detectable pore-water Fe(II) and $\Sigma S(-II)_{(aq)}$ concentrations are consistent with published Fe-S solubility data (Morse et al., 1987). For example, the observed pore-water $\Sigma S(-II)_{(aq)}$ concentration at equilibrium with amorphous FeS, having a solubility product of $10^{-2.95}$ ($K_{sp} = \{Fe^{2+}\}\{HS^{-}\}/10^{-pH}$), are expected to buffer pore-water Fe(II) to low concentrations at near-neutral pH. Even lower Fe(II) concentration would exist if more crystalline Fe-S phases, such as mackinawite, greigite or pyrite, controlled Fe(II) and $\Sigma S(-II)_{(aq)}$ solubility (Morse el al., 1987). The saturation indexes for the more important mineral phases show that the pore waters in both reservoir sediments are supersaturated in some common metallic sulphides such us covelline (SI>14), chalcocite (SI>23), chalcopyrite (SI>22), pyrite (SI>13), galena (SI>5), sphalerite (SI>4), greigite (SI>3) etc., Al-hydroxides like alunite (SI>1.3), basaluminite (SI>4) and amorphous aluminium hydroxide (SI>1.3).

In the pore-water the molar ratio Fe^{2+}/S is higher in the Sancho sample (24) than in the Olivargas (1.5). The saturation indexes for the more important Fe(III)-hydroxides phases performed by the Phreeqc program show that the pore-waters are supersaturated in ferrihydrite, (only in Olivargas dam) and goethite (SI>2.6). The elevated proportion of Fe(II) in the Sancho can be due to the reduction of the Fe(III)-hydroxides by organic matter following the equation 1 (Lovley, 1991), causing an increase of the pH.

$$4Fe(OH)_3 + CH_2O + 7H^+ \rightarrow 4Fe^{2+-} + HCO_3^- + 10H_2O \qquad (1)$$

4.2.2. Solid phases

Table 2 shows the results obtained in the sequential extraction of both sediment samples. The main elements are Fe (3.9% in Olivargas and 4.5% in Sancho), Al (1.6% in Olivargas and 2% in Sancho), S (0.5% in Olivargas and 0.2% in Sancho) and Zn (0.3% in Olivargas), following of Cu, Mn, Pb and As.

The extracted percentages of some elements in each sequential extraction step are represented in Fig. 4. For Fe and As the residual fraction prevailed with higher percentages in the Sancho reservoir (more than 70% of total Fe and 80% of total As. Previous works have shown the primary sulphides are not totally extracted in the step associated to the sulphides (step 3) and some could be removed with the residual fraction (Förstner, 1985). In Olivargas sample a considerable amount of Fe (29%) and As (26%) was also extracted in step 2.

Co, Mn and Zn displayed the highest solubility. In both reservoirs more than 55% of the total Zn was extracted with acetic acid, whereas it was less than 35% in the step 2. However the acid-extractable fraction of Co and Mn was very variable: 35 and 47% of the total Cd-content in Sancho and Olivargas, respectively, and 45 and 69% of the total Mn content in Sancho and Olivargas. Cu is associated with the steps 2 and 3 (more than 69% in Sancho and more than 91% in the Olivargas, for both steps). The maximum total S content prevailed in step 3 (more than 46% in both samples). The rest is associated mainly with the steps 1 and 4.

In Olivargas sediments the concentrations of toxic elements in relative abundance in the first fraction (F1) are in the following order: Zn (55%) > Co (47%) > Cd (33%) > As

(10%) > Pb (9%) > Cu (4%). Alike, in Sancho sediments are: Zn (55%) > Co (35%) > Cu (21%) > As (6%) > Pb (4%). These sediments are toxic and harmful since this step concerns the bioavailable fraction, the most dangerous for the environment, consisting of exchangeable metals and those soluble in water or in slightly acidic conditions.

Fractions 2 and 3 may also be a threat depending on the environmental conditions. Fraction 2 represents metals bound to oxides that can be released if conditions change from oxic to anoxic state. Fraction 3 is made up of metals bound to organic compounds and sulphides, which may be released under oxidizing conditions. Finally, fraction 4 corresponds to those metals strongly associated with crystalline structures of minerals, which are therefore unlikely to be released from the samples.

