RESEARCH ARTICLE

Impacts on effluent contaminants from mine sites: risk assessment, fate, and distribution of pollution at basin scale

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Abstract The environmental implications of mining activities are of worldwide concern. An environmental evaluation at the basin level was conducted because of widespread mining in Cajamarca in Northern Peru. A sediment monitoring program was developed at the Jequetepeque basin, located in Cajamarca. A total of 16 sites were monitored at three different times between June 2009 and July 2010, and a total of 42 samples were collected. All samples were analyzed by microwave digestion and by a sequential extraction scheme following the three-stage European Community Bureau of Reference (three-stage BCR) protocol. Trace element mobilization from the sediments to the water column was assessed by the risk assessment code (RAC). Spatial and temporal distribution of trace elements was evaluated by principal component analysis and hierarchical cluster analysis. Cd, Zn, As, and Pb showed the highest concentrations independent of season. Notably, Cu concentration and mobility increased during the wet season for all samples. Additionally, Hg concentration and mobility increased during the wet season near the mine sites. According to the enrichment factor, the highest enrichments of Cd, Zn, Pb, and As were related to mine runoff. The effect of trace elements near the mine sites at the Jequetepeque basin was considered a significant threat to the environment due to Cd, Zn, Pb, and As, and the concentrations of Cu and Hg were also considered a concern. This work establishes a baseline for the environmental quality status of the Jequetepeque basin that may support water quality management in Peru.

Introduction

Environmental efforts in the Andean region need to focus on water quality management and evaluation of impacts and pressures on the aquatic ecosystem due to mining activities. The environmental plans and measures for efficient water quality management need an assessment of the pollution and periodic evaluation of the ecosystems (Barrios 2006; Borja 2005). Local, regional, and state administrations and local stakeholders (civil society organizations, indigenous, professionals, ONGs, etc.) have to be involved in these plans and measures and work together to resolve the socio-environmental conflicts of mining activities. For this purpose, knowledge of the water quality status related to current mining pressures and impacts is essential.

The European Water Framework Directive (WFD; European Commission 2000) was widely recognized as innovative (Sigel et al. 2010) for the protection, improvement, and sustainable use of the water environment. The core of the directive focuses on the environmental objective of good status, long-term perspective, and integrated water resources management. The WFD precipitated a fundamental change in

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management objectives from only pollution control to ensuring ecosystem integrity as a whole (Hering et al. 2010).

Polluted sediments from mining activities impact river water quality because they prolong the residence time of pollutants at the basin scale. The continuous exchange between sediment and water during settlement and re-suspension phases of contaminated particles during transport has potential to impact downstream regions (Förtsner and Salomons 2010). Therefore, the risk of bound contaminants being spread within the river basin, e.g., during situations of high water discharge, is growing because of increasing amount of sediment trapped in the basin (Förstner and Müller 1973; Chen and Liu 2006; Cánovas et al. 2008).

Sediment monitoring was conducted in this work to identify the water bodies at risk and to enable measures that improve the quality of water bodies. A total of 16 sites along the Jequetepeque basin were monitored in June and November 2009 and July 2010 following the criteria and considerations of a previous study (Yacoub et al. 2012). The grade of pollution of different substances, the sources of contamination, and the potential effect of the trace elements were determined by comparing obtained data to the regional background levels and to levels obtained in other environments affected by mining (Borja et al. 2004) and by the enrichment factor indicator (Chen et al. 2008; Idris 2008; Kartal et al. 2006; Luo et al. 2012; Reimann et al. 2005).

The mobilization of trace elements and their bioavailability gives valuable information for risk assessment by providing details on the distribution or partitioning of trace elements in soils and sediments. The modified three-stage European Community Bureau of Reference extraction procedure (three-stage BCR) is a useful predictor for the short- and long-term mobility of trace elements in contaminated sediments (Pérez-López et al. 2008; Oyeyiola et al. 2011). Therefore, the three-stage BCR protocol was applied in this study to assess the availability, mobility, or persistence of trace elements (Pérez and Valiente 2005; Kartal et al. 2006; Arain et al. 2008; Pérez-López et al. 2008).

The modified three-stage BCR extraction procedure was developed and applied to evaluate the environmental implications of trace element mobilization from the sediments to the water column (further details are available in the "Electronic supplementary material", sub-section S1). The spatial and temporal distribution of trace elements along the basin was also assessed to evaluate the risk of pollution at the basin for middle- to long-term periods. This analysis was developed by obtaining values of trace elements at sampling points and sample partitioning.

The purpose of this study was to evaluate the environmental impact of mining activities in terms of the pollution at the basin level. The enrichment factor (EF) was calculated as a geochemical index to determine polluted sites and to estimate the impact of anthropogenic activities (Chen et al. 2008; Idris

2008; Kartal et al. 2006; Luo et al. 2012; Reimann et al. 2005). The risk assessment code (RAC) was also used to estimate the grade of environmental risk associated to trace elements bound to exchangeable and carbonate fractions that can be easily released to the water column (Andrade et al. 2010; Canuto et al. 2013; Ghrefat and Yusuf 2006; Jain 2004). These approaches reported information about trace element patterns along the basin and their environmental implications, thus establishing their spatial and temporal distribution.

The spatial and temporal distribution from the developed methodology and the statistical analysis were reported in this work (shown in Fig. 1). Principal component analysis and hierarchical cluster analysis were carried out as statistical analyses (reported in the "Electronic supplementary material", sub-section 7). The trace element concentrations from the analytical methods were included in the statistical analysis. The same results were obtained by both the spatial and temporal distribution assessment methodologies, emphasizing the pollution trends at the basin.

