

# **Experimental Study of Mobility and Kinetic Characterization of Trace Elements in Contaminated Sediments from a River Basin in Northern Peru**

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Received 8 March 2014; revised manuscript accepted 21 June 2014

## **ABSTRACT**

In the Jequetepeque basin (Peru), gold extraction activity has been performed in the last decades, leading to a release of metals and metalloids into the environment. Sediment samples were taken in the vicinity of two mines and analysed. Extraction of metals and metalloids from sediments was carried out using single extraction procedures, acidic ( $\text{HNO}_3$ ), and complexation (EDTA) leaching, in order to determine the mobility of trace elements. Results indicated that acidic extraction at low pH values increased the leachability of trace elements. EDTA showed a higher bioavailability of metals in sediments than acidic extraction under similar pH conditions because of its greater leaching capacity. This is an important issue in view of risk assessment analysis. The highest extractability was observed for Cd in all sediments with up to 90% of extraction after 1 hour. The mobility index analysis indicated that faster kinetic leachability of some trace elements leads to a higher mobility in sediments, especially those near the active gold extraction mine. The ecological risk assessment suggested that the four river sediments were at high and very high risk levels, indicating that sediment contamination is an issue of environmental concern in the Jequetepeque basin of northern Peru.

**Key Words:** single-extraction procedures; sediments; EDTA, diffusion coefficient; ecological risk index; mobility index.

## INTRODUCTION

An accurate estimation of metals' bioavailability in soils and sediments is gaining importance in ecological risk assessments (Chen *et al.* 2009). In this sense, the use of selective chemical extractions is the usual approach for understanding the interaction of heavy metals with soil and sediment components and to assess their mobility and availability to plants (Sahuquillo *et al.* 2003; Ure 1996). Single-extraction schemes provide a simpler generic approach by dividing the sorbed phases into just two categories: labile and non-labile (Young *et al.* 2005). Acidic or chelating agent solutions are usually used as extractants because of their effectiveness in removing a wide range of heavy metals (Chen *et al.* 1998; Fangueiro *et al.* 2002). Moreover, weak acids simulate the effect of an acid input (*e.g.*, through acid rain or an accidental spill) onto soils and sediments (Sahuquillo *et al.* 2003). Kinetic extraction by a single reagent can be defined as the proper methodology to determine the distribution of species in natural environments (Fangueiro *et al.* 2002, 2005; Gismera *et al.* 2004). The most widely utilized reagents for single-extraction schemes are powerful chelating agents, such as ethylenediamine tetra-acetate (EDTA) and diethylenetriamine penta-acetate (DTPA) (Madrid *et al.* 2007; Young *et al.* 2005).

Trace elements stored in floodplains and channel sediments have the potential to serve as future sources of pollution and depend on factors such as the proximity of contaminated sediment to the active channel (lateral and vertical) and the intensity of the geomorphic activity along the river (Martin 2004). Published literature on sediment-associated trace elements' dispersion processes in rivers can be used to understand the processes and the space and timescales over which they operate; this knowledge can be used in a practical way to help river basin managers more effectively control and remediate basins, particularly those affected by current and historical mining of trace elements (Macklin *et al.* 2006).

It should be pointed out that trace elements can exist in different forms in the environment, where they may be transformed from one form to another or exist in different forms simultaneously. The form or chemical speciation of trace elements varies widely depending on environmental conditions. Such differences in chemical speciation affect the environmental fate, bioavailability, and environmental risk of trace elements. The mobility of such hazardous trace elements is highly dependent on their specific chemical forms or different binding forms rather than on the total element concentrations. Consequently, knowledge of trace

element partitioning between the different geochemical fractions is particularly useful for determining the bio-available fraction and the risk of eco-toxicity (Cánovas *et al.* 2007, 2008; Galan *et al.* 2003; Kraus and Windegand 2006, Lynch *et al.* 2014).

In that sense, previous studies were applied in the Jequetepeque basin, where the chemical quality of the surface waters was the focus following the ecological and chemical approaches under the water framework directive requirements (EC 2000; Yacoub 2013). It was evaluated using classical chemical monitoring methods for trace-level pollutants present in water and sediment (Yacoub *et al.* 2012; Yacoub *et al.* 2013; Yacoub *et al.* 2014). From these findings, the present study seeks to deepen the knowledge about the most polluted sites in environmental terms by an accurate estimation of metal bioavailability and potential risk.

In the present work, the mobility of trace elements from river sediments was evaluated by single-extraction treatments, nitric acid (under different pH), and EDTA, and compared the labile with non-labile amount obtained by each extractant. Additionally, kinetic experiments were performed using time-based extraction experiments with EDTA as the added extractant. A diffusion kinetic model adapted to the sediment system was used to describe the experimental data. Finally the environmental assessment (in ecological and mobility terms) was performed through the potential ecological risk and mobility index.

## **METHODOLOGY**

### **Site Selection and Sample Collection**

The sediment samples were obtained from the upper-middle part of the Jequetepeque basin, located in Northern Peru, as shown in Figure 1. Two study areas, the Llapa and Rejo sub-basins, were selected on the basis of the criteria determined in previous studies: i) U.S. Environmental Protection Agency (USEPA) guidelines (USEPA 1991, 1994, 1998, 2001, and 2002); ii) proximity to the main mining activities; iii) hydrology, geology, geomorphology, erosion, and topography (CARE 2007; CAO 2007; DIGESA 2008; PEJEZA 2005); iv) previous evidence of toxicology or spillage; v) available data from studies of water quality (CAO 2007; DIGESA 2008; Stratus 2003); and vi) feasibility of monitoring activities, particularly regarding physical access to sites and approval of local residents (Yacoub *et al.* 2012). Sampling points M1 and M2 were located near the Sipán SL mine (closed in 2005), and M3 and M4 were located

near the Minera Yanacocha SRL mine (active since 1993). The cyanide leaching process was the extraction method for both gold mines.

