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Developing tools to evaluate the environmental status of Andean basins with mining activities

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PhD Thesis

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ABSTRACT

Water quality was characterised and the pressures of anthropogenic activities were evaluated in an Andean basin to obtain information on the environment within an ecosystem approach in Peru. This investigation was developed as a first step toward introducing river management plans and water quality programmes. A continuous simulation model and an environmental monitoring program were developed, taking into account the requirements of the European Water Framework Directive. The dynamics of the basin were characterised using the Soil and Water Assessment Tool. The results obtained from analysis of water and sediment data indicated trace element pollution near mine sites, mainly As, Cd, Cu, Pb, and Zn. The impact of this pollution on the basin was quantified. The ecological status reported was good or very good for all the samples. Nevertheless, points located near mines exhibited the same trends as observed in the water and sediment monitoring.

Keywords: Hydrological modelling, environmental pollution, model calibration, spatial discretization, spatio-temporal distribution, sequential extraction, statistical analysis, risk assessment, trace element, water quality.

RESUMEN

Estado de la calidad del agua fue caracterizado y las presiones de las actividades antropogénicas fueron evaluadas en una cuenca andina con el fin de promover y mejorar el conocimiento del medio ambiente dentro de un enfoque eco-sistémico en el Perú. Esta investigación fue desarrollada como un primer paso para introducir planes de gestión de programas, específicamente de calidad del agua. Para ello, un modelo de simulación continua y un programa de vigilancia ambiental se han desarrollado teniendo en cuenta las exigencias de la Directiva Marco del Agua (DMA). La dinámica de la cuenca se caracteriza por la Herramienta de Evaluación de Suelo y Agua (SWAT). Los resultados obtenidos a partir del agua y datos de sedimentos visualizan la contaminación de elementos traza cerca de las minas y cuantificar el impacto en la cuenca, principalmente para As, Cd, Cu, Pb y Zn. El estado ecológico reportado fue bueno o muy bueno para todas las muestras. Sin embargo, los puntos localizados cerca de las minas mostraron alteraciones con las mismas tendencias observadas en los monitoreos de agua y sedimento.

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LIST OF PAPERS AND PROJECTS RELATED TO THIS THESIS

This thesis is a summary of the following papers and projects:

I. Yacoub, C., Pérez-Foguet, A. (2012) Slope effects on SWAT modeling in a mountainous basin. Journal of Hydrological Engineering. doi: 10.1061/(ASCE)HE.1943-5584.0000756

II. Yacoub, C., Pérez-Foguet, A., Miralles, N. (2012). Trace Metal content of sediments close to mine sites in the Andean region. The Scientific World Journal, 2012, 12 pages. doi:10.1100/2012/732519

III. Yacoub, C., Pérez-Foguet, A., Miralles, N. (2013). Spatial and temporal trace metal distribution of a Peruvian basin: recognizing trace metal sources and assessing the potential risk. Environment Monitoring Assessment. Accepted. EMAS-D-12-11133. DOI: 10.1007/s10661-013-3147-x

IV. Yacoub, C., Miralles, N. and Valderrama C. (2013). Experimental study of trace elements mobility and kinetic characterization in sediment samples from Peru. Water Environment Research. Submitted.

V. Yacoub, C., Pérez-Foguet, A., Miralles, N. and Valderrama C. (2013). Environmental assessment of trace element sediments from a Peruvian mine basin. Science of the total environment. Submitted.

VI. Yacoub C., Pérez-Foguet A., Miralles N., (2011). Risk assessment and seasonal variations in southern countries: Trace metal emissions in the Upper Basin Jequetepeque, Peru. In the proceedings of *IWA Watermatex,* June 2011, San Sebastian, Spain. pp 870-877.

VII. Yacoub C. and Pérez- Foguet A. (2011). Assessing Hydrologic Impact of Anthropogenic Activities Located at the Upper Part of Jequetepeque River Basin, Peru. *International SWAT Conference*. June 2011. Toledo, Spain.

VIII. Yacoub, C.; Miralles, N. (2011). Propuesta de un sistema de control de calidad ambiental en cuencas mineras. *V Congreso Universidad y Cooperación al Desarrollo*. Universidad de Cádiz, April 6-8, 2011. Cádiz, Spain. *pp 134-135.*

IX. Yacoub, C., Pérez-Foguet, A. (2010). Assesing slope influence in ArcSWAT model of Andean watersheds. In the proceedings of *XVIII International Conference of Computational Methods in Water Resources*, June 2010, Barcelona, Spain.

X. Yacoub, C., Pérez-Foguet, A., Miralles, N. (2009). Análisis de impactos ambientales en la cuenca del Jequetepeque, Perú, producidos por actividades mineras. *II Congrés UPC Sostenible 2015. Centre per a la sostenibilitat de la UPC*, 9 i 10 de juliol de 2009, Barcelona (España).

XI. Yacoub, C., Pérez-Foguet A. (2009). Assessment of terrain slope influence in SWAT modeling of Andean watersheds. *European Geosciences Union General Assembly*. Vienna, Austria, April 2009.

XII. Yacoub, C., Cortina, J.L. (2008). Identificación y Cuantificación de impactos medio ambientales generados por Minera Yanacocha en Cajamarca-Perú. *IV Congrés Universitat i Cooperació al*

Desenvolupament, Universitat Autònoma de Barcelona, 12 al 14 de novembre de 2008, Bellaterra, Spain, pp 137.

XIII. Yacoub C. Agua y medio ambiente. In: Pérez-Foguet, A., Jiménez, A. (Coords.). El agua como elemento clave para el desarrollo, Canal Educa. Canal de Isabel II. Madrid, 2012, pp77-89.

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Glossary

ABI Andean Biotic Index

BCR Community Bureau of Reference (now Standards, Measurements and Testing Programme, SM&T)

CAO Compliance Advisor Ombudsman

CCME Canadian Council of Ministers of the Environment

CRM Standard reference material

CV Cumulative Variance

DEM Digital Elevation Model

DESA Dirección Ejecutiva de Salud Ambiental del Perú

DTPA diethylenetriamine penta-acetate

ECOSTRIAND Ecological Status River Andean protocol

EC European Commission

EC Electrical Conductivity

EDTA ethylenediamine tetra-acetic acid

EEA European Environment Agency

EF Enrichment Factor

EQSD Environmental Quality Standards Directive

GIS Geographic Information System

HCA Hierarchical Cluster Analysis

HRU Hydrological Response Unit

HQ Hazardous Quotient

IBMWP Iberian Biological Monitoring Working Party index

ICP-MS inductively coupled plasma mass spectrometry

ICP-OES inductively coupled plasma optical emission spectrometry

IHF Fluvial Habitat Index

INRENA Instituto Nacional de Recursos Naturales del Perú

ISO International Organization for Standardization

IWRM Integrated Water Resources Management

QBR-And index of the Andean riparian forest

QBR index of the riparian forest

LH-OAT Latin-Hypercube and One-Factor-A-Time

MDG Millennium Development Goals

MW Microwave

NSE Nash-Sutcliffe Efficiency

PBIAS Percent Bias

PEL Probable Effect below Level

PFTE Poly-tetra-fluoro-ethylene

PCA Principal Component Analysis

PS Priority Substances

RAC Risk Assessment Code

RE Reference Element

RfD Reference Dose

RSE observations of standard deviation ratio

SCE Shuffled Complex Evolution Method

SCS Soil Conservation Service

SD Standard Deviation

SENAMHI Servicio Nacional de Meteorología e Hidrología

SES Sequential Extraction Scheme

SSQ sum of squared residuals

SPSS Statistical Package for the Social Sciences

SWAT Soil and Water Assessment Tool

TDS Total Dissolved Solids

TE Trace Element

TEL Threshold Effect Level

TSS Total Suspended Solids

UA Uncertainty Analysis

UN United Nations

UNE Una Norma Española (the Spanish Association for Standardization and Certification)

USDA - ARS U.S. Department of Agriculture - Agricultural Research Service

USEPA United States Environmental Protection Agency

WAD Weak Acid Dissociable

WFD Water Framework Directive

WHO World Health Organization

1. Introduction

1.1 Mine pollution in Andean Basins

Mine water pollution is a widespread, international problem and is one of the most severe forms of aquatic pollution (Jarvis and Younger, 2000). Specifically, acid mine drainage is one of the primary causes of water pollution worldwide and has emerged as a major environmental problem over the last few decades (Jarvis and Younger, 2000; Lin et al., 2007; Pérez-López et al., 2008; Romero et al., 2006; Tarras-Wahlberg and Nguyen, 2008).