Methods

Site characteristics

Natural erosion and mining are the possible major sources of trace metal pollution of the site. Furthermore, considering the hydrological dynamics of the basin, the areas selected were placed at the nearest points to the mine sites, at the upper part of the basin, and at the middle part of the basin, where the river flows into the reservoir. Three study areas from the Jequetepeque river basin located in Northern Peru were evaluated in three sub-basins: Llapa, Rejo, and Alto Jequetepeque. A total of 16 monitoring sites were established during three campaigns, and 42 samples were collected on the basis of criteria defined in a previous study (Yacoub et al. 2012). That previous study has been developed in November 2008, and this work complemented it with three consecutive campaigns since then. Two campaigns were developed in the dry season (June 2009 and July 2010) and one campaign at the beginning of the wet season (November 2009).

The Ll samples were located in the Llapa sub-basin, near the Sipán SL Mine; the R samples were from the Rejo sub-basin, close to the Minera Yanacocha SRL Mine; and the T samples were either before or after the reservoir at the Alto Jequetepeque sub-basin. Gold extraction was performed with cyanide leaching from both mines. Yanacocha SRL Mine has been active since 1993, whereas Sipán SL Mine was closed in 2005. Ll samples are near perennial pastures, while R samples are near reforested forests and T samples are in the river bank.

All of the sites from the upper part of the basin presented the same climatic and hydrologic characteristics (Yacoub and Foguet 2013). Their soils are Andosols (tertiary soils with the

Fig. 1 Scheme of the analysis performed in the present study. It shows the relation between the analytical procedures, the environmental indicators developed, the spatial and temporal distribution analyzed, and the statistical analysis performed
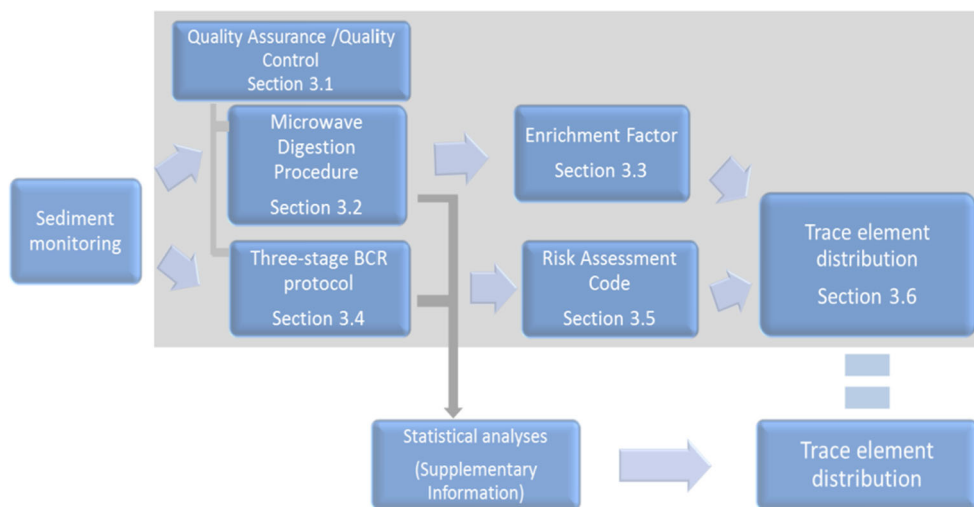
same stratigraphic unit), while the T sample soils is Miscellaneous Bank. Samples collected from the R3 monitoring site were considered unaffected by the mine because of its location (Fig. 2). Considering also the similarities on soil, ecology, and climatology between samples from the upper part of the basin, R3 was considered a background sampling point.

Sample collection

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 sub-samples 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 was achieved and sieved to obtain two particle sizes (ISO 5725-1:1994). The coarse particle size ranged between 1 and 0.5 mm and was used to determine enrichment factor. The fine size had a particle size of <63 μm (UNE Standard 7050) and retained most of the trace elements (Butler 2011; Margí et al. 2004; Prudencio et al. 2007; Varejao et al. 2009). This

Fig. 2 Map of the Jequetepeque basin in Peru. Monitoring points cited for each sub-basin. Monitoring points and sub-basins placed at the basin
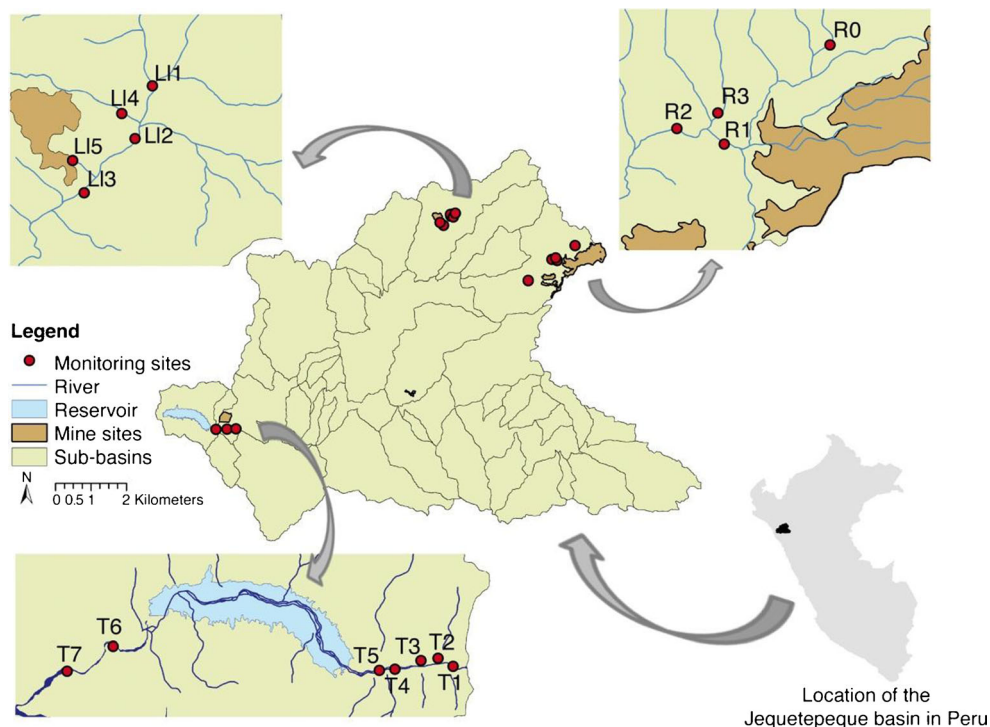
particle size was used for microwave digestion and BCR procedures. Dried samples were stored in polyethylene bottles.