Sediment samples were collected in plastic bottles using a core sampler. Samples were taken from the nearest point on the river bank, from the superficial layer (ca. 10 cm) of sediments covered by approximately 20 cm of water. The sediments were kept cool in the field. Three sediment subsamples were collected and mixed at each site to ensure homogeneity (Yacoub *et al.* 2012). The sediment samples were dried at 105°C until a constant weight and stored in polyethylene bottles (Yacoub *et al.* 2014). Particles that were < 63 µm in size and which retained trace metals (Chen *et al.* 2007) were considered for all the extraction procedures.

### **Experimental Procedure**

To determine trace element content in sediments, a digestion procedure by microwave (MW) was carried out following the USEPA Method 3051A (USEPA Method 3051A). The MW digestion procedure chosen does not dissolve all of a sample matrix, such as quartz, silicates, titanium dioxide, alumina, and other oxides. Therefore, this digestion procedure is not considered total digestion and is referred to as pseudo-digestion (Yacoub 2013). A total of 0.5 g of sediment sample was taken. The reagents added to the sediment sample were 9 mL of HNO<sub>3</sub> and 3 mL of HCl. No detectable contamination was found when blank vessels were processed. The experiments were performed in duplicates. The final digested solution obtained was filtered through 0.45 µm cellulose acetate membrane filters and stored in polyethylene bottles at 4°C until analysis. All reagents used were of analytical reagent grade and were purchased from Merck. Ultra-pure water (Milli-Q system Millipore) was used throughout the study.

### **Extraction Experiments**

The HNO<sub>3</sub> and EDTA extraction experiments were performed under the same methodology. Initial pH solutions were varied from 1 to 6 in order to i) avoid the precipitation of metals, and ii) to determine the concentration between low pH values (which are typical from mine pollution) and pH values that are common for rivers. Batch experiments were carried out at room temperature 21 ±0.5°C.

First, 0.25 g of sediment was put in contact with 15 mL of the extracting solution and shaken in a rotary Intelli-Mixer RM-2. Suspensions were then centrifuged for 30 min at 3000 rpm before

filtration in a Selecta Centronic-BL centrifuge. The equilibrium pH was measured and the extract was separated from the sediment by filtration with 0.45 micrometer filter membrane (Millipore Corporation). Then, the extract was acidified with 10% HNO<sub>3</sub> to pH less than 2, to avoid precipitation. Finally, the extract was stored in refrigerant (less than 4°C) until analytical determination. Replicates of the extraction procedure were made for each sediment sample extraction; being discarded if some precipitate appears during the extraction.

The kinetic extraction of trace elements by the EDTA for the four sediment samples were carried out by considering the optimum operating conditions obtained in previous studies (Fangueiro *et al.* 2002; Fangueiro *et al.* 2005); thus, 15 mL of an extracting solution of 0.0125 mol·L<sup>-1</sup> of EDTA was mixed with 0.25 g of sediment sample in 20 mL glass tubes by a rotary shaker at 25 rpm for different extraction time (shaking time) varying from 5 min to 24 hours. Suspensions were then centrifuged for 40 min at 3000 rpm in a Selecta Centronic-BL centrifuge. Equilibrium pH was measured using a Crison potentiometer (model GLP 22) before filtration.

The concentrations of Cd, Cu, Pb, and Zn were determined by inductively coupled plasma mass spectrometry and optical emission spectrometry (ICP-MS model Elan 6000 and ICP-OES Perkin Elmer model Optima 3200RL) while As and Ni were analysed by ICP-MS. It was necessary to use two instruments for Cd, Cu, Pb, and Zn quantification due to the wide range of concentrations obtained by the pseudo-total and single extraction procedures for the four sampling points. The efficiency of the analysis was assessed by replicates, with standard deviations less than 10%. Based on these, the obtained results from the performed analytical methods were considered adequate.

### **Kinetic Modelling**

The diffusion model assumes that the complexation reaction of metals (M) by an added ligand (L) is fast, and that the rate-limiting step is the intra-particle diffusion of the complex (ML) (Chen *et al.* 1998). Studying metal desorption from sediments, Fangueiro *et al.* (2005) considered that, in the initial stages of the desorption process; the Fickian diffusion equation that describes the diffusion in and out a cylinder could be simplified to:

$$\frac{M_t}{M_\infty} = q_t = k_d \sqrt{t} \quad (1)$$

where  $M_\infty$  is the amount of complex ML entering or leaving the sphere after infinite time, the total amount  $M_t$  is the complex ML (diffusive substance) entering or leaving a sphere at time  $t$ , and  $k_d$  is the intraparticle diffusion rate constant ( $\text{mg g}^{-1} \text{min}^{-1/2}$ ).

The intraparticle diffusion model developed by Weber and Morris (1963) was used as a first approach for describing desorption processes on sediments. The mathematical dependence of uptake  $q_t$  of solids on  $t^{1/2}$  is obtained if the desorption process is considered to be influenced by diffusion in the spherical solid and by convective diffusion in the metal solution (Valderrama *et al.* 2010). The fractional approach to equilibrium changes is according to a function of  $(D_t/R^2)^{1/2}$ , where  $R$  is the particle radius and  $D_t$  is the diffusivity of metal within the solid at time,  $t$ . (Senthilkumaar *et al.* 2006).