South America, with a long history of mining (prior to Spanish colonisation in the 16th century), is no exception in creating mine water pollution. Mine production in this region has increased dramatically over the last fifteen years, accompanied by changes in public policy, many of which are related to social conflicts, shifts in natural resource patterns and land ownership, and a rapid expansion of business-led social responsibility that includes promoting community development programs. Today, the mining industry is booming in such countries as Peru and Bolivia due to (i) the actual high costs of metals in the international markets and (ii) the low cost of production in these countries, which is also promoted by favourable social and environmental policies. Perhaps for this reason, both historical and present-day mine development sharply contrasts with present poverty in the extractive zones. Environmental damage, great inequality (coupled with evidence of rather concentrated forms of accumulation) and limited economic diversification are several factors associated with actual mine areas in the Andean context (Bebbington et al., 2007).

The water quality is recognised as a factor directly related to poverty. Poor water quality is not equally redistributed at local or regional scales. In the context of economic growth boosted by mining activities, water quality is also related to increases in social gaps. These facts escalate the social problem, where local stakeholders are the most affected by the impoverished conditions, inequality and exclusion, which also increase the conflict and hinder the eradication of poverty. This reality is self-evident in the Andean region where numerous, active social conflicts are against mining activities, where water contamination is their greatest grievance (Bebbington et al., 2008; Budds and Hinojosa, 2012; Panfichi and Coronel, 2011).

As a result of current and historical metal mining, river channels and floodplains in many parts of the world have become contaminated by trace elements in concentrations high enough to pose a hazard to human life and sustainable development (Macklin et al., 2006). Additionally, aquatic flora and fauna are highly impoverished, and most likely as a consequence, a number of socioeconomic impacts are associated with mine waters (Jarvis and Younger, 2000).

Due to the geomorphologic characteristics of the Andean region, there is a strong presence of trace elements in the environment. For this reason, mining activities are sometimes understood as just one more contributor to the total amount of trace elements. It should be mentioned that streams and rivers affected by acid mine drainage are complex systems in which hydrological and geochemical processes interact to determine the fate and transport of trace elements. Study of the trace element behaviour in these systems is further complicated by spatial and temporal variability in the relevant processes (Kimball and Runkel, 2002). In terms of the Andean social conflicts, focusing on water quality and its relationship with mining, the differentiation between natural and anthropogenic pollution is a concern. In this sense, information regarding the source of pollution may be helpful to take remedial actions to improve and protect water quality.

Additionally, water quality will be a key issue in the near future, when water will become one of the most critically stressed resources. Therefore, further increases in surface water pollution due to mine pollution would seriously affect the quality of drinking water because surface water is providing more and more of the drinking water supply. Accordingly, surface water quality represents an international concern, particularly regarding future prevention and remedial actions.

The need to protect the quality and supply of freshwater resources by an integrated approach in the development, management and use of water in a sustainable way was specified in Agenda 21 of the UN Conference on Environment and Development in Rio de Janeiro in 1992 and has been developed in the European Union (EU) by the “V Action Programme” regarding sustainable development (EU, 1993-2003) and afterwards by the VI Action Programme 2003-2010, “Our future, our election: 2010 environment”. According to Macklin (2006), achieving integrated river basin management has made significant progress in the USA through the National Research Council's (1999) “New strategies for America's watersheds” document and in the EU by the new “Water Framework Directive” (WFD), which came into action on the 22nd of December 2000 by the European Commission (EC, 2000).

Actually, the EU concerns towards sustainable growth under the European 2020 strategy (EC, 2010a) are led by the “Resource efficient Europe” flagship initiative (EC, 2011) and “An industrial policy for the globalisation era” flagship initiative (EC, 2010b). Clearly, there is a direct relationship between the WFD and the 7th Goal of the Millennium Development Goals (MDGs): by 2015, reduce by half, the proportion of people without sustainable access to safe drinking water and basic sanitation to reduce poverty (UN, 2000).

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

Nevertheless, in the Andean region, there are a few publicly funded environmental plans to develop environmental monitoring programmes based on ecological assessments and/or be assessed by hydrological models. These programmes are essential to prepare river management plans and specifically, water quality programmes. In this context, the development of tools to prevent, protect and improve the water quality of fresh water resources in a sustainable way with an ecosystem approach is an initial step towards future prevention and remedial actions.

1.2 Objectives of the research

This research arises from the desire to have better knowledge regarding the presence of trace elements in the Andean environment and the effects of the pressures on the environment by open pit mining in the upper parts of basins. Characterising the water quality status and evaluating the pressures from anthropogenic activities at the basin level are the main goals of this research. This investigation is developed in a Peruvian basin and assesses the environmental status of the basin as a first step to prepare river management plans and specifically, water quality programmes.

In brief, this work develops the following assessment activities:

i. Characterise the basin with the ArcSWAT model.
ii. Develop an environmental monitoring system: water, sediment, and ecological monitoring and analysis.
iii. Assess the grade of pollution of different substances, associated risk, and potential effect on aquatic life and human health, and sources of contamination.

The environmental monitoring and tools for the water quality evaluation are developed by identifying and quantifying the sources of contamination to assess and regulate the pollution emissions. The grade of pollution of different substances, their associated risk, and the potential effect on aquatic life and human health are also relevant concerns that have been included in the development of the tools and monitoring system. This work is considered a first step to promote and enhance the knowledge of the environment within an ecosystem approach in Peru. In this sense, the objective of the study is to develop an environmental monitoring and evaluation tool that would support water quality management.

As an initial effort to prevent, protect and improve the water quality of fresh water resources in a sustainable way, the tools and monitoring system were developed. It is considered that the generation and implementation of these tools may allow stakeholders to create and enhance public policies towards environmental preservation to support the poorest sectors, avoid violating fundamental rights, promote social justice, and provide several necessary inputs for the transformation of the socio-environmental conflicts.

1.3 Overview of WFD

Plans for the protection, improvement and sustainable use of Europe's water environment was developed by the European water framework directive (WFD; Directive 2000/60/EC), where the water quality of rivers is a major management target. This directive implies that the combined impacts of water use and pollution pressures are managed in such a way that no environmental degradation occurs and sustainability is restored or maintained (European Environment Agency, EEA; 2012). Hence, the WFD has precipitated a fundamental change in the management objectives from only pollution control to ensuring ecosystem integrity as a whole (Hering et al., 2010). The directive is widely recognised as innovative, where three elements are considered the most relevant: the environmental objective of good status, long-term perspective and Integrated Water Resources Management (IWRM; Sigel et al., 2010). The WFD is a restrictive and innovative directive; highlighting the importance of the ecosystem approach and the IWRM as methods to ensure the quality of the environment. For this reason, the regulatory guidelines of the WFD are followed in this thesis.