The concentrations of toxic elements in relative abundance in the mobile phases (based on the sums of the first three fractions: F1 + F2 + F3) are in the following order: Sancho: Cu, Zn (91%) > Co (72%) > Pb (62%) > Cr (20%) > As (16%); Olivargas: Zn (97%) > Cu (95%) > Co (91%) > Pb (88%) > As (39%) > Cr (21%)

4.2.3. Sulphur species in sediments

The partitioning of the sulphur species (AVS, S^0, Py-S) from the two investigated sites is presented in fig. 5, expressed as percentages of the total reducible sulphur. Table 3 includes some chemical characteristics of the sediments examined. Iron monosulphides are the initial Fe sulphide minerals formed under reducing conditions, and are often necessary precursors for the rapid formation of pyrite (Berner, 1970; Rickard, 1975). AVS concentrations of 9.5 μmol S/g dry wt. was found in the Sancho sample, while it was not detected in the Olivargas sample. These values are consistent with unpolluted freshwater sediments (range of about 4 – 13 µmol S/g dry wt) (Gagnon et a., 1995). Elemental S was more abundant (6.8 µmol/g at Olivargas and 13 µmol/g at Sancho) than AVS. These S^0 concentrations are indicating oxidation of reduced inorganic sulphur (RIS) near the sediment surface (Troelsen and Jorgensen, 1982). The py-S is by far the most abundant sulphide component in the sediment from Olivargas (113 µmol/g) while was considerably lower in Sancho (8.9 µmol/g). This variability is related to the effects of the different limiting factor, such as the concentration of dissolved S^{2-}, the amount of Fe(II) that can be used by the reaction, the transformation of FeS in pyrite, the availability of S^0, and decomposable organic-C (Henneke et al., 1997).

In the Olivargas reservoir Py-S content is high with respect to AVS content, taking into account that it has been found at the more superficial layer of the sediment. Because of the limited thickness of the oxidised layer, dissimilatory sulphate reduction, precipitation of metastable sulphides, and formation of pyrite are therefore probably acting together, from the more superficial layers (Berner, 1970).

The degree of pyritization (DOP) and degree of sulphidization (DOS) are parameters which can be used to distinghish between situation where pyrite and Fe sulphide formation is either C- or Fe-limited (Raiswell and Berner, 1985) and to measure the completeness of reaction of reactive Fe with aqueous sulphide. DOP is defined here as:

$$\mathrm{DOP} = 100\,(\mathrm{Py\text{-}Fe}) / (\mathrm{Fe_r} + \mathrm{Py\text{-}Fe}) \qquad (2)$$

In sediments that contain a significant amount of Fe monosulphides, the DOP parameter underestimates the amount of Fe which has reacted with H_2S (Boesen and Postma, 1988). Instead, the DOS represents the degree to which reactive Fe has been transformed into sulphide and therefore provides a better indication of Fe limiting conditions. DOS is defined here as:

$$\mathrm{DOS} = 100\,(\mathrm{AVS\text{-}Fe} + \mathrm{Py\text{-}Fe}) / (\mathrm{Fe_r} + \mathrm{Py\text{-}Fe}) \qquad (3)$$

Where Py-Fe is pyrite-bound iron and AVS-Fe is monosulphide-bound iron. The reactive Fe (Fe_r) is defined as the fraction of iron that readily reacts with dissolved sulphide to produce iron monosulphides and eventually pyrite. Fe_r includes Fe present in Fe monosulphide and Fe oxyhydroxides (Canfield, 1989). The reactive Fe concentration is of 24 µmol/g in Sancho sediments and of 33 µmol/g in Olivargas.

The DOS values were close to 63 % and 50 % in sediments from Olivargas and Sancho, respectively. These relatively high DOS values indicate that large proportion of the sum of reactive and pyrite Fe are associated with suphides phases. The DOP values were 63 % and 16 % in sediments from Olivargas and Sancho dams, respectively, meaning the AVS contribution to the Fe sulphide is minimal in the Olivargas sediments.

Authors have used DOP to demonstrate iron or sulphur limitation in pyrite formation, for example, DOP values close to 100 % suggest iron limitation (Berner, 1970). In the Sancho sediments, the low DOP in relation to the DOS value indicates that reactive Fe does not limit the formation of Fe sulphide minerals but the conversion of FeS to pyrite is more inhibited (Gagnon et al., 1995) than in the Olivargas sediments. This is likely to be due to the early formation of monosulphides. This limited conversion is supported by the AVS to pyrite ratio, being zero for the Olivargas and higher than 1 for the Sancho sediments (Table 3). Middelburg (1991) explains that the conversion rate of monosulphides to pyrite in the upper sediments can be controlled by the availability of oxidants. It is clear from these results that in the Sancho sediments, neither organic matter, reactive Fe or soluble SO_4^{2-} are limiting in the upper sediments, and since there has been recent oxidation, it is likely that limited time for formation is the controlling factor. This supposition is supported by the larger oxic layer found in the water profile of the Sancho dam with respect to the Olivargas dam (Fig. 2).