### Ecological Risk Assessment

To assess the impacts of heavy metals and metalloid in the Jequetepeque basin, the Hakanson's potential ecological risk index (Hakanson 1980; Ye *et al.* 2013) was used. The potential ecological risk index methodology is based on the assumption that the sensitivity of the aquatic system depends on its productivity. The potential ecological risk index was used to assess the degree of heavy metals and metalloid pollution in sediments, based on the toxicity of these trace elements and the response of the environment. The index was calculated using the following equations:

$$C_r^i = \frac{C^i}{C_n^i} \quad (2)$$

$$E_r^i = T_r^i C_r^i \quad (3)$$

$$RI = \sum_{i=1}^n E_r^i \quad (4)$$

where  $C_r^i$ : the pollution coefficient of single metal;  $C^i$ : the measured concentration of the sample (obtained by the pseudo-digestion procedure);  $C_n^i$ : the background concentration of sediments in the study site (obtained from a sampling point considered as a background at the Jequetepeque basin) (Yacoub *et al.* 2014).  $T_r^i$  is the biological toxicity factor of different trace elements (the factors of Cd, As, Ni, Cu, Pb, and Zn were 30, 10, 5, 5, 5, and 1, respectively) (Wang *et al.* 2011; Zhang *et al.* 2012);  $E_r^i$  is the potential ecological risk factor of single metal and RI is the potential ecological risk index of all metals and metalloids present in the sample (Ye *et al.* 2013).

According to Ye *et al.* (2013), the potential ecological risk of sediments posed by heavy metals can be classified into the following categories: low risk ( $E_r^i < 40$ ,  $RI < 135$ ), moderate risk: ( $40 \leq E_r^i < 80$ ,  $135 \leq RI < 265$ ), considerable risk ( $80 \leq E_r^i < 160$ ), high risk ( $160 \leq E_r^i < 320$ ,  $265 \leq RI < 525$ ), and very high risk ( $E_r^i > 320$ ,  $RI > 525$ ).

### **Environmental Assessment of Trace Element Mobility in Sediments**

The potential ecological effect of trace mobility was assessed to estimate the resulting potential harmful effect on the trace elements obtained by EDTA and HNO<sub>3</sub> extractions. For that purpose, a mobility index (MI) was defined accordingly to Eq. (5), similar to the Hakanson ecological risk index (Hakanson 1980; Zhang *et al.* 2010).

$$MI = \sum_{i=1}^n \frac{M_i}{R_i} \quad (5)$$

where  $M_i$  is the trace concentrations in the extracts from the sediment and  $R_i$  is the threshold of this trace element considering a conservative approach.

To estimate the resulting potential harmful effect on the trace elements obtained by EDTA and HNO<sub>3</sub> extractions and considering a conservative approach, the potential ecological effect of trace mobility was evaluated. For that reason, and in view of the lack of local guidelines, the threshold used is the concentration below a probable effect level (PEL) above which adverse effects are expected to occur frequently in the aquatic life from the sediment quality guidelines developed by the Canadian Council of Ministers of the Environment (CCME 2002).

## **RESULTS AND DUSCUSSION**

### **Single Extraction by HNO<sub>3</sub> and EDTA**

Results of pseudo-total concentrations obtained by the MW digestion procedure are shown in Table 1. Aluminum and Fe were significantly more abundant compared to the other trace elements analysed for all the samples. It is well known that they are the most abundant elements in the Earth's crust. Nevertheless, the variations that Al and Fe showed were considerably different depending on the sample; Fe in M1 was more than twice the other trace concentrations obtained, while Al concentration at M4 and M2 was 7- and 5-times greater than the value obtained in M3. The great difference between concentrations depending on the sample perhaps indicates an anthropogenic source.



High Cd, Pb, and Zn values were obtained for M4 and extremely high As and Pb values were reported in M3. Similar values were obtained at sediment samples from Bolivian mine sites (Higuera *et al.* 2004) for As, Cd, and Pb, while similar As and Zn concentrations were obtained from Chilean mine samples (Salvarredy-Aranguren *et al.* 2008).

On the other side, Cu presented considerably high values in almost all the sampling points, being the concentration in M2 between 25 to 50% greater than the other obtained values. Compared with trace metal contents from mine sites in France, Chile, and Bolivia, Cu concentrations in all points are high (Coynel *et al.* 2009; Higuera *et al.* 2004; Salvarredy-Aranguren *et al.* 2008, Yacoub *et al.* 2014). Minimal variations between samples were obtained for Ni concentrations. Then, all the trace elements except Ni are considered a threat of concern in environmental terms; all them showed similar or higher concentrations than those obtained in samples from polluted mine sites.

The risk assessment of mining areas requires an accurate characterisation of the wastes due to the high metal solubility at low pH (Conesa *et al.* 2008). Based on this consideration, the single extraction by HNO<sub>3</sub> was performed under different pH. The higher amount of extracted trace elements was obtained at lower pH values, indicating an ion exchange mechanism between the protons of solution and the sediments. At a pH value of around 1, the maximum amount of these six trace elements was extracted. The extraction was greater for Cu and Zn, with concentrations around 400 mg/kg, than for Pb, As, Cd, or Ni concentrations (around 25, 15, 10, and 5 mg/kg, respectively) at this pH conditions. An increase of pH led to a rapid decrease in trace concentrations, and in fact, concentrations after pH = 4 were less than 5 mg·kg<sup>-1</sup> for most of the trace elements as can be seen in Figure 2.