The water quality of rivers requires a good status according to defined environmental objectives and ecological targets for all surface waters within the EU by 2015 (Hsu et al., 2007). The ecological quality status concept developed by the WFD is based upon the status of biological, hydro-morphological and physicochemical quality elements. To comprehensively assess the ecological status of aquatic systems, all matrices and elements should be addressed, particularly those that would most likely affect the biota of the system and those providing relevant information on impacts to them. Water, sediment and biomonitors are the matrices and elements prioritised in the WFD to determine the ecological status of superficial water and groundwater. The integration of the three matrices is not clearly defined within the WFD; however, the results of each matrix can be referenced to and compared with (i) several directly or indirectly related legislation (ICES, 2003); (ii) regional background levels (as is the case for trace elements in sediment) and proposed quality objectives in waters or biomonitors; (iii) the levels obtained from other coastal areas; and (iv) databases on toxic effects thresholds of certain contaminants and eco-toxicological approaches (Borja et al., 2004).

The WFD has impacted various levels of the environmental management of aquatic resources and has triggered the re-organisation of water management by hydrological catchments, rather than by administrative borders, with the ultimate goal being to improve the quality of surface water bodies (Hering et al., 2010); the IWRM defines the river basin as the basic unit based on four elements: characterisation and assessment of impacts on river basin districts; environmental monitoring; setting of environmental objectives; and design and implementation of the programme measures needed to achieve the objectives (EEA, 2002).

Continuous simulation models have been used in many studies to prioritise water resources planning and management as IWRM (Chung and Lee, 2009). The need for developing system models arises from the inherent non-linearity of the processes and the complexity of their interactions (Borja, 2005) and the need to understand the temporal and spatial behaviour of bound contaminants in river basins as the new requirements of the WFD demand (Hsu et al., 2007). In this work, a continuous simulation model and an environmental monitoring program are developed that considers the WFD requirements. To prioritise the IWRM, an applied environmental model characterises the dynamics of the basin, recognises possible interactions with the quality status of the water and evaluates the pressures from anthropogenic activities at the basin.

Monitoring programmes are required to classify the status of water bodies, assess the long-term changes in natural conditions or as a result of anthropogenic activities, and evaluate the extent of the impact of accidental pollution, among others. It is important to select appropriate indicators of these quality elements for monitoring purposes (Allan et al., 2006). The environmental monitoring program was conducted in this work to identify the water bodies at risk due to environmental pollution and to enable measures to improve the quality of the water bodies. This is a first effort to develop an ecological status quality index in the Andean region in a holistic way that integrates mine pollution characteristics. Water, sediment, and ecological monitoring were performed in this survey. Then, the environmental status was evaluated by statistical analyses, identification and development of indicators (from water, sediment and biota).

1.4 Overview of Hydrological Modelling

Hydrological models are mathematical representations that attempt to describe the characteristics or relationships of physical events in a quantitative manner. Modelling tools have become an important keystone for environmental assessments and play a key role in providing data and indicators needed to describe the state of, trends in and prospects for the environment (EEA, 2008). Many of these models incorporate the heterogeneity of the basin and spatial distribution of the topography, vegetation, land use, soil characteristics, rainfall and evaporation. The models are increasingly used to implement management strategies for water resources allocation, flood control, impact of land use change and climate change and environmental pollution control (Setegn, 2010). Hence, hydrological modelling has become useful for planning and managing water resources systems.

The Soil and Water Assessment Tool (SWAT) model (Arnold and Fohrer, 2005) is a physically based, spatially distributed, environmental, continuous simulator that includes hydrological modelling and has become popular for IWRM (Jayakrishnan et al., 2005; Tripathi and Panda, 2005; Mishra et al., 2007) and specifically, for the WFD requirements (Bärlund et al., 2007). Additionally, SWAT models analyse the long-term impact of land management practices for water, sediment, and agricultural chemical yields in a large basin (Arnold and Fohrer, 2005). It has proven to be an effective tool for assessing water resource and non-point pollution problems for a wide range of scales and environmental conditions (Gassman et al., 2007).

In brief, the understanding of relevant physical processes at the basin scale will be applied by the SWAT model: quantifying the fluxes from precipitation, snow-melt, interflow, overland flow, channel flow, unsaturated subsurface flow and saturated subsurface flow, transport of solid matter in subsurface and surface waters and its relationship with land use (the canopy interception, evaporation, transpiration) and climate variables (precipitation, temperature, humidity, potential evapotranspiration and wind speed.

1.4.1 Slope effects on SWAT modelling

In hydrological and water quality modelling, the manner in which the space is designated into unique units is important because these units are the smallest geographical parts for which characteristics can be entered. These units are also important because they are used to predict the simulated outputs (Migliaccio and Chaubey, 2008). However, computational cost increases when the number of spatial units increases, which does not necessarily mean better simulations.

As the number of spatial units increases, so does the number of model parameters that must be calibrated. A larger number of interacting parameters can result in unpredictable effects when multiple parameters are adjusted (Bekele and Nicklow, 2007). Calibrating large basins with a limited data series is challenging. Hence, a compromise must be considered between available data, number of computational units and the set of parameters chosen for calibration.

The SWAT model subdivides a basin into sub-basins and each sub-basin into Hydrological Response Units (HRUs). HRUs are considered homogeneous with unique values of land use, soil type, and terrain slope. Several studies have analysed the influence of basin discretisation in model predictions, either through the number of sub-basins or number of HRUs. Gassman et al. (2007) stated that many authors have analysed streamflow predictions to variations in HRUs and/or sub-basin delineations for basins ranging in size from 21.3 to 17,941 km2 and highlighted the insensitivity of the flow simulations to these variations. Other studies have analysed the sensitivity of the sub-basin division criterion (Gong et al., 2010), land use division criterion (Migliaccio and Chaubey, 2008), soil division criterion (Muleta et al., 2007), and the slope division criterion (Setegn, 2010) with respect to the model performance in streamflow and sediment; however, none have evaluated the effect of discretisation on the auto-calibration process.

The objective of this study is to evaluate (i) the effect on the calibration process of including the terrain slope as a criterion of the SWAT model discretisation on large mountain basins and (ii) the relative importance of the slope discretisation versus other discretisation criteria (sub-basin delineation and the threshold values of definition).

1.5 Overview of Environmental Monitoring

The environmental quality standards directive (EQSD) related to the WFD defines the chemical status of surface waters. The EQSD outlines environmental quality standards in fresh and coastal waters for relevant pollutants known as priority substances (PSs). These PSs include certain hazardous substances, including trace elements, that can be described as persistent, bio-accumulative and toxic, occur widely in the environment, and have well-documented detrimental effects on both environmental and human health, which potentially can be put at risk via drinking water or the ingestion of food originating from aquatic environments (EEA, 2011).

The quality of the surface water performed in this work focuses on trace elements. Water quality is assessed by ecological and chemical approaches under the WFD requirements. There is no specific requirement within the directive to link ecological or biological information or data to chemical monitoring to assess the health of the ecosystem (Allan et al., 2006). Additionally, the WFD presents a lack of information regarding sediment and biota quality instead of guidelines from the U.S. Environmental Agency (USEPA) and Canadian Council of Ministers of the Environment (CCME).