Based on a comprehensive analysis of ancient shale formations, Raiswell et al. (1988) have proposed that sediments with DOP of < 46 % indicate aerobic bottom water conditions; dysoxic or restricted conditions are implied by a DOP value between 46 and 75 % and a DOP of > 75 % suggests euxinic conditions. According to this, the Olivargas sediments would be dysoxic or with restricted conditions, whereas the Sancho sediments would be aerobic.

Besides, in acidic environments, such as in Sancho reservoir (pH around 4), the sulphide produced during the oxidation of organic matter, can react with dissolved Fe^{2+}, produced from the microbial catalysed reduction of Fe oxides/oxyhidroxides, to form insoluble Fe monosulphides (Berner, 1970). The reaction can be written as:

$$4FeOOH_{(s)} + 4SO_4^{2-} + 9CH_2O + 8H^+ \rightarrow 4FeS_{(s)} + 9CO_2 + 15H_2O \qquad (4)$$

Van der Berg et al. (1998) found that AVS concentration as low as 6 µmol/g were large enough to bind significant amounts of heavy metals. These metals can displace Fe form the monosulphides to form insoluble metal sulphides and therefore, are not considered to be bioavailable (Yu et al., 2001). This is based on the exchange reaction:

$$M^{2+} + FeS_{(s)} \rightarrow MS_{(s)} + Fe^{2+} \qquad (5)$$

As long as there is remaining FeS, aqueous metal concentration should not build up and the sediments should not be toxic with respect to metals (Cooper and Morse, 1998). Sulphides are considered the predominant solid phase controlling the concentration of metals such as As, Cd, Cu, Ni, Pb and Zn in anoxic sediments (Simpson et al., 1998). From the extracted metals by the step 3 in the sequential extraction, related to metals bound to organic compounds and sulphides, we can predict the bioavailability and toxic effects of heavy metals in these sediments, supposed that these metals in this fraction is bound to sulphides. The molar ratio of theses extracted metals in step 3 (EM, related to As, Cd, Cu, Ni, Pb and Zn) to AVS has been used by several authors (e.g. Allen et al., 1993; Clarisse et al., 2003; Otero and Macias, 2002). A molar ratio value smaller than one suggests there is excess AVS and the metals are not available. The calculated EM are 9.73 and 3.08 µmol/g for sediments from Olivargas and Sancho, respectively (Table 3). The measured AVS concentration in Sancho sediments (9.5 µmol/g) exceeds the corresponding EM, indicating that bioavailability of these elements may be low. The non existence of AVS in Olivargas sediments and the bigger EM suggest higher bioavailability and toxic effects.

Grains of pyrite has been observed (Fig. 6) by emission scanning electron microscope, after separation of the heavy fraction of the sediments. Framboid morphology dominated in the Olivargas sediments (Fig. 6a and b). However, perfectly spherical framboids were not observed in the Sancho sediments (fig. 6c), which is characteristic of fast growth (Butler and Rickard, 2000). Framboids in sediments show a size distribution with a modal size within the range 1–10 µm, and rare examples in excess of 50 µm in diameter. (Wilkin et al., 1996). The framboids found in sediments from Olivargas are mainly lower than 50 µm, while whose found in Sancho are bigger than 50 µm. The small size of many of the framboids is consistent with formation under predominantly anoxic conditions; however, the presence of larger framboids suggests brief periods of oxic bottom-water conditions (Hawkins et al., 2002). This is in accordance whit the calculated DOP from Sancho sediments, indicating aerobic bottom water conditions.

In the Sancho sediments, altered grains of framboidal pyrite has also been observed showing some oxidation (Fig. 6d). Weber et al. (2004) observed that oxidation of framboidal pyrite can be possible in a few weeks in environment with pH values less than 4-5.

5. Conclusions

Olivargas and Sancho dams behave like holomictic and monomictic lakes, having a summer thermal stratification which disappears during winter. In summer, the formation of an anoxic bottom layer is observed and removed by winter homogenization. This anoxic bottom layer is greatly lesser and less marked in the Sancho dam.