Analytical methods

Microwave digestion

A microwave oven (Berghoff MWS-2) with a capacity of ten poly-tetra-fluoro-ethylene 60-ml vessels and a power of 1,350 W was used following USEPA Method 3052. To 0.5 g sediment sample, 9 ml of HNO_3 and 3 ml of HCl were added and digested for 30 min as shown in the "Electronic supplementary material" (Table S1.1). The final solution was filtered through 0.45-µm cellulose acetate membrane filters and stored in polyethylene bottles at 4 °C until analysis.

Sequential extraction

A sequential extraction scheme proposed by the European Community Bureau of Reference (BCR) (Ure et al. 1993) was used because of the geomorphological characterization with Mn and Fe hydro-oxy-oxides and the low organic matter content associated with volcanic soils in the study area. The modified three-stage BCR extraction procedure was used to predict the short- and long-term mobility of trace elements in contaminated sediments (Pérez-López et al. 2008; Oyeyiola et al. 2011; Guevara-Riba et al. 2004; Margí et al. 2004; Gismera et al. 2004; Sahuquillo et al. 1999; Ure et al. 1993). Further details are available in the "Electronic supplementary material" (Table S1.2). The final solution obtained was filtered through 0.45-µm cellulose acetate membrane filters and stored in polyethylene bottles at 4 °C until analysis.

Determination of trace element concentrations

Trace element concentrations in the extracted and digested samples were determined using inductively coupled plasma mass spectrometry and optical emission spectrometry (ICP–MS model Elan 6000 and ICP-OES Perkin Elmermodel Optima 3200RL).

A standard reference material, CRM 320R, was used for the quality control of the analytical data, quantifying the recovery of the analyte spikes due to the extractants obtained from the BCR procedure. Additionally, 25 % of the samples were replicated, giving a standard deviation of less than 9 %.

Enrichment factor determination

The purpose of determining the EF is to identify the trace metal origin by distinguishing the anthropogenic source from natural inputs and quantifying the impact of anthropogenic contributions (Chen et al. 2008; Idris 2008; Kartal et al. 2006;

Luo et al. 2012; Reimann et al. 2005). This factor is a geochemical approach based on the assumption of the linear relationship between a reference element and the other elements of interest under natural sedimentation conditions and identifying and quantifying human intervention on the natural cycle of the elements (Reimann et al. 2005). The EFs were calculated according to the following equation:

$$EF = \frac{(C_M/C_{RE})sample}{(C_M/C_{RE})reference\ material} \qquad (1)$$

where the numerator is the ratio of the concentration of the element being determined, C_M, to that of the reference element, C_{RE}, in the sediment sample, whereas the denominator is the same ratio but in the reference material. The reference element should have the same matrix as the samples and should be free of trace metal pollution.

In this study, the EF was calculated with the concentrations obtained by the MW digestion procedure. Fe was chosen as the reference element based on the homogenized data related to the sediment matrix of all samples, which are a silicate matrix, and the findings in the literature (Deely and Fergusson 1994; Idris 2008; Kartal et al. 2006). Additionally, the concentration of the reference element in the coarse particle size (between 0.5 and 1 mm) was used because it is considered to be free from anthropogenic pollution (Idris 2008). For the same reason, the reference material used was determined from the concentrations of the coarse particle size. Specifically, the reference material chosen was the mean concentration from the R3 monitoring site. As described before, the monitoring site was located at the upper part of the basin and was isolated from any productive activity. Because of that, the site was considered a better reference material than the earth's crust, and the enrichment factor related to the variability of the rocks' composition, the natural fragmentation in the sampling site, and the differences between the analytical methods used can be avoided (Reimann et al. 2005; Reimann and de Caritat 2005).

Environmental implications and risk assessment

The BCR was used to evaluate the environmental implications of trace elements present in sediments. Because the elements are presented in different bounded phases, the risk should be evaluated for each cumulative step of the BCR. First, the three fractions of the BCR were summarized as potential threats to the environment. Then, a risk assessment was performed according to the Risk Assessment Code (RAC). RAC was obtained by dividing the amount of element in exchangeable phase by the total amount of the element (Andrade et al. 2010; Canuto et al. 2013; Ghrefat and Yusuf 2006; Jain 2004):

$$RAC = \frac{C_{exchangeable\ phase}}{C_{pseudo-total\ digestion}} \qquad (2)$$

where $C_{exchangeable}$ and $C_{pseudo-total}$ are the metal concentration in the exchangeable phase and in the pseudo-total content of the trace element in the sample, respectively.

Statistical methods

First, data treatment was carried out to maximize the data and to minimize error. The data were checked for gaps and statistical outliers prior to statistical analysis. The detection limit was used as a threshold value for the results below the detection limits (Bengraine and Marhaba 2003), and a decimal logarithmic transformation was used to improve the statistical analysis. The kurtosis and skewness statistics indicated that the transformed variables were closer to a normal distribution than the original variables for almost all analytes.

