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CHARACTERISATION OF HEAVY ELEMENTS PARTITIONING BETWEEN GROUNDWATER AND SUSPENDED PARTICLES AFTER THE COLLAPSE OF A MINE TAILING DAM (AZNALCÓLLAR, SOUTH SPAIN)

Maria Jesús Turrero, Antonio Garralón, Paloma Gómez, Ana Melón and Francisco Fernández

CIEMAT
Avda. Complutense, 22
28040 Madrid, Spain
Phone: + 34 91 3466138, Fax: + 34 91 3466542
e-mail: mariaje@ciemat.es

ABSTRACT

A sequential filtration procedure has been used to investigate the partitioning and the degree of association of metals (As, Cd, Cu, Fe and Pb) with the coarse-grained fraction (>0.45 μm) and the colloidal fraction (0.002-0.45μm) in water samples from an area affected by the collapse of a mine tailing dam (Aznalcóllar, Southern Spain). The elemental composition and the concentration of particles and colloids in the water were determined by SEM/EDAX after filtration and microelectrophoresis analyses were carried out to determine the charge properties of the particles. Sampling was performed both in waters affected and unaffected by the toxic spill (polluted and unpolluted waters, respectively). SEM/EDAX studies indicate that particles are mainly composed of inorganic matter, even though certain differences in the elemental composition of particles and colloids between polluted and unpolluted samples have been detected. In polluted waters the presence of pyrite (S, Fe), sphalerite (S, Zn) and Pb associated with Fe-oxyhydroxides stands out. In unpolluted samples, the significant carbonate contents must be pointed out. Colloids occur in relatively low concentrations, ranging from 10^8 to 10^{11} colloids per litre and the zeta-potential values vary from –0.7 to –6.8 mV. Both colloid stability and concentration are higher in those samples taken far away from the zone affected by the toxic spill.

The rapid depletion of heavy elements from the water is due to their association with particles and colloids, which can function as carriers within certain distances. At the pH of these waters (5-8), 50-70% of the total iron occurs as Fe-oxyhydroxides within a size range of 0.45 and 8 μm, 25-40% is found as colloidal iron, and the remaining 7% is in solution. Sorption onto these iron-rich particles or colloids seems to control the heavy element partitioning between dissolved and particulate phases.

INTRODUCTION

The tailing dam of Aznalcóllar pyrite mine collapsed on April 25, 1998 and 4 Hm^3 of sulphide slurry flooded the Agrio and Guadiamar valleys. A significant number of open wells were also flooded, and, consequently, their water became polluted. An important amount of heavy metals, which were present in the slurry, were dissolved in the waters, specially: Zn, Cd, Cu, As and Pb. The retention of these heavy metals by the suspended particles and colloids in the waters has been studied, in order to quantify the potential transport of these elements in colloidal form.

The study of the association of heavy metals with colloids has received much attention recently in environmental investigations (Smith, et al., 1992; Skei, et al., 1996; Lead et al., 1997). Colloids are generally considered as particles whose sizes vary between 1 nm and 450 nm. Due to their small size and consequently, their high surface area per unit mass, they can function as highly effective sorption substrates.

Several authors have investigated the pH dependence of the partitioning of heavy metals between water and sediments in mine drainage and have correlated this effect to sorption reactions onto iron-rich precipitates (Smith, 1991). The amount of toxic elements sorbed onto colloids is related to the number of available surface sites for sorption. This process is affected by many factors: pH of the solution, ionic strength, number and size distribution of particles, the presence of competitive ligands as sulphate, carbonate species, etc.

Nine water samples, which correspond to polluted and unpolluted waters of the Aznalcóllar spill mine, were collected from the Guadiamar valley. High concentrations of heavy metals were determined in waters and iron-rich precipitates were detected in soils. A mineralogical, physical and chemical characterisation of the colloids and suspended particles has been carried out, in order to determine their sorption capacity and their potential mobility in the aquifer.