The effect caused by the AMD loads into the reservoirs is mainly important in the sediments of the bottom. The sediments from Olivargas dam have concentrations of toxic elements higher than the Sancho, especially As, Pb and Zn. The concentrations of toxic elements in relative abundance in the most labile fraction are in the following order: Zn (55%) > Co (47%) > Cd (33%) > As (10%) > Pb (9%) > Cu (4%) in Olivargas, and Zn (55%) > Co (35%) > Cu (21%) > As (6%) > Pb (4%) in Sancho. As a result, these sediments are toxic and harmful since this fraction concerns the bioavailable fraction, the most dangerous for the environment, consisting of exchangeable metals and those soluble in water or in slightly acidic conditions.

The calculated DOS and DOP values point out the AVS contribution to the Fe sulphide is minimal in the Olivargas sediments, remaining the toxic elements in its most mobile fraction. In fact, the non existence of AVS in Olivargas sediments and the relatively high concentration of extracted metals suggest higher bioavailability and toxic effects.

In the Sancho sediments, the low DOP in relation to the DOS value indicates a fast formation of monosulphides. However, the DOP value as well as the presence of larger framboids suggests periods of oxic bottom-water conditions. As a result, the oxidation of these sulphides upon exposure to oxygen, can lead to the liberation of associated trace metals to the water column.

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Tables

Table 1. Physicochemical parameters and chemical composition of the pore-water sediments and the overlain water.

	Sancho dam		**Olivargas dam**	
	Overlain water	Pore water	Overlain water	Pore water
pH	4.30	6.62	7.00	7.05

EC (µS/cm)	362	325	223	260
DO (mg/l)	7.70	<dl	5.20	<dl
Eh (mV)	548	57.6	419	64.5
T (ºC)	11.4	16.9	9.3	15.0
Al (mg/l)	2.10	1.53	<dl	4.05
As (µg/l)	<dl	<dl	<dl	11.0
Co (µg/l)	65.0	<dl	<dl	<dl
Cu (mg/l)	0.44	0.40	<dl	<dl
Fe^{2+} (mg/l)	<dl	6.11	<dl	3.11
Fe^{3+} (mg/l)	<dl	17.4	<dl	21.7
Mn (mg/l)	1.70	1.31	0.37	3.33
Ni (µg/l)	28.0	<dl	<dl	<dl
Pb (µg/l)	<dl	36.0	<dl	171
Sn (µg/l)	56.0	<dl	6.40	<dl
Zn (mg/l)	1.40	<dl	0.95	1.29
S^{2-} (mg/l)	<dl	0.25	<dl	2.11
SO_4^{2-} (mg/l)	117	<dl	66.0	<dl
HCO_3^-(mg/l)	<dl	5.49	20.0	18.0

EC: electrical conductivity; **DO:** disolved oxygen; **<dl:** below detection limit

Table 2. Amount of some elements released in the different steps of the BCR sequential extraction procedure (values in mg/kg dry wt.; nd: not detected).

	Al	**As**	**Cd**	**Co**	**Cr**	**Cu**	**Fe**	**Hg**	**Mn**	**Pb**	**S**	**Zn**
F1												
Olivargas	183	10.5	1.12	10.4	nd	28.9	5338	4.00	415	26.0	949	1705
Sancho	440	2.30	nd	6.82	nd	83.3	2262	1.54	121	5.45	385	270

F2												
Olivargas	3420	26.4	1.99	7.50	2.55	332	11519	nd	78.3	221	100	1108
Sancho	3232	4.32	nd	4.13	2.43	133	8333	nd	27.0	75.4	107	124
F3												
Olivargas	1539	2.50	0.31	2.17	3.39	389	1119	0.59	10.3	16.3	2510	225
Sancho	1636	nd	nd	2.83	4.36	141	987	0.60	8.58	3.94	1095	49.7
F4												
Olivargas	10676	61.6	nd	1.95	21.9	39.7	21087	0.51	94.0	35.9	1845	87.9
Sancho	14550	34.7	nd	5.45	27.9	36.0	32965	0.21	113	52.0	346	44.7

Table 3. Selected chemical characteristics of the sediments examined

	AVS (µmol/g)	Py-S (µmol/g)	Fe_r (µmol/g)	DOP (%)	DOS (%)	AVS/CRS (%)	AVS/Py-S	EM (µmol/g)	EM/AVS
Sancho	9.5	8.9	24	16	50	51	1.07	3.08	0.32
Olivargas	nd	113	33	63	63	-	-	9.73	-

AVS: acid volatile sulphur; Py-S: pyrite sulphur; Fer: reactive Fe; CRS: Cr reducible sulphur; DOP: degree of pyritization; DOS: degree of sulphidization; EM: extracted metals

Figure 1.