The data determined for each phase were processed using multivariate statistical analysis by SPSS v15.0 software package. Principal component analysis (PCA) was performed to ascertain the spatial and temporal trends of the elements in the basin. Additionally, hierarchical cluster analysis (HCA) was developed to facilitate the interpretation of the data related to the sampling sites. The Varimax normalized algorithm was used for the rotation of principal components, PCA, which facilitates interpretation of the principal component by maximizing the variance of the extracted factors and reducing the uncertainties of initial unrotated factor loading. HCA was applied using Ward's method of agglomeration and squared Euclidean distance as the measurement of similarity (Yacoub et al. 2012).

Results

Method efficiency

The efficiency of the digestion procedure was considered acceptable when obtained recoveries varied between 70 and 130 % (Kartal et al. 2006; Martínez2008). The recoveries for all trace metals analyzed by MW digestion are shown in the "Electronic supplementary material" (Table S2.1). Since all values were reported within this range, the results were considered valid, except for Cr which had only 61 % recovery. Low recoveries for Cr could be due to difficulties in the total release of the Cr present in the sample, mainly related to alumino-silicates and to the slow kinetics of the Cr.

It has to be noted that the literature does not give any values for the three-stage BCR extraction procedure performed for CRM 320R. To obtain data at the extraction procedure, three samples of CRM 320R were included in the analysis. Except for Cu at the exchangeable phase and for Ni and Cd at the oxidizable phase, acceptable results were achieved based on standard deviation and cumulative variance obtained for each

trace element (Table S2.2 in the "Electronic supplementary material").

Total element concentration

The pseudo-total trace element contents of all samples collected along the basin and analyzed by MW digestion are shown in the "Electronic supplementary material", subsection S3. The results are means of three samples and standard deviations.

Al and Fe were present in abundance (40,399 and 36,135 mg/kg on average, respectively) compared to the other elements. Ni and Cr concentrations showed minimal variations between samples from Jequetepeque basin (see Table S3.1 in the "Electronic supplementary material"). The concentration of Cr was significantly lower than the concentrations found in the literature (Coynel et al. 2009; Goldhaber et al. 2009; Medici et al. 2011). However, the concentration of Ni was within the range found in the literature (Coynel et al. 2009; Goldhaber et al. 2009; Medici et al. 2011).

Pb concentration, with an average of approximately 64 mg/kg, fluctuated notably between 13.6 and 1,026 mg/kg. Similar concentrations of metals were obtained in the Bolivian mine sites, with slightly higher mean concentrations (Salvarredy-Aranguren et al. 2008). In contrast, higher mean values were obtained in this study than those from anthropogenic impacted areas (Goldhaber et al. 2009; Medici et al. 2011).

The higher variations obtained for As and Hg, from 5.4 to 581.7 mg/kg and from 0.5 to 11.4 mg/kg, respectively, were, to a large extent, greater than the findings in the Bolivian and Chilean mine sites (Higueras et al. 2004; Salvarredy-Aranguren et al. 2008) and similar to the values obtained in a basin affected by a mine in France (Coynel et al. 2009).

Cu ranged from 10.7 to 861 mg/kg, with an average value of 189 mg/kg. This concentration was considerably high compared with the values obtained from the mine sites in France, Chile, and Bolivia (Coynel et al. 2009; Higueras et al. 2004; Salvarredy-Aranguren et al. 2008).

Zn varied between 64.5 to 547.3 mg/kg, with an average value of 145.4 mg/kg. Similar average values were found in sediments near the Chileanmine sites (Higueras et al. 2004), whereas the values obtained in this study were significantly lower than the values obtained near the mine sites in Bolivia (Salvarredy-Aranguren et al. 2008).

The Cd contents of sediment samples ranged from 0.2 to 11.4 mg/kg, with an average value of 1.5 mg/kg. The mean concentration was in agreement with findings in the literature, showing similar mean concentrations in areas affected by the anthropogenic activities as metal working industries, handicraft factories, and engineering and chemical industries in Italy, and mining in Bolivia and France (Coynel et al. 2009; Medici et al. 2011; Salvarredy-Aranguren et al. 2008).

However, it should be noted that the highest values of Cd reported in the literature were higher than those obtained in this study. On the other hand, average values and higher concentrations are similar than obtained for Cd in California due to mining (Goldhaber et al. 2009).

As a preliminary study carried out in the upper parts of the Jequetepeque basin in November 2008 (Yacoub et al. 2012) has shown, the concentration of trace elements was within the range of those reported in this work, where Ll5 and R1 were the most polluted monitoring sites for As, Cd, Cu, Hg, Pb, and Zn. These trace elements reported exposure on the aquatic life to toxicity, following the Canadian Guidelines (CCME 2002; Burton 2002).

Origin of trace elements

The calculated EF values were used to assess the origin of the trace elements from sediment samples. A total of 12 sites were evaluated from the first sampling conducted in June 2009 from the three sub-basins (Ll1-Ll5, R1-R3, and T1-T4) of the Jequetepeque basin (Fig. 2). Once the EF was calculated, the pollution grade of the monitoring sites was defined by using the scale shown in Table S4.1 of the "Electronic supplementary material" (Cáceres-Choque et al. 2013; Kartal et al. 2006; Sutherland 2000).