The results indicate that the highest amounts of trace elements are leached with pH values ≤1, which can be considered as extreme conditions; thus, trace element mobility in sediments was evaluated by the most common treatments, weak acid and strong complexant solutions (Sahuquillo *et al.* 2003). Acid nitric extraction can solubilize metals complexed with organic matter, adsorbed or co-precipitated to oxyhydroxides, carbonated or sulphides (Martinez-Sanchez, *et al.* 2008) and it is a function of pH value (Rigol *et al.* 2009). EDTA is a complexing reagent capable of extracting metals in similar conditions, which means, metals bound to organic matter, carbonate, and Fe and Mn oxides (Gismera *et al.* 2004).

In order to evaluate the leachability of trace elements, the results of HNO<sub>3</sub> extraction at pH = 4, were compared with those of EDTA extraction under similar pH conditions (Table 2). Thus, the EDTA extraction resulted in higher concentrations of leached trace elements than the acid extraction. Furthermore, extraction by EDTA showed extremely higher values of As and Pb than acid nitric extractions (above 30-times greater in most of the samples). Additionally, almost all the samples showed Cu and Zn concentrations higher from EDTA extractions; in most cases values were 4-fold that of the concentration leached by acid treatment.

The trace elements showed different ratios of extraction with respect to the total amount of elements in the sediments as can be seen in Figure 3. For HNO<sub>3</sub> extraction, Cd extraction was around 40% in all sediments, while extractions of Zn and Cu were less than 20%. In general, sediment sampling point M3 resulted in higher ratios. Such difference in leachability could be related to how trace elements are associated with the fractions of the sediments. The Cd with the highest leachability would therefore be released mostly from the oxide-bound fraction, since a large proportion of Cd is associated with oxide fraction; similar results were obtained by Nguyen *et al.* (2010). The low leachability of Pb and (to a lesser extent) Cu can be related to the fact that these metals are capable of forming complexes with organic matter at pH values greater than 3.

The higher EDTA leachability than HNO<sub>3</sub> can be explained through the complexation extraction mechanism that is favoured at pH values around 4-6, while ion exchange, the extraction mechanism of a weak acid is not favoured at this levels of pH (Nguyen *et al.* 2010). In general, sediment sample M4 resulted in greater values by EDTA extraction than other sediments samples. This may be due to the higher amount of organic matter (Table 1) in this sediment, which makes the bioavailability of the trace elements higher compared with other sediments.

### **Kinetic Modelling**

The extraction rate curves for Cu, Zn, and Pb were similar in shape and two regions can be distinguished: a first one for short extraction times, corresponding to faster extraction of trace elements and a second for higher extraction times where the extraction kinetics are slower. The amount of trace elements associated with a short extraction rate is related to the fraction easily extracted, while the second fraction is related to extraction of complexes that requires more time to dissociate (Fangueiro *et al.* 2005).

On the other hand, As, Ni, and Cd observed a lineal behaviour, which indicates that little amounts of trace elements are extracted and only the exchangeable and weakly adsorbed species are released. The same trend was observed for other sediments. The amount of trace element released by the EDTA extraction after 1 hour is relatively significant compared to the total trace elements' content determined by the MW digestion procedure (Table 1) as can be seen in Figure 4. The fraction of most of the trace elements and for all sediment sampling points is below than 20%, except for Zn (M4) and Cu in M2, M3, and M4 and Cd for all samples.

The diffusion equation was used to fit the kinetic curves of EDTA extractions of As, Cd, Cu, Pb, Zn, and Ni in the four sediments studied. The values of  $r^2$  and SEE are presented in Table 3. For the diffusion equation, the mean values of  $r^2$  is greater than 0.94, with most values greater than 0.98; furthermore, the relative error follows the same trend observed for the  $r^2$ . Thus, the diffusion model can properly describe the extraction rate data for these trace elements, as shown in Figure 5. The results obtained indicate that higher diffusion coefficients were obtained for Cu, closely followed by Zn and Pb, while the lowest diffusion coefficients were reported for Cd. It is important to pointing out that Cd extraction after 1 hour by EDTA reached almost 85% of total leached amount of this metal at 24 hours; then, the diffusion coefficients are clearly affected for the metal remaining 15% which is slowly mobilized by EDTA after 1 hour of extraction in four sediments.

### **Ecological Risk Assessment**

Summarized in Table 4 are the calculated values of  $E_r^i$  and RI for trace elements in the sediments from the Jequetepeque basin, northern Peru. Among the six heavy metals and metalloid, Cu presented the highest ecological risk on average, followed by Cd, As, and Pb (in decreased order of potential ecological risk). The  $E_r^i$  values for Cu showed high risk for almost all the samples, while Cd reported very high risk at M4, suggesting high potential of ecological risk. Sampling point M3 reported considerable risk from As, Cd, and Pb, while M1 showed a moderate risk from As and Cd. Arsenic and Pb posed a low risk ( $E_r^i < 40$ ) at other sediment samples, followed by Ni and Zn.

RI values suggested that the four river sediments were at high and very high risk levels ( $265 \leq RI < 525$  and  $RI \geq 525$ , respectively), indicating that the potential of pollution is an issue of concern. Then, RI suggested a very high potential ecological risk in sediments near the Minera

Yanacocha SRL mine site and sediments from the Llapa mine site indicated high ecological risk due to the trace elements concentrations found in the sediment samples.

### **Environmental Assessment of Trace Element Mobility in Sediments**

In Table 5 are summarized the obtained MI values for trace elements in the sediments from the Jequetepeque basin. MI values less than 1 are not considered hazardous while values above suggested a potential concern to the environment.