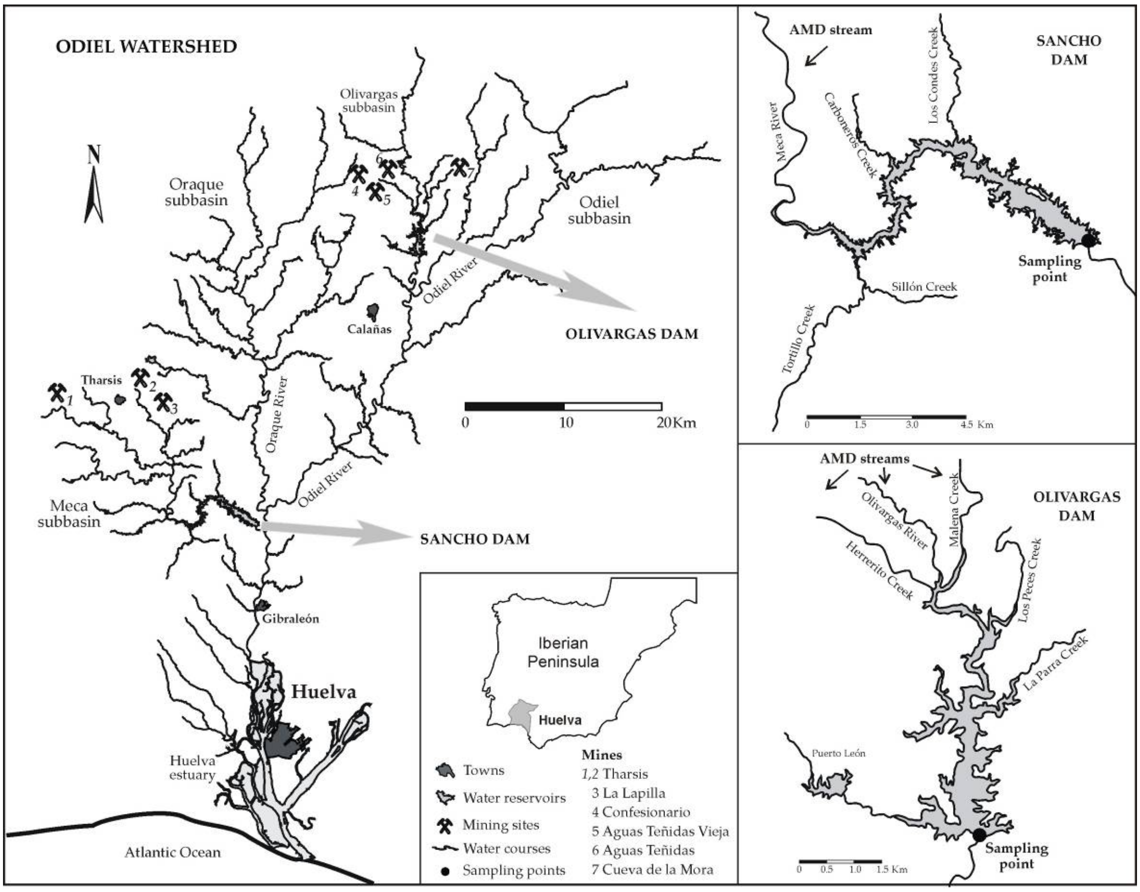
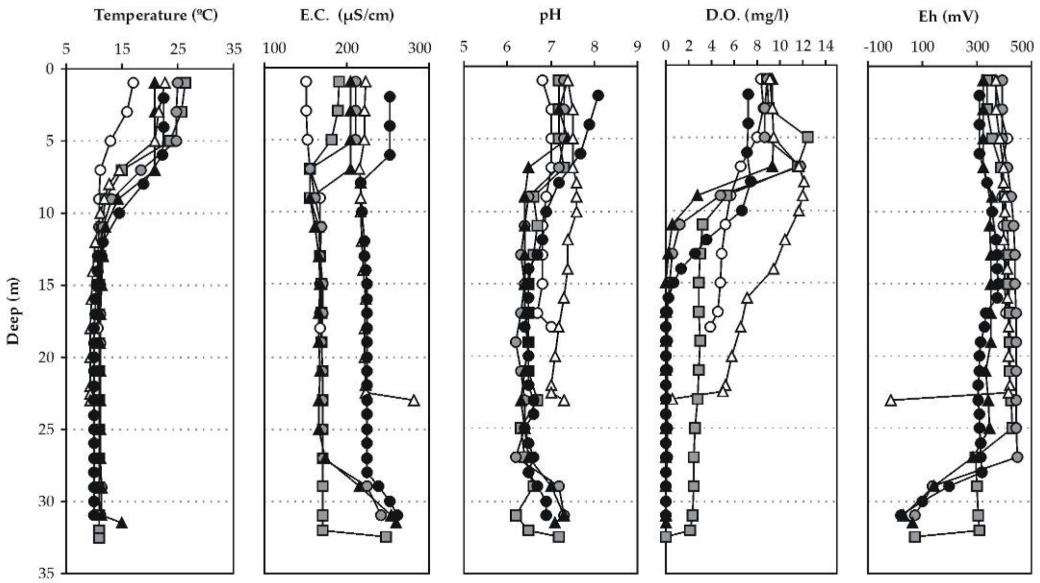