MATERIALS AND METHODS

Sampling and fractionation of suspended particles and colloids

Nine water samples were collected from the Guadiamar valley and Entremuros area (Sevilla, Spain) distributed as follows: three were taken from wells, which were affected by the sulphide slurry spill mine (samples: 17, 32, 43), five from the unpolluted area (samples: 2, 3, 31, 33, 34,) and one (P2M6) in the channel where the toxic waters were retained before their release to the Guadalquivir river. The collapsed tailing dam is located in the northernmost part of the area and all the samples have been ordered sequentially, by their closeness to the dam, in a N-S profile.

Physico-chemical parameters (pH, Eh, electric conductivity and temperature) were measured in situ. The samples were collected in 2 liters containers and were kept at 4 ºC until their chemical analyses. Each container was connected to an 8 µm filter situated inside a glove-box purged with 99%N_2 + 1%CO_2, in order to maintain an oxygen concentration of 200-500 ppm and to prevent possible air contamination of particles and degassing. The filtration procedure worked continuously in a cascade from the bigger pore membrane (8 µm) to the smaller pore ultrafiltration membrane (2 nm) (Figure 1). The size range, that was used in this work to study the association of heavy metals with suspended particles, was 8 µm, 3 µm, 0.8 µm y 0.45 µm. The size limit between suspended particles and colloids is 0.45 µm and filters of 0.22 µm and 0.1 µm were used, in order to characterise the heavy metals retention by colloids.

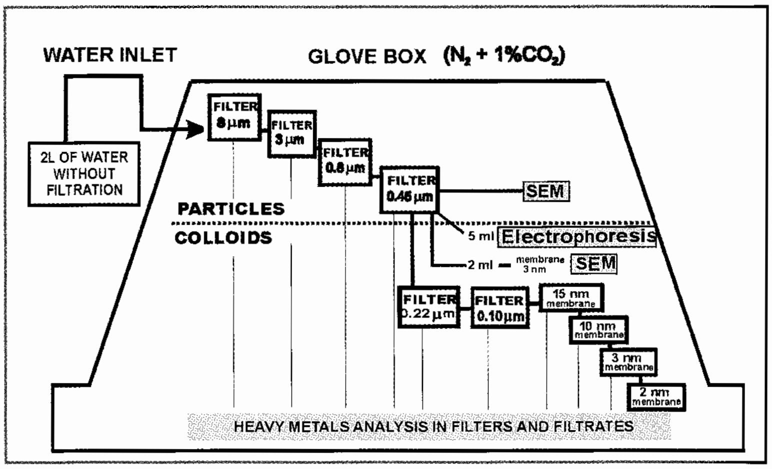

Figure 1. Suspended particles and colloids fractionation system in a glove box to characterise the association of heavy metals in the waters affected by the spill of Aználcollar mine.

This prefiltered water is then ultrafiltered in teflon cells of 25 mm diameter by transverse filtration driven by a peristaltic pump through four different nominal molecular weight cut-off limit (MWCL) membranes (15 nm, 10 nm, 3 nm and 2 nm) (Gómez and Turrero, 1992; Gómez et al., 1993). All the membranes are washed before use for at least 24 h with Milli-Q water. Aliquots of all the ultrafiltrates were preserved for the measurements of heavy metals. The chemical composition was determined both in retentates and filtered water. Elemental analysis of colloids was conveniently carried out by ICP-AES or ICP-MS.

A set of membrane samples for the determination of colloid concentration by SEM counting was made. The preparation of these membranes for the measurements of the colloid concentration was carried out by passing 2 and 5 ml of prefiltered water through a Diaflo Amicon XM50 (polyacrylamide, 3 nm) membrane. They were also soaked in Milli-Q water for at least 24 h prior to their introduction in the teflon cell. The membranes were then dried in N2 atmosphere and under vacuum inside the glove box. Moreover, samples were collected, after 0.45 µm filtration, for the determination of electrophoretic mobility.