In this survey, the chemical quality of the surface waters is the focus and is evaluated using classical chemical monitoring methods for trace-level pollutants present in water and sediment in a Peruvian basin. In addition to the sediment standards, a biota standard may be required along with the water column when the environmental target is a chemical with a tendency to bio-accumulate and one which may therefore pose a risk through secondary poisoning resulting from food chain transfer (EEA, 2011). Therefore, the ecological status is developed by a protocol for the assessment of the ecological status of the Andean rivers (Acosta et al., 2009).

Sediment in rivers polluted by acid mining drainage consists of a complex mixture of various geochemical fractions containing potentially toxic trace elements. Polluted sediments are important to the water quality of rivers because they prolong the residence time of pollutants in river basins by accumulating organic and inorganic contaminants, by retarding their transport in river basins, and by the decreased degradation of organic substances under anoxic conditions. The continuous exchange between the sediment and the water during the settlement and re-suspension phases of the contaminated particles during transport has the potential to impact previously non- or less contaminated areas (Förstner, 2004). Therefore, the risk of bound contaminants being spread within the river basin, e.g., during situations of high water discharge, is growing because of the increasing amount of sediment trapped in river basins (Cánovas et al., 2008; Chen and Liu, 2006; Förstner and Müller, 1973; Viers et al., 2009).

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). Recent literature on sediment-associated trace element 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).

Note 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; Cánovas et al., 2008; Galan et al., 2003; Kraus and Windegand, 2006).

In this sense, sequential extraction schemes (SES) is widely used to assess the trace element mobilisation and its bioavailability by providing details on the distribution or partitioning of trace elements in soils and sediments. Certainly, this is valuable information in terms of risk assessment that is not available from a pseudo total digestion procedure. Therefore, the retention and release of trace elements (relative to re-adsorption and redistribution processes) was obtained by this methodology and evaluates the availability, mobility or persistence (Arain et al., 2008; Kartal et al., 2006; Pérez-López et al., 2008; Pérez and Valiente, 2005; etc.).

In 1987, the Community Bureau of Reference (BCR, now the Standards, Measurements and Testing Programme, SM&T) produced a standard protocol for the extraction of trace elements from soils and sediments to resolve the problems caused by the wide variety of SES in existence at that time and the lack of comparable results (Adriano et al., 2004; Arain et al., 2008; Kartal et al., 2006; Pérez-López et al., 2008; Pérez and Valiente, 2005;Sahuquillo et al., 1999). The protocol uses fixed operation conditions (i.e., extractant agents, time and form of shaking, operation sequence, etc.), which ensures that results obtained in different laboratories can be compared accurately (Thomas et al., 1999). Therefore, the BCR protocol, normally used to study trace element distribution in sediments (Pérez and Valiente, 2005; Nannoni et al., 2011; Pagnanelli et al., 2004; Routhm and Hjelmquist, 2011; Ure et al., 1993; Vareajo et al., 2011; Villalobos-Castañeda et al., 2010) was developed in this work.

The amount of dissolved trace element depends on characteristics of the solid as well as the aqueous phase and – non-linearly – on the kinetics of the solid/solution interactions. Sequential extraction protocols are performed in equilibrium conditions, then, the thermodynamic information is obtained. However, the mobility rate of trace element is not considered (Gismera et al 2004). Kinetic extraction by a single reagent can be defined as the proper methodology to determine distribution of species in natural environment (Fangueiro et al., 2002; 2005). The most widely utilized reagents for single-extraction schemes are powerful chelating agents, such as ethylenediamine tetra-acetate (EDTA) and diethylenetriamine penta-acetate (DTPA) (Young et al., 2005; Chen et al., 1998; Fangueiro et al., 2002 and 2005; Gismera, 2004; Madrid et al., 2007). In the present work we evaluated the mobility of trace elements from river sediments by single-extraction treatments; nitric acid (under different pH) and EDTA are evaluated, and comparing 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. Different kinetic models adapted to the sediment system are used to describe the experimental data. The parameters determined by the kinetic approaches were applied to the experimental data and the trace elements results were evaluated in mobility terms.

2. Description of the study area

The Jequetepeque river basin contributes significantly to the livelihoods of 389,859 people (INEI, 2005). This is an important area in Peru because it supplies water to major cities and production activities in the lower part of the basin. Additionally, the Jequetepeque river basin contains the most important gold mine in South America, the Yanacocha S.R.L Mine. There are other mine projects in the upper-middle part of the basin, with the most significant mine in terms of size being a closed gold mine, the Sipán S.L Mine.

This is also a basin of critical national significance because of current socio-environmental conflicts in the region that may spread throughout the country (Bebbington et al., 2008; Panfichi and Coronel, 2011; Sosa and Zwarteveen, 2012). After two decades of the mining, Cajamarca, the region in which the upper part of the basin is located, is controversial due to conflicts between the central and local government, the most serious of which is related to complaints by residents of the region about mine water pollution (Bebbington et al., 2007). This is an open conflict that is relevant not only locally but globally, as reflected in the international press from 2005 to the present time (Associated Press, 2012; Folks, 2012a, 2012b; Owles and Murray, 2005; Perez and Bergman, 2010; Ximenez de Sandoval, 2012).

In this context, efforts to prevent, protect and improve the quality of fresh water resources in a sustainable way, in accordance with the requirements of the WFD, are considered especially relevant. It should be noted that the Peruvian government has made some such efforts. The new environment and water law reflects the importance of taking into account the sustainability and integration of the ecosystem and the importance of the water quality (Government P., 2009a and 2009b). Nevertheless, the lack of water facilities and the lack of consistent baseline data in the basin are obstacles that must be overcome to avoid planning decisions based on false assumptions (Pérez-Foguet and Giné Garriga, 2011). The development and implementation of management tools for the Jequetepeque basin may facilitate the expression of stakeholders' views, enhance public policies, to support the poorest sectors, avoid violations of residents' fundamental rights and provide information necessary to resolve socio-environmental conflicts.

The Jequetepeque basin (4,372.5 km2) is located at 7° 6′ S/ 78° 30′ W in the northern part of Peru (Figure 2.1). The Jequetepeque River flows from east to west into the Pacific Ocean. The annual average precipitation ranges from 0 to 1,100 mm/year, the altitude of the river basin ranges from 0 to 4,188 meters above sea level (m.a.s.l.), and the mean average water discharge is 816.49 Mm3. The Gallito Ciego reservoir (400 m.a.s.l.) separates the upper-middle part of the basin from the lower part. The river basin supplies water to the large cities on the coast and to agricultural fields. Erosion produced by extreme events such as the 1997–98. El Niño Phenomenon is responsible for the reservoir silting up faster than expected. Due to the significance of this reservoir to one of the most important agricultural areas in the country, the Jequetepeque river basin has been the object of several studies by the government (INRENA, 2005).