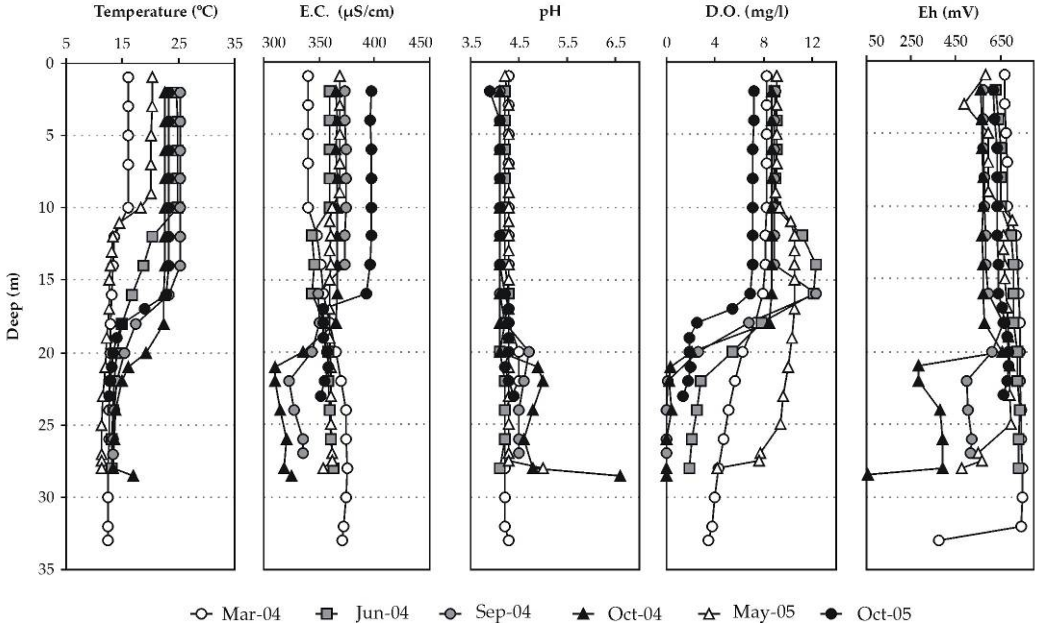