ANALYTICAL TECHNIQUES

Microelectrophoresis may be used to measure the colloid electrophoretic mobility which is related to the colloid surface potential (Hiemenz, 1986), which in turn, can give information on the colloid stability. Microelectrophoresis was used to measure the colloid electrophoretic mobility function (model-related to charge) and colloid population in terms of number of particles per litre. The equipment used was a Malvern Zetamaster

The colloid population may be assessed in terms of sizes and density by scanning electron microscopy (SEM) using a membrane filter to obtain a suitable target. It is assumed that there is no colloid/membrane reaction and that all colloids are recovered. The size detection limit is 50-80 nm

(Longworth and Ivanovich, 1990; Degueldre et al., 1990) under specific conditions of the microanalyses (accelerating voltage: 15 kV and working distance: 39 mm); the analysed volume was 1 μm^3 and the detection limit is 0.1% in atomic weight. All the membranes were coated with gold prior to counting image and EDAX analysis.

The main cations and some trace elements were determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES). Analytical emission lines, including background measurements positions and correction of spectral interference, were selected from U.S. Environmental Protection Agency method 200.6, combining a Jobin Yvon JY 48 simultaneous instrument and a Jobin Yvon JY 38 VHR monochromator.

Trace and ultratrace elements in filters and filtrates were determined using a Finnigan MAT SOLA quadrupole ICP-MS. Three different internal standards (Ga, In and Lu), based on aqueous standard solutions, were used to correct matrix effects in samples. Isotopes selected for elemental quantification were previously checked for isobaric and polyatomic interferences according to U.S. EPA method 200.8.

The methods were validated with certified reference materials of the Community Bureau of Reference (BCR) of the Commission of the European Communities.

RESULTS AND DISCUSSION

Colloid concentration obtained by SEM counting in polluted and unpolluted samples varied from 108 to 1011 colloids per litre (Figure 2) and the results of the zeta potential ranged from -0.7 to –6.8 mV (Table 1). Low results, both in colloid concentration and in surface net charge, can be observed in both kinds of samples. However, polluted samples located in the Southern part of the studied area showed lower zeta potential values than those located in the Northern part, due to their higher stability. An increase of colloid concentration of more than three orders of magnitude is also observed towards the South (Figure 2). In contrast, colloid concentration in unpolluted waters shows slight variations.

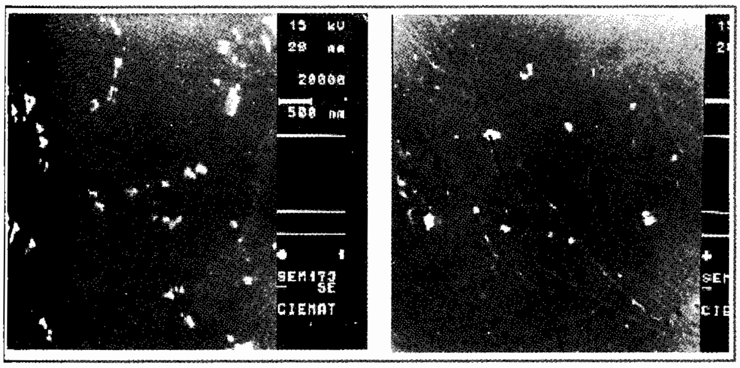

Figure 2. Scanning electron micrograph of ultrafiltration membranes, where colloid concentration and elemental analysis were determined by SEM. Left: sample 43 (1.5 1011 colloids/l). Right: sample 33 (2.1 1010colloids/l).