The results indicated that Cd enrichment values were the highest in all samples from the Jequetepeque basin (Table 1). The highest enrichment Cd value was found in the Rejo sub-basin as very high enrichment and significant values were also determined at the R1 and R2 (downstream of R1) monitoring sites, respectively. Additionally, all the T samples showed significant enrichment values. In the Llapa sub-basin,

Table 1 Enrichment factors obtained for all trace elements in all sites monitored at the Jequetepeque basin

	Al	As	Cd	Cr	Cu	Fe	Ni	Pb	Zn
Ll1	2.0	0.4	1.2	1.7	0.6	1.2	1.0	1.0	1.1
Ll2	1.9	0.4	1.6	1.5	0.8	1.1	1.0	1.0	1.3
Ll3	1.5	1.9	**7.0**	1.9	1.5	1.3	1.6	1.3	2.0
Ll4	1.4	1.8	1.3	1.3	*3.1*	1.0	1.0	1.0	1.7
Ll5	0.6	**6.2**	*3.5*	0.7	1.7	1.2	1.0	1.9	0.9
R1	1.2	*4.5*	***39.4***	1.9	2.2	0.8	2.1	**14.1**	*4.0*
R2	1.9	2.5	**7.5**	2.0	1.1	1.3	2.1	*3.5*	1.7
R3	1.8	2.7	2.9	1.8	1.0	1.3	1.9	*3.3*	1.5
T1	1.6	1.4	**6.2**	2.9	1.0	1.2	1.8	2.3	1.8
T2	1.1	1.2	**6.0**	1.8	0.5	1.0	0.9	2.1	1.6
T3	1.1	1.1	**5.2**	1.9	0.8	1.0	1.0	2.0	1.5
T4	1.2	1.3	**6.2**	2.1	0.8	1.1	1.5	2.3	1.6

Upright values are associated to minimal enrichments, italicized values to moderate enrichments, bold values to significant enrichments, and the bold italicized value to high enrichment

significant enrichments were found for the Cd in Ll3 and for As in Ll5, and moderate enrichments were obtained in Ll5 for Cd, suggesting that the presence of As and Cd at these points is due to anthropogenic activities.

The Pb concentrations also showed moderate enrichment values in R1 and decreased approximately four times the enrichment in R1 for the other R samples, suggesting that the moderate Pb enrichment values found in R1 were mainly due to mining activities. Additionally, moderate enrichment values were detected for As and Zn at R1. The highest enrichment values of Cd, Cu, Ni, Pb, and Zn were obtained at this site, indicating severe pollution. Taking into account the location of the samples and the determined EF values, the anthropogenic source for Cd, Pb, and Zn was the mining activities at the Yanacocha Mine. Furthermore, As and Cu enrichments were higher near the Sipán Mine, suggesting it to be the main pollution source in the Jequetepeque basin. The EF values for Al, Fe, Cr, and Ni showed deficiency to minimal enrichments; therefore, these concentrations were associated to a greater extent to depleted sediments. It has to be mentioned that there is a lack of agreement in the literature about the significance of EF close to 1. In this case, we consider that the approximations done in the EF (relative to the reference element and material) are consistent enough to consider it as indicative of geogenic or natural origin (Luo et al. 2012; Villalobos-Castañeda et al. 2010).

Trace element partitioning

The relative percentages of trace element partitioning with respect to the pseudo-total concentration at the monitoring points in the Jequetepeque basin are shown in Fig. 3. The residual fraction was calculated as the difference between the sum of the three-stage BCR steps and the pseudo-total concentration of the digestion procedure (Butler 2011; Luo et al. 2012; Martínez 2008; Mester 1998; Oyeyiola et al. 2011).

Cr and Ni were mainly in the residual fraction, accounting for 81 and 63 % of the total content, respectively. Thus, Cr and Ni were mainly bounded to the oxidizable fraction and to a lesser extent to the reducible and exchangeable phases. In the R0 sample, the oxidizable fraction was 43.4 and 99 % for the Cr and Ni, respectively. Similar values were observed in sediments from Po River, one of the most polluted basins in Italy (Malferrari et al. 2009), and for Ni in polluted Spanish mine (Galán et al. 2003).