ODIEL WATERSHED
N
Olivargas subbasin
Oraque subbasin
Odiel subbasin
Odiel River
OLIVARGAS DAM
Calañas
Tharsis
1
2
3
4
5
6
7
Oraque River
Odiel River
Meca subbasin
SANCHO DAM
0
10
20Km
Gibraleón
Huelva
Huelva estuary
Atlantic Ocean
Iberian Peninsula
Huelva
Towns
Water reservoirs
Mining sites
Water courses
Sampling points
Mines
1,2 Tharsis
3 La Lapilla
4 Confesionario
5 Aguas Teñidas Vieja
6 Aguas Teñidas
7 Cueva de la Mora
AMD stream
SANCHO DAM
Meca River
Carboneros Creek
Los Condes Creek
Sampling point
Sillón Creek
Tortillo Creek
0
1.5
3.0
4.5 Km
AMD streams
OLIVARGAS DAM
Olivargas River
Malena Creek
Herrerito Creek
Los Peces Creek
La Parra Creek
Puerto León
0
0.5
1.0
1.5 Km
Sampling point

Figure 2.



a) OLIVARGAS DAM



b) SANCHO DAM

Figure 3.

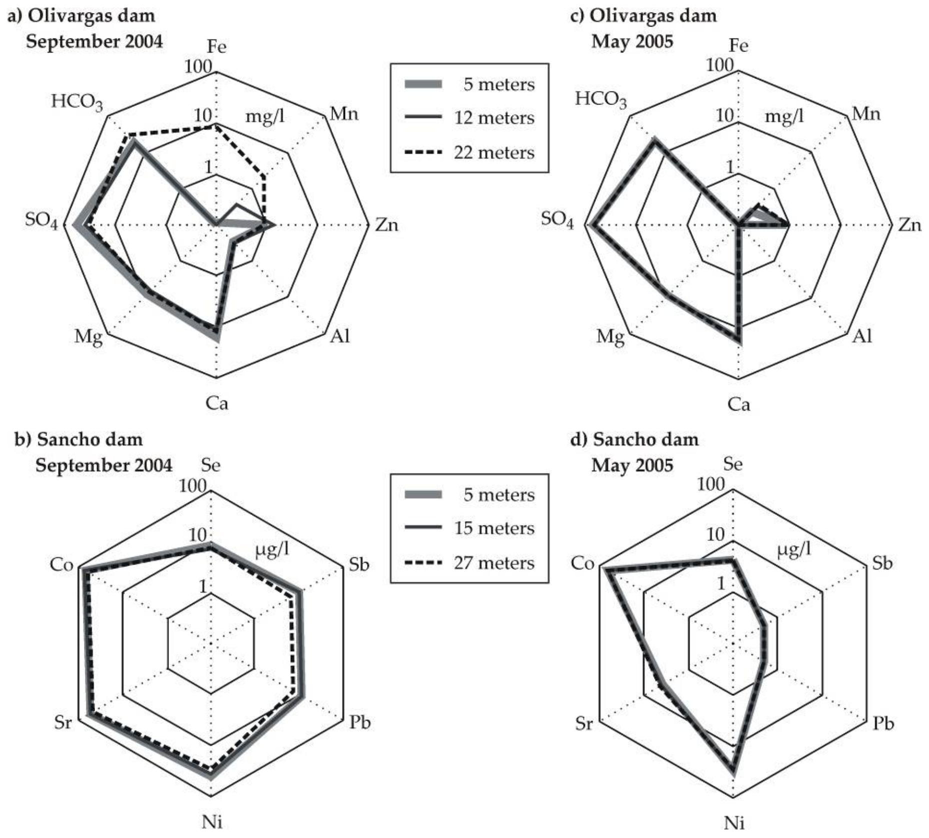

a) Olivargas dam
September 2004
c) Olivargas dam
May 2005
b) Sancho dam
September 2004
d) Sancho dam
May 2005
Fe
Mn
Zn
Al
Ca
Mg
SO_4
HCO_3
100
10
1
mg/l
5 meters
12 meters
22 meters
Se
Sb
Pb
Ni
Sr
Co
μg/l
15 meters
27 meters

Figure 4.