Sample without filtration	Zeta Potential	Concentration (colloids /l)	pH field	Type water
17 (polluted)	-0.9	$1.2\ 10^{9}$	6.53	SO_4-Ca
32 (polluted)	-1.9	$3\ 10^{10}$	6.34	SO_4-Ca
43 (polluted)	-6.0	$1.5\ 10^{11}$	7.3	Cl-Na
P2M6 (polluted)	-6.5	$4.5\ 10^{9}$	6.15	SO_4-Ca
2 (unpolluted)	-7.0	$2.0\ 10^{10}$	4.39	SO_4-Ca
3 (unpolluted)	-1.7	$9.8\ 10^{9}$	6.62	SO_4-Ca
31 (unpolluted)	-1.9	$4.9\ 10^{8}$	7.2	HCO_3-Ca
33 (unpolluted)	-2.8	$2.1\ 10^{10}$	7.27	HCO_3-Ca
34 (unpolluted)	-2.6	$9.0\ 10^{9}$	7.62	HCO_3-Ca

Table 1. Results of zeta potential, colloid concentration, pH and type of water in polluted and unpolluted samples.

The SEM/EDAX determination of the colloid elemental composition and suspended particles was carried out with some difficulties, due to the size of the colloids and their low concentration in the waters (Table 2). The colloids of polluted waters are mainly constituted by inorganic particles, clays (illite: K-Si-Al silicates), silicic acid (chalcedony), gypsum (SO_4 Ca), pyrite (S, Fe) and sphalerite (S, Zn). Pb and As are strongly adsorbed onto the iron oxy-hydroxides. Colloids from unpolluted waters fundamentally consist of fine clay particles, the presence of carbonates (Ca) being the main difference with the colloids of polluted waters. These results are in agreement with the chemical composition of the waters, since polluted waters are Ca-SO_4^{2-} type waters, whereas the unpolluted ones are Ca-HCO_3^- type waters.

Polluted samples	Unpolluted samples
Si, Fe, Mg, Al (chlorite)	K, Si, Al (illite)
K, Si, Al (illite)	S, Ca (gypsum)
S, Ca (gypsum)	Cl, Na
S, Fe (pyrite)	**Ca (carbonates)**
S, Zn (sphalerite)	S, Pb (galena)
Si (chalcedony)	Si (chalcedony)
Cl, Na	
Fe, As	
Fe, Pb	

Table 2. SEM/EDAX elemental composition of the colloids and particles retained in the filters and in membranes during the fractionation procedure.

A filtration and ultrafiltration study was performed in order to examine the retention reactions of metals between dissolved and particle fractions. These reactions are pH-dependent and the amount of binding sites in the sorbent determines the retention capacity of the colloids. The highest contents of Cd, Cu, As, Fe and Pb in polluted samples are associated with fractions, whose pore size is greater than 0.22 μm. However, in waters located in the Southern part of the studied area, these