The MI obtained following the same trend observed by the ecological risk index, considering the concentrations obtained at the HNO<sub>3</sub> and EDTA extractions, suggesting greater environmental risk for sample M4. The EDTA extraction reported higher leaching capacity than for the HNO<sub>3</sub> extractions at the same pH. As discussed before, the pH influence on acidic extraction is also relevant for environmental risk evaluations due to the increase in the leaching capacity at lower pHs (Figure 2). Additionally, pH  $\leq 3$  potentially can be found in environments affected by mining activities. Then, leachability will increase significantly for elements with an intermediate mobility (*e.g.*, Cu and Ni) and especially for fixed elements (*e.g.*, Pb), confirming that an increase in acidity causes a considerable increase in extractability (Sahuquillo *et al.* 2003).

The effect of the concentration and mobility of Cd, Zn, Pb, and As, near mine sites suggested a significant issue for the environment, and as the results obtained from the RI and MI analysis indicated, that sediment sampling points (M3 and M4) near the active mine (Minera Yanacocha SRL) reported greater risk than those (M1 and M2) obtained at the closed mine (Sipán SL). These results are in agreement with previous research developed on sediment samples analysed by BCR sequential extractions and MW digestion procedures, at 16 sites from the Jequetepeque basin monitored between June 2009 and July 2010 (Yacoub *et al.* 2014).

The mobility index was also estimated as a function of time kinetic extractions performed by EDTA procedure. As can be seen in Figure 6, the mobility of trace elements reported the same temporal trend for all the samples, indicating the same behaviour in a possible scenario of trace element release from the sediments to the river. The mobility in sediment sampling points M2 and M3 is greater compared with sampling point M1. It should be pointed out that sampling point M4 reported the highest mobility, which is in agreement with ecological risk index and also with data reported in previous studies at the basin.

It must be mentioned that the release of trace elements in most of the samples occurred after 10 minutes of the extraction (Figure 6). The amount of trace elements released is quite significant as was discussed previously (Figure 4) and it is related with the higher mobility index obtained for sediments M3 and M4. This fact can be correlated with the results reported by Yacoub *et al.* (2013) in which high concentrations of the trace elements were detected and measured in water samples from 2003 to 2010 in several sampling campaigns at the Jequetepeque basin. Concentrations of Cd, Pb, As, and Cu in water were estimated (following the hazard quotient methodology) to be of significant risk to human health and also to the environment at the river basin (Yacoub *et al.* 2013). Then, a potential linkage between these metals and metalloids in sediment and water samples in view of the mobility analysis points out that these trace elements could easily be released from sediments to the water column.

## **CONCLUSIONS**

The extraction experiments indicated that EDTA caused greater mobility of trace elements' acid treatment under similar pH conditions. The acid extraction under lower pH increased the leachability for elements with an intermediate mobility (Cu, Ni), with acidity causing a considerable increase in extractability especially for fixed elements (Pb). The extraction by EDTA extraction showed a higher bioavailability of metals in sediments because of its higher leaching capacity than acidic extraction, which is an important issue in view of risk assessment analysis. The highest extractability was observed for Cd in all sediments, either by acidic or EDTA extraction, with an extraction up to 90% after 1 hour. The parameters obtained by the kinetic model show that the remaining 10% Cd is the slowest to be extracted, requiring 24 hours, followed by Ni, As, Pb, Zn, and Cu. The mobility index analysis indicated that faster kinetic leachability of some trace elements leads to a higher mobility in sediments, especially those near the active gold extraction mine. The ecological risk assessment suggested that the four river sediments were at high and very high risk levels, indicating sediment pollution as an issue of environmental concern.

## **ACKNOWLEDGMENTS**

This research was financially supported by MEC Projects CTM 2012-37215-C02-02 (Spanish Ministry of Education and Science), the Catalan government (project ref

2009SGR905), and the Center for Development Cooperation of UPC. We also thank Ana Maria Cadenato Matia for the thermogravimetry analysis and special thanks to M. Mar Martínez Planas and Regina Isern Rosselló for their contribution in obtaining experimental data

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**Table 1.** Total elements concentration (expressed in  $\text{mg}\cdot\text{kg}^{-1}$ ) determined by the MW digestion and organic matter content for four sediments.

Sediment	Al	As	Cd	Cu	Fe	Ni	Pb	Zn	Organic matter %
M1	37138	234.3	1.3	563.3	70753	16.3	46.1	134.6	6.19
M2	57534	45.4	0.3	861.0	40881	16.8	16.8	197.8	6.30
M3	10743	581.7	1.6	681.1	34660	3.4	1026.0	155.5	4.85
M4	76688	84.5	8.2	393.8	40026	14.1	103.5	376.7	8.72

**Table 2.** Amount of trace elements extracted by  $\text{HNO}_3$  and by EDTA treatment on the four sediments concentration expressed in  $\text{mg}\cdot\text{kg}^{-1}$ .

sediment		As	Cd	Cu	Ni	Pb	Zn
M1	$\text{HNO}_3$	0.04	0.61	39.14	0.88	0.15	19.96
	EDTA	0.50	0.71	152.00	1.88	5.56	43.73
M2	$\text{HNO}_3$	0.10	0.16	82.38	0.67	0.14	27.95
	EDTA	3.17	0.22	328.25	1.70	4.75	42.20
M3	$\text{HNO}_3$	0.77	0.69	215.91	0.97	2.78	40.61
	EDTA	3.86	0.65	258.58	0.46	90.18	39.00
M4	$\text{HNO}_3$	0.12	2.64	8.65	0.82	0.32	91.97
	EDTA	5.39	7.84	273.56	2.62	18.73	200.52

**Table 3.** Coefficient of determination ( $r^2$ ) and relative error (SEE) associated to diffusion model fitting for trace elements extraction by EDTA in four sediments.