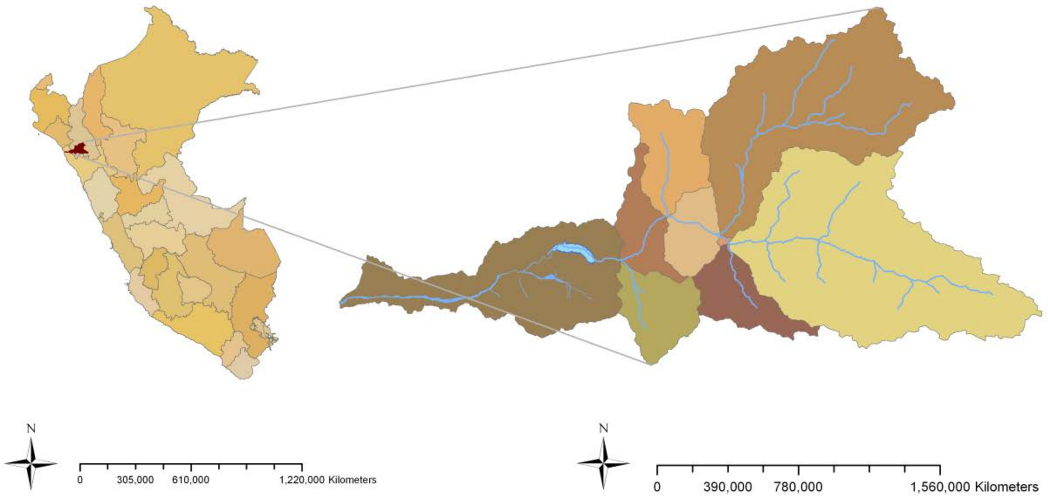


Figure 2.1: Location map of the Jequetepeque basin.

The upper-middle part of the basin covers an area of 3,564.8 km2. Approximately 80% of the population are farmers. The main activities are agriculture, rising livestock, and mining, and there are no other productive activities, such as tanning or intensive farming, that produce pollution (CARE, 2007; INRENA, 2005). The annual mean temperature ranges from 25.4 ºC at the reservoir to less than 4 ºC in the upper part of the basin. The areas of highest rainfall variability are found in the upper-middle part of the basin. The land use map of the Jequetepeque basin indicates that 23% is cultivated for field crops, 23% is pasture land and 53% is forest land (Figure 2.2a). The geology of the basin is illustrated in Figure 2.2b. The majority of the soil types of the basin are leptosols (53%), andosols (26%), regosols (7%) and phaeozems (7%).

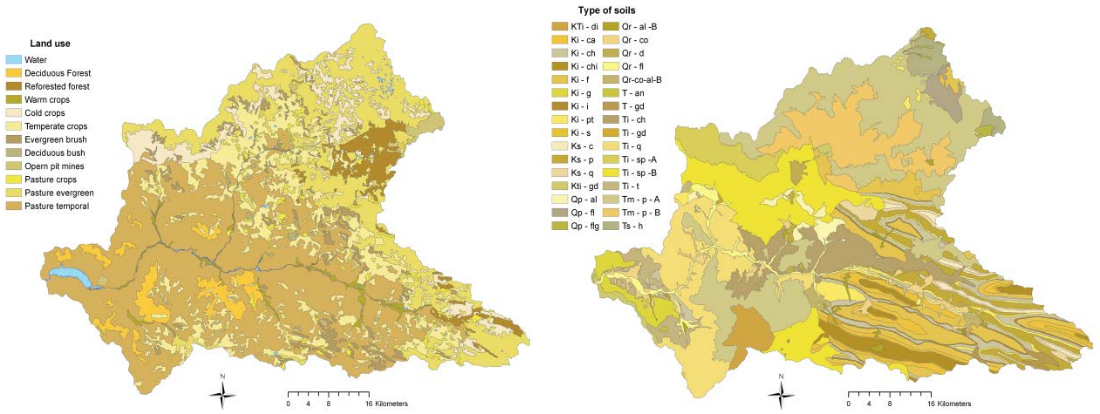


Figure 2.2: a) left side - Land use map, b) right side - Soil map of the middle upper part of the Jequetepeque basin. K, Q and T are cretaceous, quaternary and tertiary soils respectively, with inferior (i), medium (m), superior (s), and Pleistocene (p) series. The stratigraphic unities are: ancient alluvial (al), ancient fluvial (fl), ancient fluvioglacial (flg), andesita porphyritic (an), Cajamarca (c), carhuaz (ca), Chimu (chi), chilete (Ti-ch), chulec (ch), diorite porphyritic (di), farrat (f), granodiorite (gd), goyavisguizga (g), huambas (h), inca (i), parlatambo (st), pullulcana (p), porculla (Tm-p), quinden (Ti-q), qullquinan (q), recent coluvial (co), santa (s), san Pablo (sp), sliding (d), and tembladera (t).

Páramo ecosystems, found above 3,000 m.a.s.l., are characterised by strong UV isolation and cold and humid weather with strong daily temperature fluctuations. They are also characterised by volcanic soils, rich organic matter, a few adapted species of flora and fauna, and high vulnerability to small changes in climate and anthropogenic activities (Buytaert et al., 2006). Páramo ecosystems can notably influence the hydrologic regime of a drainage basin. Their role in hydrological terms is considered important because of their large capacity to retain and drain out water.

3. Methods

The objectives of this study were the application of a physically based hydrological model, SWAT, and the environmental assessment of the water quality status of the basin, with respect to the WFD guidelines, by environmental monitoring. In this section, the methodology used in this study is described.

3.1. Hydrological Modelling

The application of the SWAT hydrological model involved calibration, validation, sensitivity analysis, and uncertainty analysis. For this purpose, a Latin hypercube and one-factor-at-a-time sensitivity method and a parasol calibration method were developed, as described below.

3.1.1. Description of the Soil and Water Assessment tool (SWAT) Model

The Soil and Water Assessment Tool (SWAT) is a public-domain, spatially distributed, physically based continuous-event hydrologic model (Arnold and Fohrer, 2005), developed by the U.S. Department of Agriculture's Agricultural Research Service (USDA ARS) to predict the impact of land management practices on water, sediment, and agricultural chemical yields in large basins with varying soils, land use and management over long periods of time (Neitsch et al., 2001a, 2001b). It has proven to be an effective tool for assessing water resource and nonpoint pollution problems for a wide range of scales and environmental conditions (Gassman et al., 2007). The SWAT model has been applied previously in Peru (CARE et al., 2007). It was subsequently used as an IWRM tool. Because the model is in the public domain, it is easily used by some agencies and NGOs. For these reasons, the SWAT model was the tool chosen for hydrological modelling in this study.

The SWAT model simulates a basin by dividing it into sub-basins on the basis of differences in soils and land use (Green et al., 2008). The SWAT model divides each sub-basin into homogeneous areas with unique soil, land use and slope properties. These homogeneous areas are the model calculation units, referred to as the hydrological response units (HRU). The input information for the sub-basins is aggregated to simulate the hydrological behaviour of the basin. The SWAT model has proven to be an effective tool for assessing water resources and nonpoint pollution problems for a wide range of scales and environmental conditions (Gassman et al., 2007). ArcSWAT2005 v2.3.4 of the model, in which the SWAT model is embedded in a geographic information system (GIS), was used in this study.

3.1.2. SWAT Model Input

ArcSWAT's input requirements include weather data and spatially distributed data: digital elevation model (DEM) data, soil data and land use data. Data on river discharge is also used for calibration purposes. A study developed by CARE et al. (2007) compiled the minimum data required to model the Jequetepeque basin. In this study, these data were updated to calibrate the model to study long-term impacts. The spatially distributed data were projected in the WGS 1984 UTM Zone 17S projection using ArcGIS 9.3. The DEM data define the topography of the basin by describing the elevation of any point in a given area at a specific spatial resolution (Setegn, 2010). A 90-m digital elevation model, developed by CARE et al. (2007), was used to describe the basin (Figure 3.1).