The As residual fraction varied from 76 to 99 % from the total amount. The remaining concentrations were mainly in the reducible fraction. As observed in Fig. 3, the sum of the three extractable fractions was higher in samples collected far away from the mine sites, especially in samples from the alto Jequetepeque sub-basin (T samples) (see Fig. S5.2 in the "Electronic supplementary material"). Similar As levels were found in polluted sediments from India (Routh and Hjelmquist
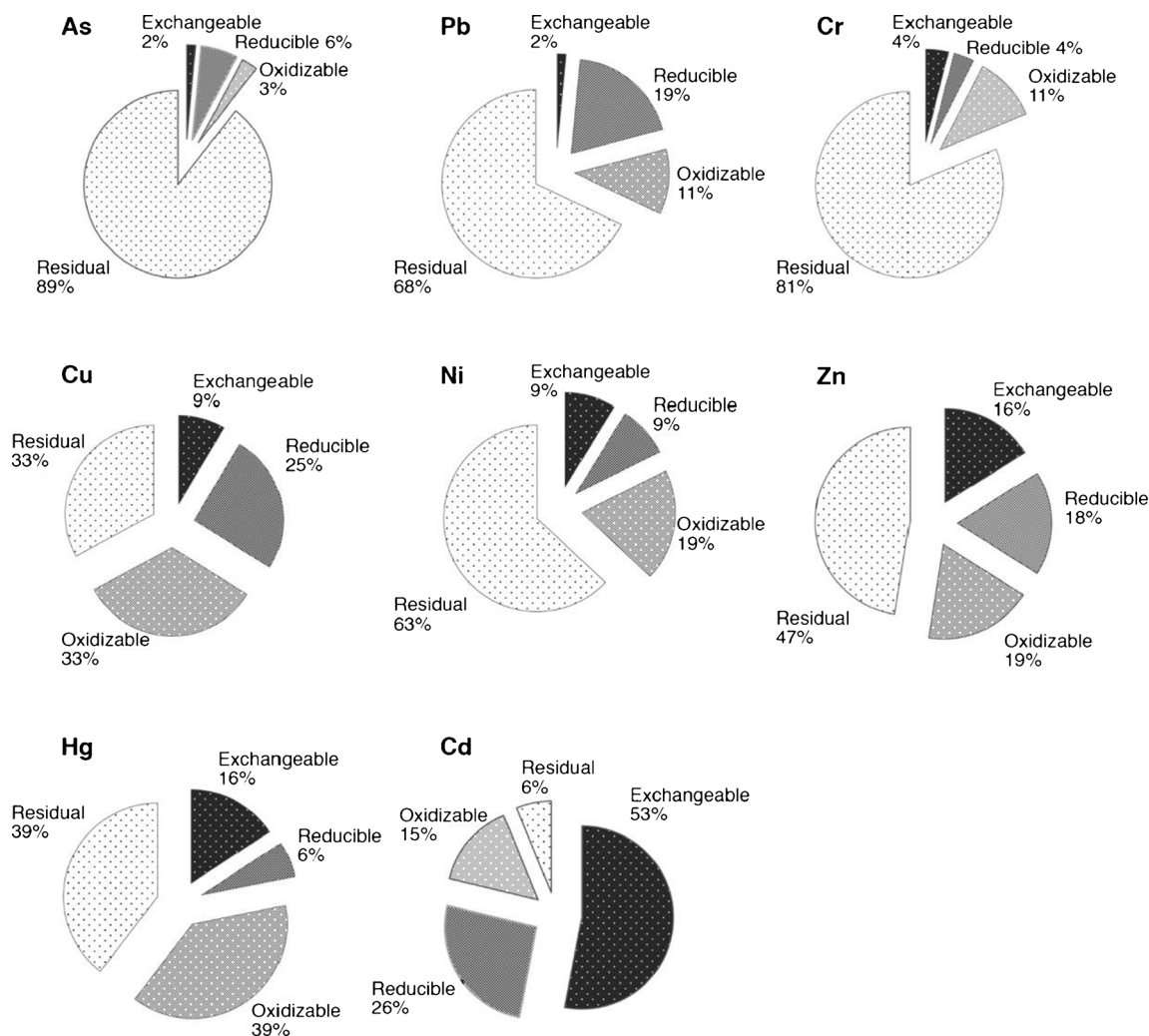
Fig. 3 Percentages of each phase of the three-stage BCR (exchangeable, reducible, oxidizable, and residual) obtained for all trace elements. They are presented as the average values of all the 42 samples monitored for each trace element

2011) and in rivers from Kosovo that were impacted by mines (Nannoni et al. 2011).

The Pb partitioning illustrated the same pattern as the one obtained for As (Fig. 3) from these places (shown in Figs. S5.2 and S5.9 in the "Electronic supplementary material"). This trend was also observed in mining areas in Kosovo (Nanoni et al. 2011), and comparable percentages were also found in a contaminated basin in Italy (Malferrari et al. 2009).

The fractionation of Hg in surface sediments showed a wide range of variation (Fig. S5.7 in the "Electronic supplementary material"). The residual and oxidizable phases were on average 39 % of the total amount, whereas the exchangeable phase accounted for 16 % and the reducible phase for 6 % of the total.

The partitioning of Cu was higher in the mobile than in the residual fraction (Fig. 3). The values for Cu in the mobile fractions ranged widely depending on the source of sediment. The oxidizable and residual fractions varied from 1 to 99 %,

whereas the exchangeable fraction ranged from 0 to 24 %. A high heterogeneity has been reported for Cu partitioning by other investigators (Galán et al. 2003; Passos et al. 2010).

Almost half of the concentration of Zn was in the residual phase, and the rest was in the mobile fractions in proportions of 19 % in the oxidizable phase, 18 % in the reducible phase, and 16 % in the exchangeable phase. The exchangeable phase was higher in R1 samples, suggesting an anthropogenic source (Fig. S5.10 in the "Electronic supplementary material"). This is in agreement with the results obtained in sediments from the Po River in Italy (Malferrari et al. 2009).

The highest mobility was mainly in the exchangeable phase for Cd (53 % on average), ranging from 34 to 72 % depending on source of sample. The fractionation profile of Cd was as follows: exchangeable (53 %)>> reducible (26 %)>oxidizable (15 %)>residual (6 %). Similar trends were found for Cd in street sediments from Turkey, in sediments affected by mining areas from Spain,

and in polluted Italian rivers (Kartal et al. 2006; Margui et al.2004; Malferrari et al. 2009; Mediciet al. 2011).

Environmental implications

The first three extracted sediment phases represent bioavailable fraction that may be released to the water column depending on environmental conditions. The pollution observed due to element partitioning in the Jequetepeque sediment samples was evaluated using a conservative approach to assess its environmental impacts. The order of mobility from sediments to water column was as follows: Cd (94 %) >>Cu (67 %)>Hg (61 %)>Zn (53 %) >>Ni (37 %)>Pb (32 %) >> Cr (19 %)>Fe (12 %)>As (11 %)>Al (10 %). The mobility of Cd, Cu, Hg, and Zn was a serious concern for the environment at almost all monitoring sites of the basin.

Because the exchangeable phase is a weakly bounded phase, making it easier to release the trace elements to the water column, the RAC value was considered in the evaluation. The RAC evaluates the potential risk of trace elements in the environment by using the criteria described in Table S6.1 of the "Electronic supplementary material" (Andrade et al. 2010; Canuto et al. 2013; Ghrefat and Yusuf 2006; Jain 2004; Villalobos-Castañeda et al. 2010).