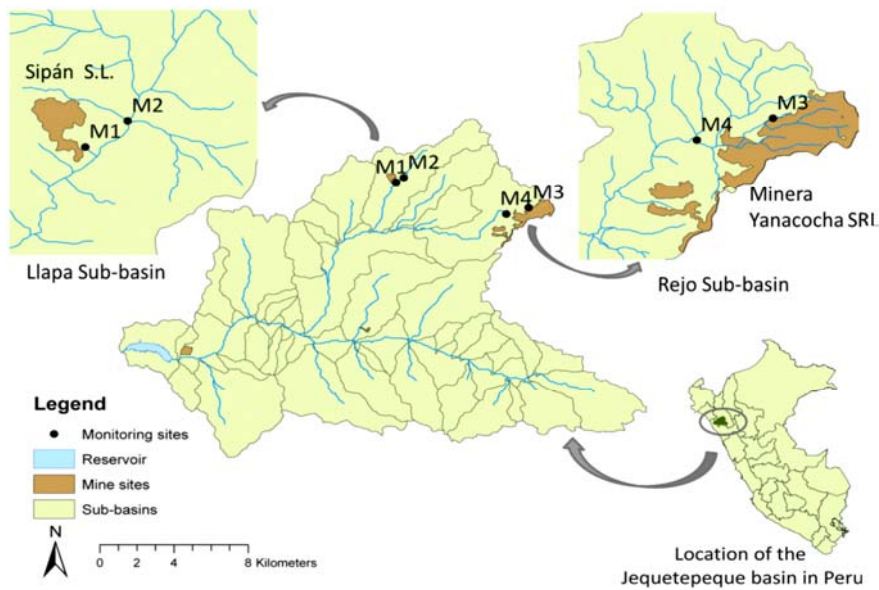
	Sediment	SEE	$r^2$	$D_t$ ( $\text{cm}^2 \cdot \text{s}^{-1}$ )
As	M1	0.04	0.93	$3.74 \times 10^{-7}$
	M2	0.08	0.99	$3.57 \times 10^{-9}$
	M3	0.02	0.98	$1.53 \times 10^{-9}$
	M4	0.06	0.99	$9.86 \times 10^{-9}$
Cd	M1	0.02	0.94	$1.21 \times 10^{-7}$
	M2	0.02	0.80	$5.18 \times 10^{-7}$
	M3	0.02	0.93	$1.58 \times 10^{-7}$
	M4	0.01	0.98	$1.00 \times 10^{-9}$
Cu	M1	0.02	0.99	$2.52 \times 10^{-6}$
	M2	0.02	0.99	$1.07 \times 10^{-5}$
	M3	0.02	0.98	$5.93 \times 10^{-6}$
	M4	0.03	0.95	$3.99 \times 10^{-6}$
Ni	M1	0.19	0.90	$1.27 \times 10^{-9}$
	M2	0.08	0.99	$8.61 \times 10^{-7}$
	M3	0.06	0.99	$7.28 \times 10^{-7}$
	M4	0.03	0.98	$1.15 \times 10^{-9}$
Pb	M1	0.02	0.97	$3.59 \times 10^{-9}$
	M2	0.03	0.97	$2.29 \times 10^{-9}$
	M3	0.04	0.96	$1.10 \times 10^{-6}$
	M4	0.06	0.96	$6.51 \times 10^{-8}$
Zn	M1	0.12	0.94	$8.54 \times 10^{-7}$
	M2	0.08	0.92	$2.79 \times 10^{-7}$
	M3	0.05	0.94	$2.34 \times 10^{-7}$
	M4	0.03	0.98	$4.04 \times 10^{-6}$

**Table 4.** Ecological risk factor ( $E_r^i$ ) and potential risk index (RI) of the Jequetepeque basin sediments estimated from their heavy metal and metalloid contents.

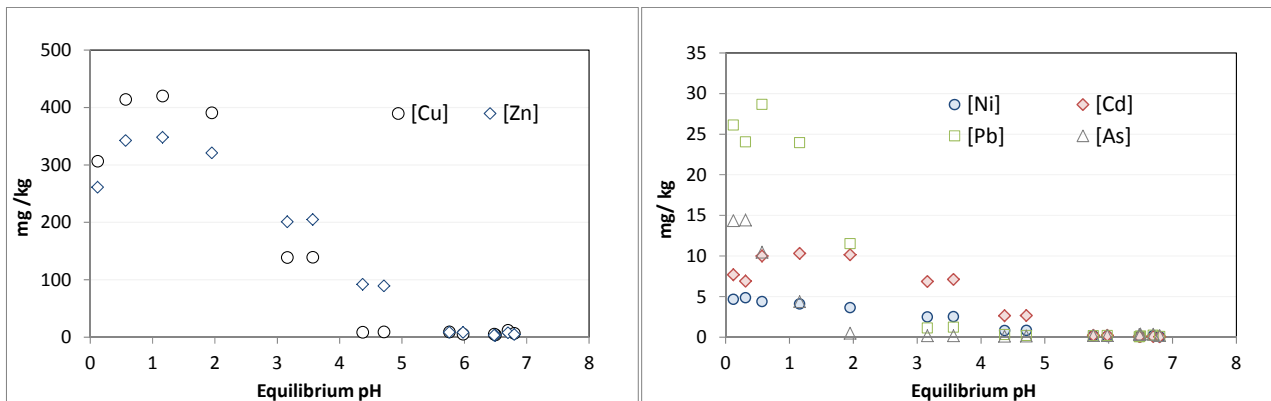
Sediment	As	Cd	Cu	Ni	Pb	Zn	RI
M1	52	75	166	7	6	1	308
M2	10	19	253	8	2	2	294
M3	129	98	200	2	143	2	573
M4	19	491	116	6	14	4	650

**Table 5.** Mobility index (MI) of sediments in Jequetepeque basin estimated from their trace metal contents extracted by EDTA and HNO<sub>3</sub>.