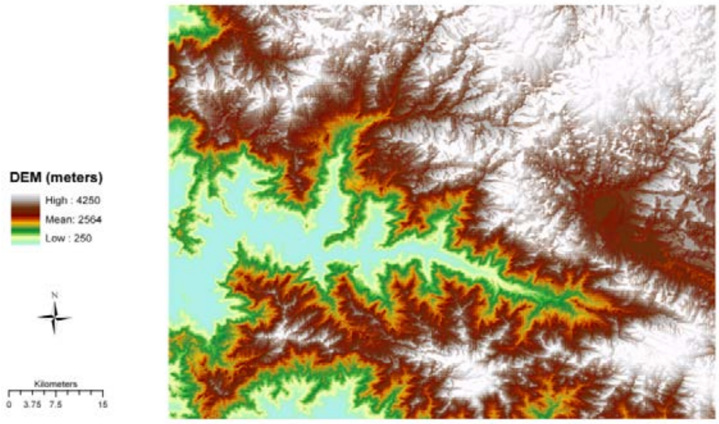


Figure 3.1: DEM of the Jequetepeque Basin (meters above sea level)

The soil map was obtained from the same source. The soil data included the physical and chemical soil properties for each layer of each soil type. The inputs for the soils' physical properties (the maximum rooting depth of the soil profile, depth of the soil profile, moist bulk density, available water capacity, saturated hydraulic conductivity, erodibility factor, etc.) govern the movement of water and air through the profile and influence the cycling of water, whereas the soils' chemical characteristics (the fraction of porosity from which anions are excluded, organic carbon content, etc.) determine the initial levels of the various chemicals in the soil. Land use is a significant factor in hydrological modelling because it is related to evapotranspiration, runoff and surface erosion processes in a basin (Winchell et al., 2007). The land use map obtained from CARE was improved with land use maps provided by Peruvian Instituto Nacional de Recursos Naturales, INRENA. The land use and soil maps entered into the ArcSWAT model are shown in Figures 3.2a and 3.2b, respectively.

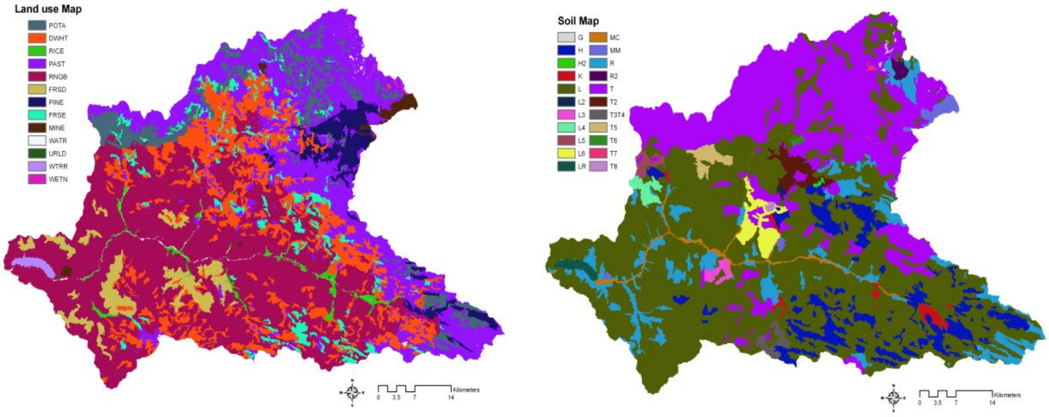


Figure 3.2: a) left side - Land use map, b) right side - Soil map of the middle upper part of the Jequetepeque basin introduced into the model: G- Gleisol, H- Phaozem, K- Kastanozem, L- Leptosol, MC-Miscellaneous Bank, MM - Miscellaneous mine, R-Regosol, T- Andosol. DHWT-Durum wheat, FRSD- Forest deciduous, FRSE- Forest evergreen, MINE- Mine, PAST-Pasture, PINE- Pine, Pota-Potato, RICE- Rice, RNGB- Range bush, URLD- Residential low density, WATR- Water, WETN- Wetlands non forested, WTRR- Water reservoir.

SWAT is a continuous model that requires daily precipitation data and maximum and minimum air temperature data. It also has embedded in it a weather simulator that can generate weather data. The available data from one daily maximum and minimum temperature station, located in the middle of the basin, six daily precipitation stations distributed within the basin, and one daily flow station located in the upper part of the basin were used to generate the weather data inputs required (Figure 3.3).

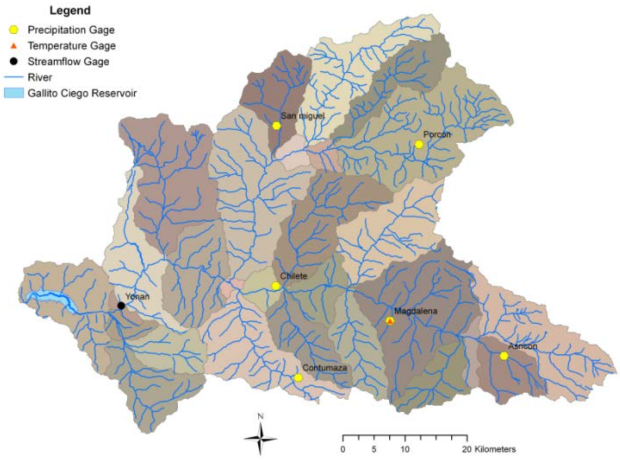


Figure 3.3: Gauge stations of the Jequetepeque Basin

A nine-year weather generation database was incorporated to generate representative climatic data and fill gaps in the weather data (Figure 3.4). These data included the probability of occurrence of a wet or dry day; the average, standard deviation and skew of daily precipitation in a month, the average and standard deviation of maximum and minimum air temperature in a month, the average daily solar radiation for a month, the average daily dew point temperature in a month and the average daily wind speed in a month.

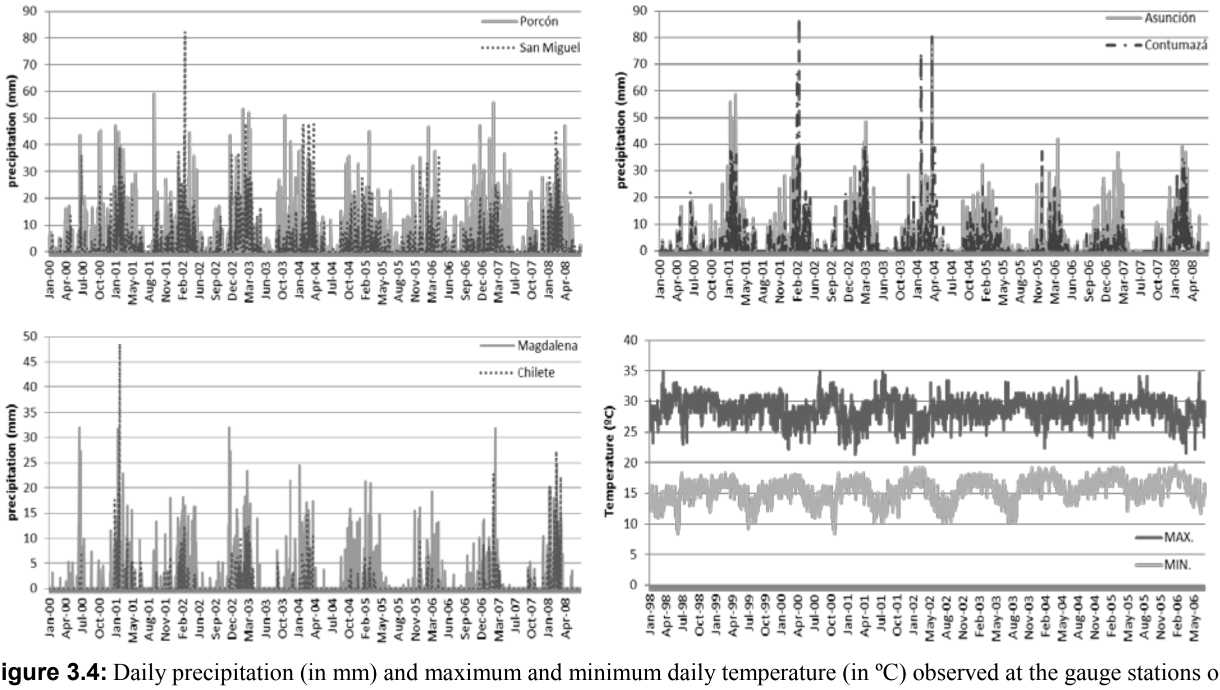


Figure 3.4: Daily precipitation (in mm) and maximum and minimum daily temperature (in ºC) observed at the gauge stations of the Jequetepeque basin

The time period of the meteorological data obtained from CARE et al. (2007) extended by three years the data obtained from the Peruvian meteorological and hydrological administration (Servicio Nacional de Meteorología e Hidrología, SENAMHI). The data period was therefore 1996 to 2009. Data from 1996 to 1998 were used to train the model, data from 1999 to 2005 were used for calibration, and data from 2006 to 2009 were used for validation.