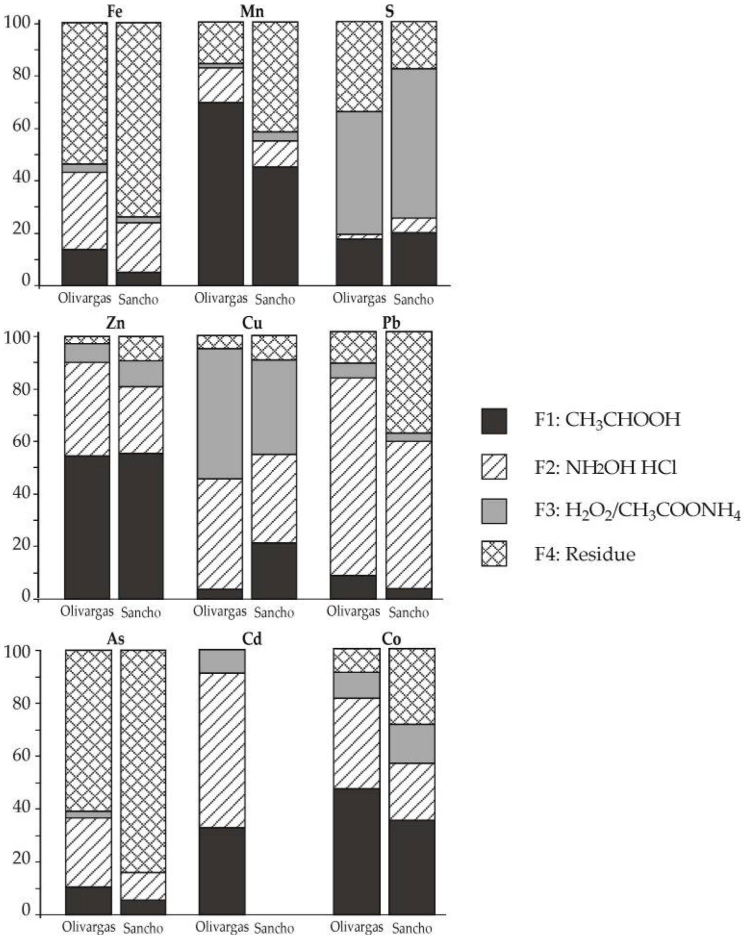


Figure 5.

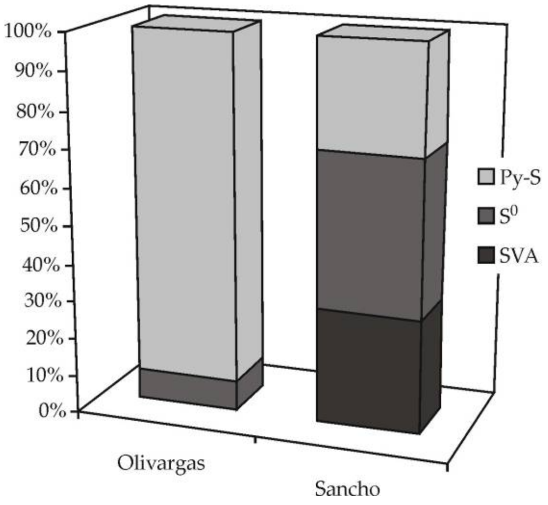
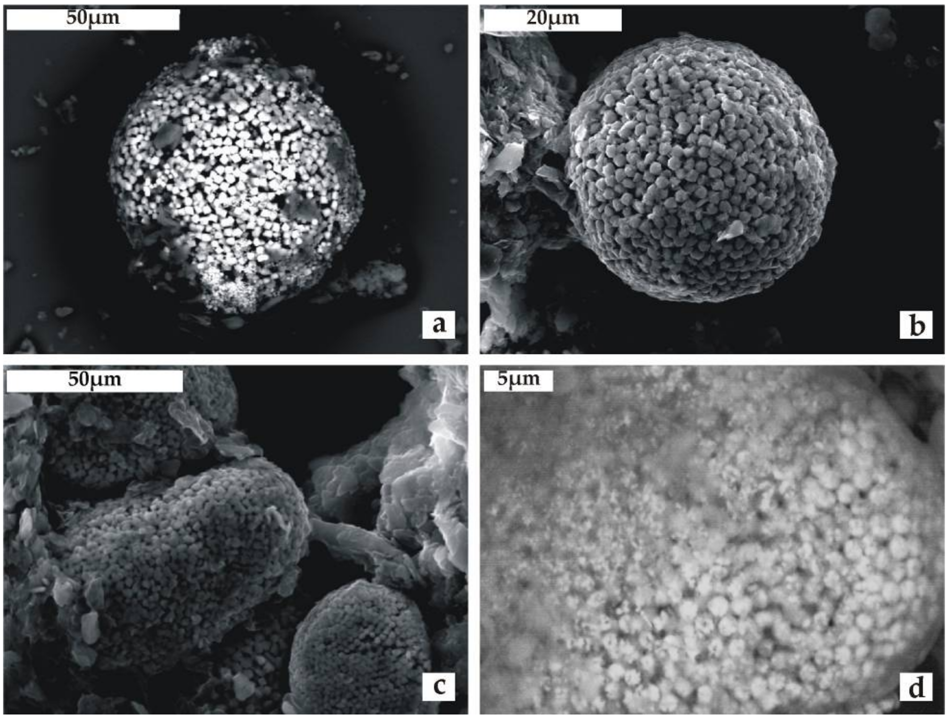


Figure 6.


50µm
a
20µm
b
50µm
c
5µm
d