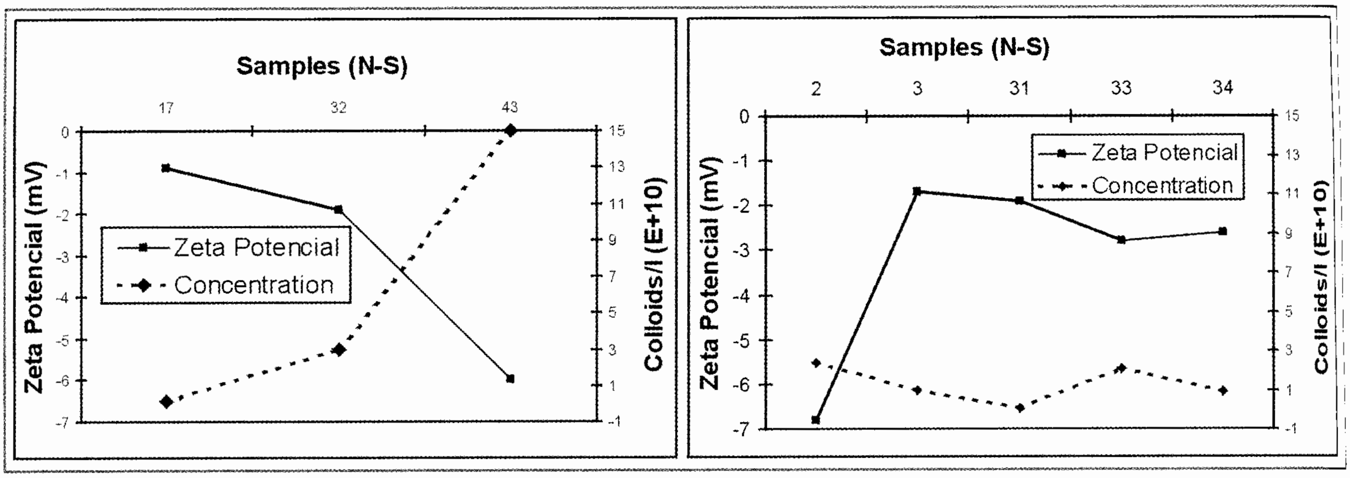

Figure 3.- Physico-chemical characteristics of colloids in polluted and unpolluted waters in a N-S profile.

elements are associated with pore sizes less than 0.22 µm. EDAX analysis shows that iron oxy-hydroxides are the main sorbent material of the heavy elements present in the waters.

The pH in polluted samples ranges from 6.1 to 7.3 (Table 1). The total iron concentration analysed in these waters varies from 19 mg/l to 61 mg/l and the results obtained from the fractionation system show that 50-70% of the total iron is retained in the size range from 0.45 to 8 µm. Approximately, 25 to 40% of the iron is associated with colloids (<0.45 µm) and around 7% is in solution (Figure 3). The retention process generally increases with increasing pH, but in some cases the sorption of heavy metals may be affected by competitive processes between aqueous sulphates and hydroxo species.

Sorption of Cd, Cu, As, and Pb seems to be controlled by the presence of iron-rich particles or colloids, given the high correlation degree found between As and Pb with the iron particles (r=0.97 and r=0.96, respectively). Table 3 shows the correlation ratio of some of these heavy metals detected in polluted samples.

Sample	**As-Fe**	Cd-Fe	Cu-Fe	**Pb-Fe**
17	**0.97**	0.77	0.39	**0.96**
32	**0.88**	0.57	**0.88**	0.74

Table 3. Correlation ratio of some heavy metals detected in the polluted samples.

The arsenic concentration in unpolluted samples is below the detection limit, in contrast to the polluted samples, where it ranges from 200 mg/l to < 6 mg/l from north to south. These differences are pointed out in the fractionation of this element. The results of the arsenic retention are shown in Figure 5. Sample 17 shows a high concentration of dissolved arsenic (200 mg/l), the water pH being 6.5. The retention reactions caused by suspended particles (>0.45 µm) accounts for 77% of the total As, whereas the colloid retention decreases to 22% of the total As present in the water. Sample 43 presents a different behaviour, due to the low As concentration present in the water, which is, in turn, related to the increase of pH observed in this water.