3.1.3. SWAT Model setup

SWAT simulation consists of the following steps: (1) data preparation, (2) definition of the drainage area and its sub-basins, (3) definition of the hydrological response units (HRU), (4) calibration and uncertainty analysis, and (5) verification.

Some refinements were made to the data required by the model. A mask of the Jequetepeque basin was created to delineate the basin. The improved land use map was incorporated into the SWAT land cover and plants database, which required changes in the lookup tables that identifies the SWAT code for each land cover used. The soil SWAT database was modified to include the soil types of the basin identified by CARE et al. 2007.

The mask and DEM describe the topography and the streams of the basin, and therefore the sub-basins, for the model. The flow direction and flow accumulation steps are tied to the stream definition processes (Winchell et al., 2007 – user's guide). The origin of a stream is defined by the minimum drainage area. The ArcSWAT interface allows the user to fix the number of sub-basin by deciding the initial threshold area (Setegn, 2010). To evaluate the relative importance of the slope discretisation in the Andean Jequetepeque basin and its effect on the calibration process, four different sub-basin delineations were performed using the same required data. The first case (C1) was created using the default sub-basin delineation with a size threshold of 6.89 km2 and resulted in 28 sub-basins. Size thresholds 12.8, 9.4 and 5.2 km2 for Cases 2, 3 and 4 resulted in 12, 19 and 35 sub-basins, respectively.

The sub-basins were further divided into the model calculation units, the HRU, which are the product of overlaying soil, land use and slope boundaries. The HRUs within the sub-basins were defined on the basis of three threshold values introduced into the model: (i) the percentage of land use over the sub-basin area; (ii) the percentage of each soil class over each land use area; and (iii) the percentage of each slope class over each soil area. These thresholds were used to discretise the sub-basins and create the HRUs as a function of the land use, soil and terrain slope criteria. For all four sub-basin discretisation cases, the HRUs were defined with a threshold of 20% for land use and 10% for soil type, as suggested in the literature (Winchell et al 2007). Additionally, a fifth case (C5), was considered using the same 28 sub-basins identified for C1, but applying half of the threshold values used in the other four cases (10% for land use and 5% for soil type). A single slope parameter was computed for each HRU as the dominant one.

For the purpose of evaluating the terrain slope as a criterion for HRU definition, each case of sub-basin discretisation with a unique slope value was compared with the same sub-basin discretisation but including the slope as a criterion of HRU discretisation. As the land use and soil information was not changed, the variation of the HRU discretisation was only due to the slope discretisation. The ArcSWAT interface allows the user to divide the HRUs into 5 intervals of slope. The most homogeneous ranges of the 5 slope intervals were designated (Figure 3.5 and Table 3.1).

Table 3.1: Percentage Area for each slope range defined

Slope Ranges	% Area	
	Total	2% Threshold
0 -15	19.89	19.79
15 -24	18.86	20.33
24 -35	20.40	20.99
35 -49	19.02	19.06
49 -999	20.86	19.82

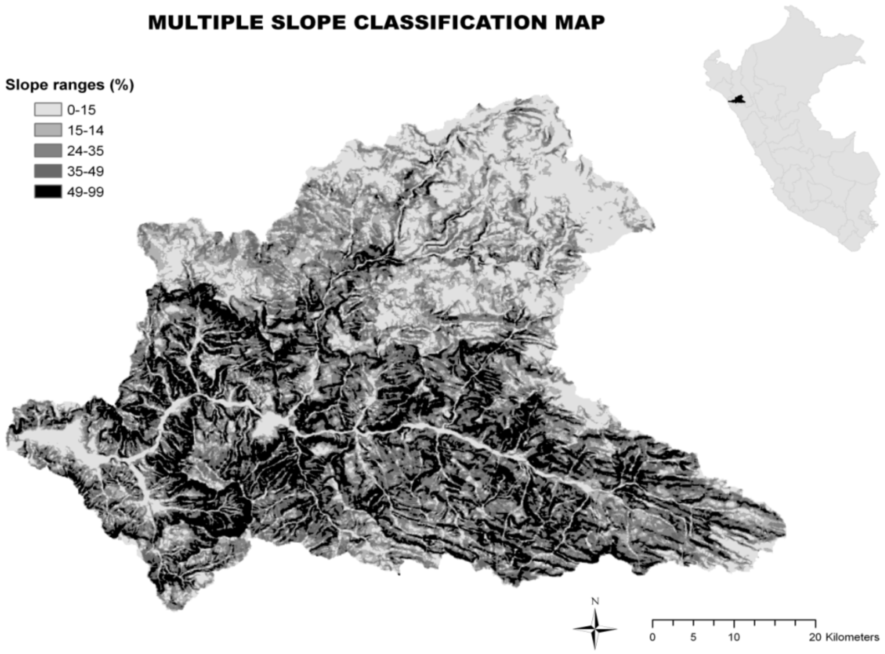


Figure 3.5: Map of slope classification used for the fine discretization case (equivalent to 486 HRU).

A threshold of 2% of the slope class over the soil area was considered for all cases (decreasing this threshold did not increase the number of HRUs) to compare no slope consideration with the maximum number of HRUs related to the slope variation. The same thresholds of land use and soil used for the discretisations without taking into account slope were used. The numbers of HRUs, land uses and soil types considered in this study are summarised in Table 3.2.

Table 3.2: Definition of each case of discretization, with the number of sub-basins, HRUs, land uses, types of soils, slope ranges and the threshold values used for the definition of the five cases with their respective sub-cases: the coarse discretization, (C.) and the fine discretization (F.)

Discretization case	nº Sub-basins	nº HRUs	nº land uses	nº soil types	nº slope ranges	% threshold values land use	 soil type	 slope
C1C	28	94	5	11	1	20	10	
C1F	28	436	5	11	5	20	10	2
C2C	12	44	3	7	1	20	10	
C2F	12	208	3	7	5	20	10	2
C3C	19	62	5	7	1	20	10	
C3F	19	293	5	7	5	20	10	2
C4C	35	119	7	12	1	20	10	
C4F	35	538	7	12	5	20	10	2
C5C	28	188	8	14	1	10	5	
C5F	28	859	8	14	5	10	5	2

3.1.4. SWAT Model Calibration and Evaluation

The steps in the calibration process are the following: (i) parameter identification, which consists of defining and choosing the most sensitive parameters of the model; and (ii) parameter estimation, which consists of fixing the values of the parameters chosen.