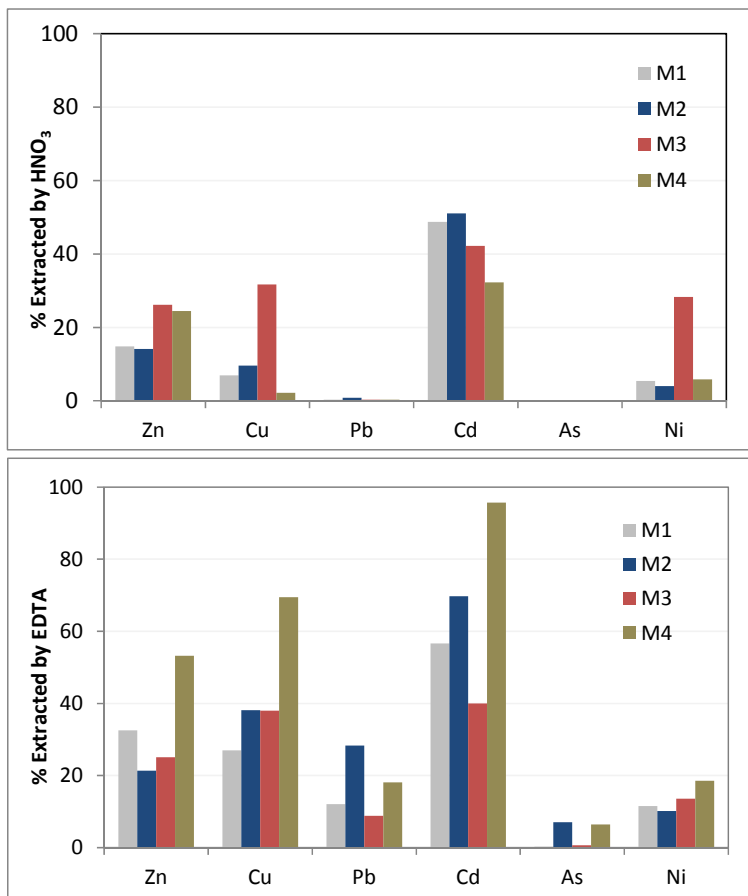
	As	Cd	Cu	Pb	Zn	MI
<b>EDTA</b>						
<b>M1</b>	0.030	0.203	0.77	0.061	0.16	1.3
<b>M2</b>	0.184	0.062	1.66	0.049	0.13	2.1
<b>M3</b>	0.227	0.187	1.31	0.991	0.12	3.1
<b>M4</b>	0.317	2.239	1.39	0.206	0.64	4.8
<b>HNO<sub>3</sub></b>						
<b>M1</b>	0.002	0.174	0.20	0.002	0.06	0.5
<b>M2</b>	0.006	0.047	0.42	0.002	0.09	0.6
<b>M3</b>	0.045	0.198	1.10	0.030	0.13	1.5
<b>M4</b>	0.007	0.755	0.04	0.004	0.29	1.1



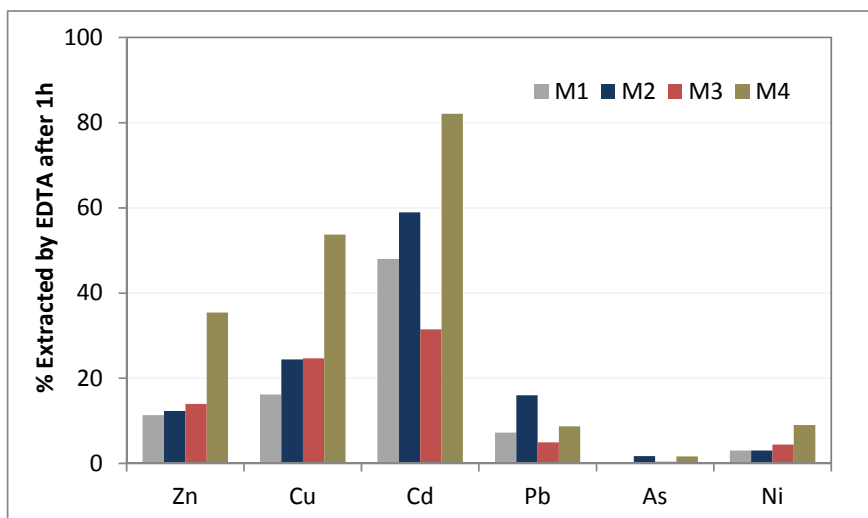
**Figure 1.** Map of the four monitoring sites at the Jequetepeque basin (Perú).