According to Fig. 4, RAC showed a very high risk for Cd in samples from Ll4, Ll5, R1, and R2 monitoring sites, which are the closest to the mine sites (Sipán SL and Yanacocha SRL). Samples from R1 were also risky to the environment because of high concentration of Zn and Cu especially those taken during the wet season. Further details are available in sub-section S6 of the "Electronic supplementary material".

Furthermore, Hg was also present at very high concentration in samples taken during wet season in R3 and during dry season in R2 and T1. The potential release of these elements to the environment from these locations at different seasons

suggests that some of the contamination might be of anthropogenic origin. Further details are available in the "Electronic supplementary material" in S6.

Sediments always act as reservoir for metals; their potential risk of pollution to the environment must be considered. Additionally, there is presence of extremely acidic pH in some of the river monitoring sites (with pH close to 1.5). Therefore, the trace elements bound to the second fraction of the three-stage BCR protocol were also considered as an aspect of concern and its associated risk evaluated. Then, Cd and Zn increased the environmental risk for most of the samples, whereas the risk for Hg was the same than from RAC assessment.

It should be noted that Cu concentrations also increased in concentration significantly in the reducible phase during the wet season in Ll1, R3, T1, T3, and T5 monitoring sites. Similar trends were observed for Pb, where samples taken during the dry season showed high concentrations in this phase, being an aspect of environmental concern in the Alto Jequetepeque basin (T monitoring sites). The effect of the reducible phase on the environment was noticeable for Cu during the wet season and Pb during the dry season. This behavior was also reported in an Italian basin characterized by metal working industries and handicraft factories (Medici et al. 2011).

Spatial and temporal distribution of trace elements along the basin

Figure 5 shows the findings of this study by taking into account the values of the sample partitioning and distribution along the basin.

The same trend was observed for Cd and Zn at all monitored sites for the three-stage BCR and pseudo-total concentration procedures. The trend suggested that there was one source for these elements, as indicated by the enrichment factor, especially for the R1 sample. Thus, both species were the most mobile elements, and consequently, the risk associated with them is considered as very high as the RAC code suggested. Therefore, the presence and mobility of Cd and Zn due to mining activities are considered as a significant concern from an environmental point of view.

All the high concentrations observed for As and Pb were mainly near mine sites. Thei rconcentrations were primarily in the residual phase and less in the bound reducible phase. High Pb levels were more pronounced in the Yanacocha SRL Mine, whereas high As levels were found in the Llapa SL Mine. These results were in agreement with those estimated by the EF and RAC methods where similar trends were observed. Nonetheless, As and Pb were not considered to be high risk to the environment because of their low mobility. However, their high concentrations due to mine activities are an issue of concern.
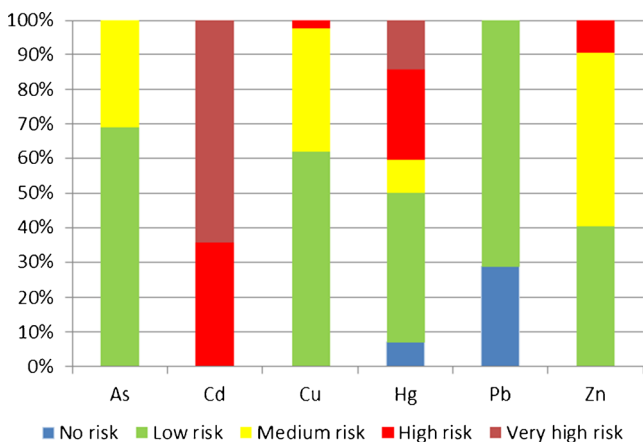

Fig. 4 Risk assessment code obtained for As, Cd, Cu, Hg, Pb, and Zn. They are presented as the sum of all the 42 samples monitored for each trace element

Fig. 5 Map of the Jequetepeque basin showing the points with great, significant, and moderate concentrations of trace elements (points in *red*, *orange*, and *yellow*, respectively) and the element speciation for trace elements (As, Cd, Cu, Ni, Pb, and Zn) for each step of the three-stage BCR protocol at the most contaminated points (*R1*, *Ll4*, and *Ll5*) of the basin
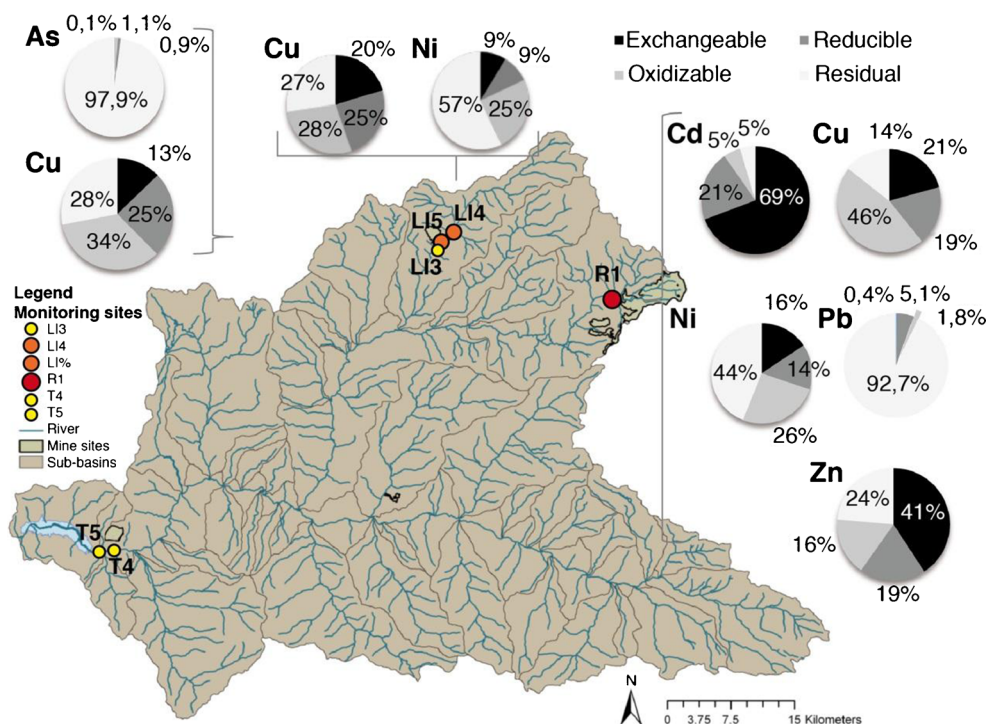
High levels of Ni and Cu were found in the Ll4 and R1 monitoring sites. This was in agreement with the EF and RAC results for Cu, which indicated moderate enrichment and a very high risk. Despite the high concentrations in the residual fraction, considerable mobilities for Ni and Cu were observed in Ll5 and Ll3, mostly in the reducible and oxidizable phases. According to RAC values, these trace elements showed high mobility and could be potentially very high risk to the environment. However, their concentrations are low, as well as their impact.