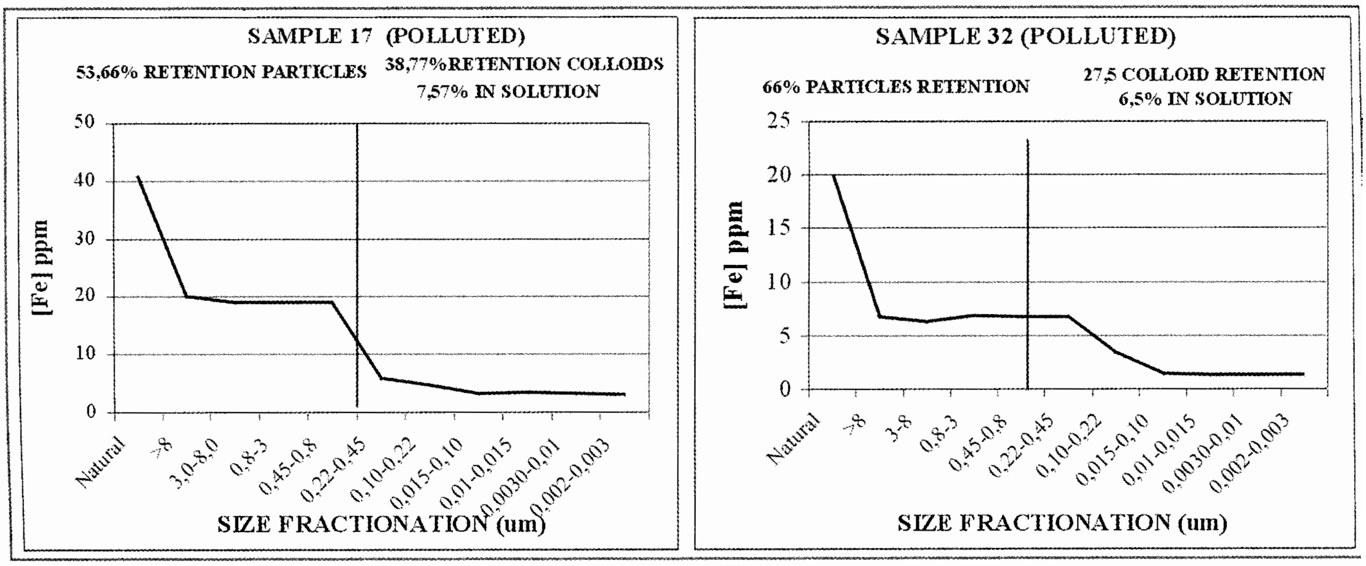

Figure 4. Fe fractionation as a function of the colloid and particle size in polluted samples.

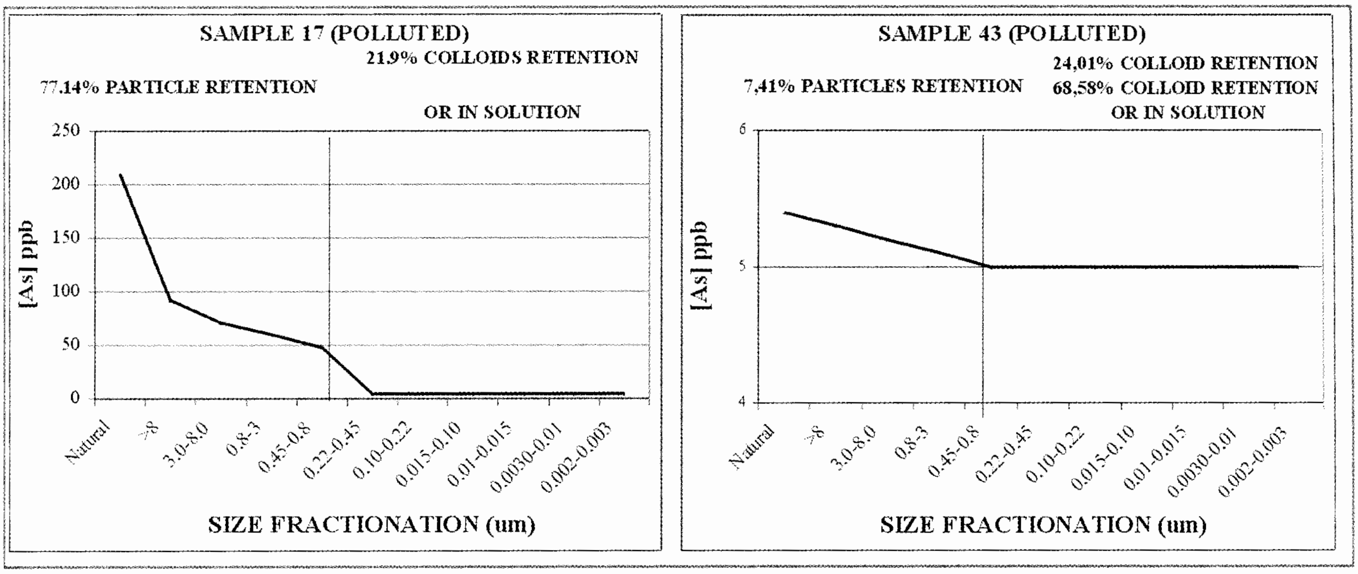

Figure 5. Arsenic fractionation as a function of the colloid and particle size in polluted samples (sample 17 is located in the northern part and sample 43 in the Southern part of the studied area).