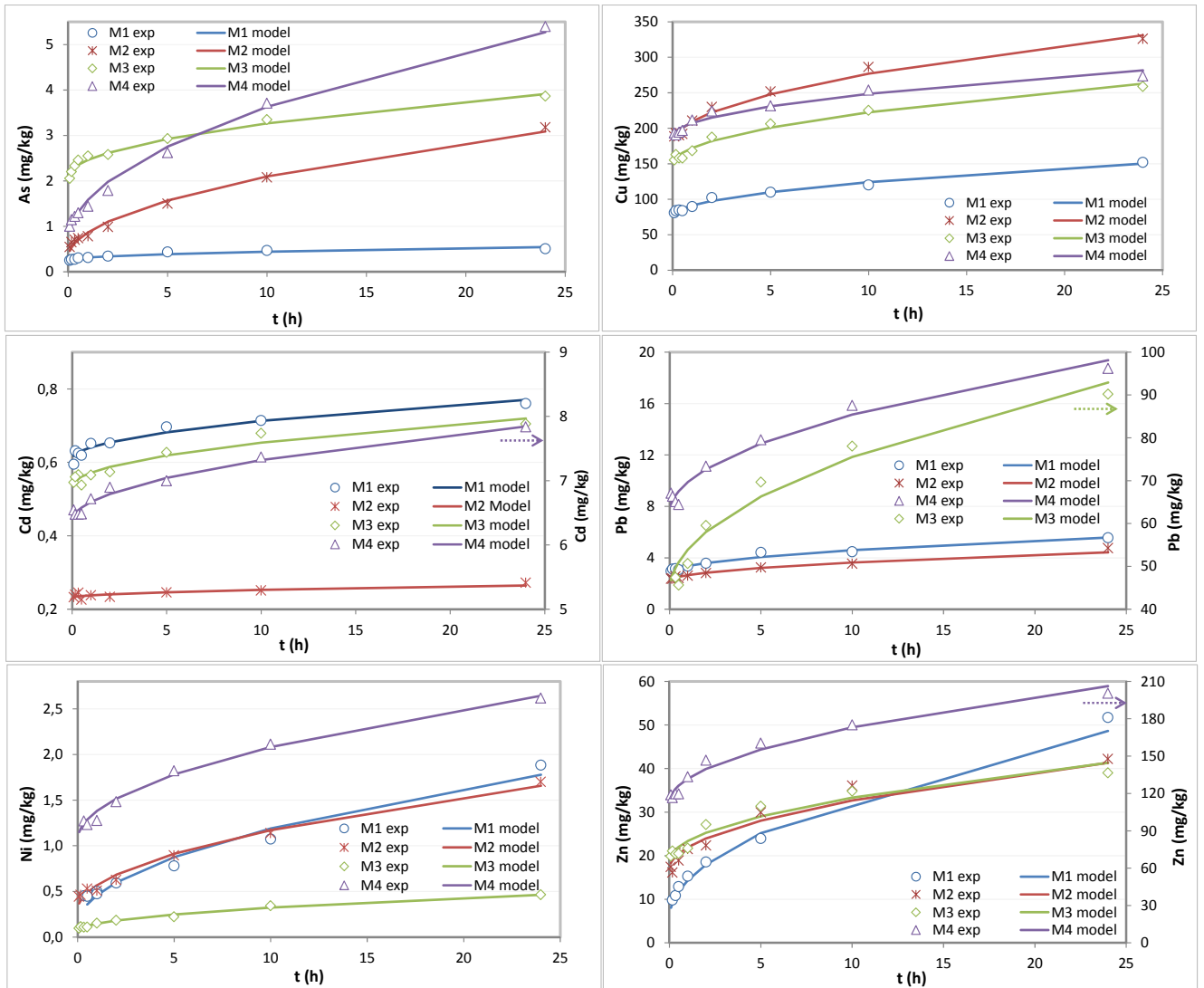
**Figure 2.** Influence of pH in trace elements extraction of Cu, Zn, Ni, Cd, Pb, and As from sampling point M4. Concentration expressed in  $\text{mg} \cdot \text{kg}^{-1}$ .



**Figure 3.** Ratio of trace elements leachability of four sediments sampling points after HNO<sub>3</sub> and EDTA extraction.

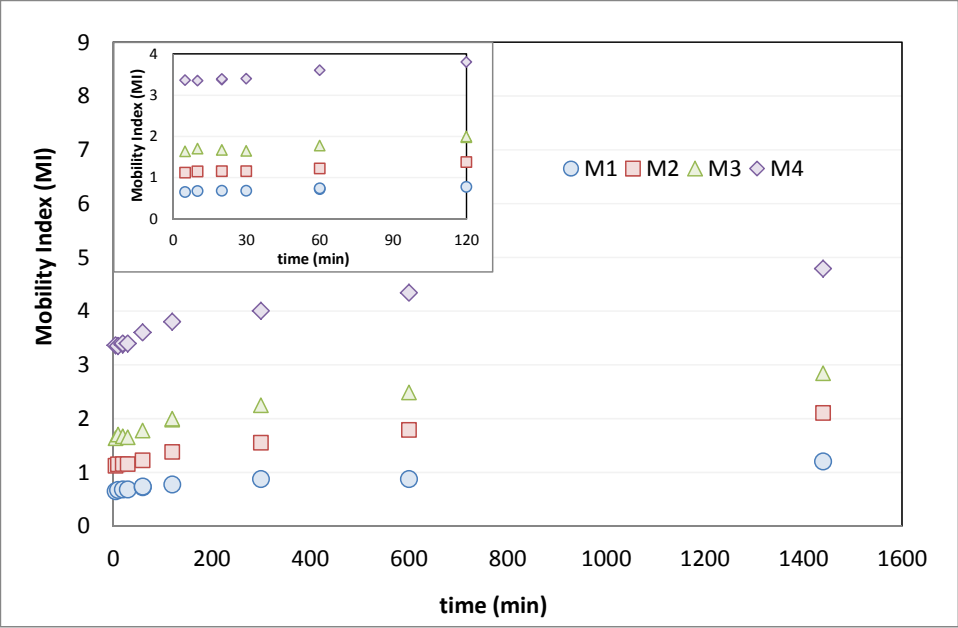


**Figure 4.** Fraction of trace elements extracted by EDTA (1 h) considering the  $Q_{\text{tot}}$  = total content of trace elements obtained in MW digestion procedure.



**Figure 5.** Experimental and fitted extraction rate data of As, Cd, Ni, Cu, Pb and Zn from four sediments by the diffusion model.





**Figure 6.** Mobility index of the Jequetepeque basin sediments estimated from kinetic extraction of trace elements content.