Remarkably high levels of Cu were also reported in the T4 and T5 samples in the oxidizable phase. These results were in agreement with those previously obtained in a preliminary study performed at the same monitoring sites (Yacoub et al. 2012). Despite differences in analytical methods, the spatial distributions of the trend elements and their concentration ranges were similar for the three sampling periods, confirming the spatial distribution of the trace elements at the basin.

The temporal changes in elemental distribution were evaluated by differences observed among the three sampling periods. The same trends were found for all trace elements in June 2009, November 2009, and July 2010. Cd and Zn concentrations and trends over all sampling periods were similar, and the same was observed for As and Pb. These elements showed the highest concentrations, and according to the EF values, higher enrichments were due to mining activities.

Furthermore, Hg and Cu concentrations and their mobilities increased during the wet season in all samples. However, Hg concentrations were higher in samples located

downstream of the mine sites (Ll5, R0, and R1), but their mobilities were lower. Higher concentrations of Cr were obtained in the mobile fraction during the dry season, specifically for the R1 and T samples, in contrast to Cu and Hg. Increased levels of Cu during the wet season and of Pb and Cr during dry season were also reported in rivers affected by the metal working industries and handicraft factories in Italy (Medici et al. 2011).

We conducted extensive statistical analyses on the MW digestion and the three-stage BCR data as observed in subsection S7 of the "Electronic supplementary material". The results were in agreement with those obtained by the spatial and temporal distribution observations. The trends of trace elements at the Jequetepeque basin and their associated risk were considered useful information for water quality management of the basin.

A previous study conducted by Yacoub et al. (2013) had indicated similar results. A total of 249 water samples were analyzed with data compiled from 2003 to 2010 in order to gain knowledge on the trace element concentrations in water samples and the possible effects on human health. In particular, Cd, Pb, As, and Cu levels in water samples were an aspect of concern, complementing our study results. These trace elements were determined to be causes of significant risk to the environment at the basin. The most polluted area of the basin due to sediment was located downstream of the Yanacocha S.R.L. (an active mine), whereas the most polluted water was found downstream of the Sipán S.L. Mine (which is closed). The results obtained were dependent on the type of mining, whereby the active mine showed the highest trace

element concentrations in the mobile fractions from sediment samples, and the closed mine gave the highest concentrations in water samples.

Conclusions

The level of pollution of different trace elements, sources of contamination, and their potential effect on aquatic life and human health are relevant concerns for basins with mining activities. The environmental implications of the trace elements present in the Jequetepeque sediment samples were determined to evaluate and control pollution emissions.

The first three extracted sediment phases represented the bioavailable fraction that may be released to the water column depending on environmental conditions. The order of mobility from the sediments to the water column was as follows: Cd (94 %) >>Cu (67 %)>Hg (61 %)>Zn (53 %) >>Ni (37 %)> Pb (32 %) >>Cr (19 %)>Fe (12 %)>As (11 %)>Al (10 %).

The same trend was observed for all the monitored points for the three-stage BCR steps and the pseudo-total concentration for Cd and Zn, where a single source was suggested by the enrichment factor calculation, especially for the R1 sample, which is located near the Yanacocha SRL Mine site. Cd and Zn were the most mobile trace elements, and consequently the risk associated with them is considered very high, as suggested by the RAC calculation. The presence and mobility of Cd and Zn due to mining activities is considered a great concern to the environment.

The high values observed for As and Pb were mainly near mine sites. Their concentrations were primarily associated with the residual phase and secondarily to the bound reducible phase. The EF and RAC results for these elements were in agreement. As and Pb were not considered to be high risk to the environment because of their low mobility, but their high levels at the mine sites are an aspect of concern. Cd–Zn and As–Pb were similar for all sampling periods, maintaining the same temporal trends.

Major Ni and Cu levels were obtained at points located near the Yanacocha and Sipán Mine sites. This was in agreement with the EF and RAC values for Cu, which showed moderate enrichment and very high risk. Cu and Hg concentrations and mobilities increased during the wet season for all samples. Higher Cr mobilities were obtained during the dry season, which were the opposite for the Cu and Hg. These and other results for all trace elements were confirmed by the PCA and HCA statistical analysis.

The effect of trace elements near mine sites at the Jequetepeque basin is considered a significant issue for the environment because of the mobility of Cd, Zn, Pb, and As independent of the season. These results may be used to enhance knowledge that may support water quality management at the Jequetepeque basin as necessary steps towards future prevention and remediation actions.

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