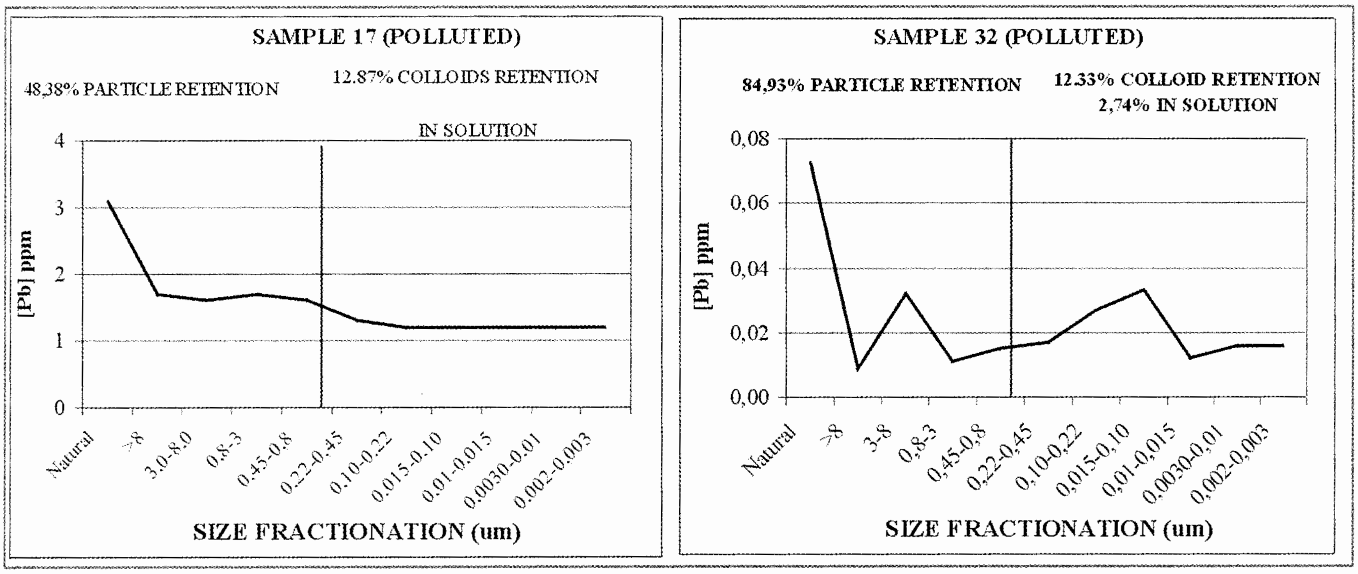

Figure 6. Pb fractionation as a function of the colloid and particle size in polluted samples

The retention behaviour of Pb is similar to that of As. Figure 6 shows the retention capacity of suspended particles and colloids by Pb. Iron oxy-hydroxides particles have a tendency to retain higher concentration of Pb than colloids.

In contrast, Cd and Cu tend to stay in solution, since only 15% of the total metal content is retained by the suspended particles. Zn is always dissolved and no retention with colloids in any range size has been found.

CONCLUSIONS

Retention capacity of suspended particles and colloids were determined in nine water samples, some of them affected by the Aznalcóllar spill mine. Sorption reactions with iron oxy-hydroxides seem to control the partitioning of As and Pb between dissolved and suspended particles or colloid fractions in these waters. The retention capacity of these Fe oxy-hydroxides must be taken into account as a retardation factor concerning the pollution of the Guadiamar River. Ultrafiltration data reveal strong retention of As and Pb (> 60%), and to a smaller extent of Cd and Cu (< 15%), onto the iron oxy-hydroxide coarse fraction, whereas the colloidal fraction contains less heavy elements, aprox. 20% of As and Pb. Zn tends to remain dissolved in all the samples.

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