Sensitivity analysis was performed in the identification of the calibration parameters by evaluating the rate of change in the output with respect to change in each input. This analysis was applied to limit the number of optimisable parameters required to obtain a good fit between the simulated and measured data. Hence, the number of free parameters to be adjusted could be considerably reduced (Eckhardt and Arnold, 2001). Additionally, this optimisation of parameters allows models to better match realistic conditions (Green and Van Griensven, 2008).

The sensitivity analysis was conducted using the combined Latin hypercube and one-factor-at-a-time (LH-OAT) sampling methods enabled in ArcSWAT and developed by Van Griensven et al. (2002) and Francos et al. (2003). The associated error of the simulations was also evaluated. The adjustment of the model outputs to the measured values was estimated using an objective function, the sum of the squared residuals (SSQ). A restricted set of 28 parameters was used for the sensitivity analysis and the evaluations of the associated error. The default ranges of the parameters were adjusted on the basis of findings reported in the literature (Holvoet et al., 2005; Muleta et al., 2005; Van Griensven et al., 2006) and the modeller’s knowledge. The final ranges used in this study are shown in Table 3.3.

The sensitivity analysis was followed by parameter estimation. This can be accomplished manually or automatically, depending on the knowledge of the modeller, the model, and the basin complexity (Gupta et al., 1999). Manual calibration can become labour-intensive when the number of parameters used in the manual calibration is large, especially for complex hydrologic models (Balascio et al., 1998). In this study, automatic calibration was considered more appropriate.

Table 3.3: Hydrological parameters and its ranges used in the sensitivity analysis

Name	Threshold values	Definition	Type of parameter
Alpha_Bf	0 – 1	Base flow alpha factor (days)	Groundwater
Biomix	0 – 1	Biological mixing efficiency	Soil
Blai	0 – 1	Leaf area index for crop	Crop
Canmx	0 – 10	Maximum canopy index	Surface Runnof
Ch_K2	0 – 150	Effective Hydraulic conductivity in main channel alluvium (mm/hr)	Channel processes
Ch_N2	0 – 1	Manning coefficient for channel	Channel processes
Cn2[1]	0.75 – 1.5	SCS runoff curve number for moisture condition II	Surface Runnof
Epco	0 – 1	Plant evaporation compensation factor	Evapotranspiration
Esco	0 – 1	Soil evaporation compensation factor	Evapotranspiration
GW_Delay	0 – 50	Groundwater delay (days)	Groundwater
GW_Revap	0.02 – 0.3	Groundwater ‘revap’ coefficient	Groundwater
GWQmn	0 – 1000	Threshold depth of water in the shallow aquifer required for return flow to occur (mm)	Groundwater
Revapmn	0 – 500	Threshold depth of water in the shallow aquifer for ‘revap’ to occur (mm)	Groundwater
Sftmp	0 – 5	Snowfall temperature (ºC)	Snow
Slope[1]	0.75 – 1.5	Average slope steepness (m/m)	Geomorphology
Slsubbsn[1]	0.75 – 1.5	Average slope length (m)	Geomorphology
Smfmn	0 -10	Min. melt rate for snow during the year (mm/ºC/day)	Snow
Smfmx	0 -10	Max. melt rate for snow during the year (mm/ºC/day)	Snow
Smtmp[1]	0.75 – 1.5	Snow melt base temperature (ºC)	Snow
Sol_Alb[1]	0.75 – 1.5	Soil albedo	Evaporation
Sol_Awc[1]	0.75 – 1.5	Available water capacity of the soil layer (mm/mm soil)	Soil water
Sol_K[1]	0.75 – 1.5	Soil conductivity (mm/h)	Soil water
Sol_Z[1]	0.75 – 1.5	Soil depth	Soil water
Surlag	0 – 10	Surface runoff lag coefficient	Surface Runnof
Timp	0 – 1	Snow pack temperature lag factor	Snow
Tlaps	0 – 50	Temperature laps rate (ºC/km)	Geomorphology

[1] these parameters are varied according to a relative change (multiplying the parameter) that maintains their spatial relationship.

In this study, the shuffled complex evolution (SCE) method embedded in SWAT and developed by Duan et al. (1992, 1993 and 1994) was used. The SCE method is a global optimisation method based on a genetic algorithm and was specifically designed to address the peculiarities encountered in conceptual basin model calibration. The automatic optimisation procedure was performed using the sum of the squared residuals (SSQ) as an objective function, and the SCE method was complemented by an uncertainty analysis (UA) as an automatic procedure. This combination is called the parasol (parameter solutions) method (Green and Van Griensven, 2008; Van Griensven et al., 2002; Van Griensven et al., 2006). The UA gives a probable interval of variation for each parameter in the SCE algorithm.

Taking into account the physical specifications of each parameter, SWAT's physically based input parameters are allowed to vary within an uncertainty range during calibration (Gassman et al., 2007). In this work, the sensitivity analysis-improved ranges were applied to the parameter estimation (Table 3.3). The UA method selects the calibrated simulations from the confidence region by defining "c" as a threshold for parameters within the probable interval by χ2-statistics:

$$\mathrm{c} = OF(\theta^{*})^{*}\left(1 + \frac{\chi^{2}_{p,0.975}}{n-p}\right) \qquad (3.1)$$

where $OF(\theta^{*})$ is the minimum value of the objective function, n is the number of observations used in the calibration, and p is the number of parameters included in the calibration (Green and Van Griensven, 2008).

It should be noted that the purpose of calibration is to determine combinations of parameter values that allow the model to adequately represent data over a certain period of time whereas the purpose of validation is to check how close the simulation is to the experimental data for the different conditions and time periods used in the calibration (Moriasi et al., 2007). Validation involves running the model with the calibrated parameters but with different data time periods and allows the user to run the model for any scenario. In this study, data from 1996 to 1998 were used to train the model, data from 1999 to 2005 were used for calibration, and data from 2006 to 2009 were used for validation.

3.1.5. Model Verification

The stream flow simulations obtained from calibration and validation were compared with the stream flow gauge data from the Jequetepeque River (Figure 3.3) using hydrographs and quantitative statistics. In this study, the Nash–Sutcliffe efficiency (NSE), percent bias (PBIAS) and observations standard deviation ratio (RSR) were the quantitative statistics used (Harmel and Smith, 2007; Moriasi et al., 2007). These indicators were defined as follows:

$$\mathrm{NSE} = 1 - \left[\frac{\sum_{i=1}^{n}(Y_i^{obs} - Y_i^{sim})^2}{(Y_i^{obs} - Y^{mean})^2}\right] \qquad (3.2)$$

$$\mathrm{RSR} = \frac{RMSE}{STDEV_{obs}} = \frac{\left[\sqrt{\sum_{i}^{n}(Y_i^{obs} - Y_i^{sim})^2}\right]}{\left[\sqrt{\sum_{i=1}^{n}(Y_i^{obs} - Y^{mean})}^{2}\right]} \qquad (3.3)$$

$$PBIAS = \left[\frac{\sum_{i=1}^{n}(Y_i^{obs} - Y_i^{sim})\cdot(100)}{\sum_{i=1}^{n} Y_i^{obs}}\right] \qquad (3.4)$$

where n is the total number of observations, Yiobs is the ith observation for the streamflow, Yisim is the ith simulation for the streamflow and Ymean is the mean of the observed streamflow. NSE assesses the relative magnitude of the residual variance compared to the measured data variance. The normalised root mean square error, RMSE, is presented by the RSR factor. PBIAS reflects the accuracy of the model by assessing the average tendency of the simulation with respect to measured data. NSE values close to one reflect good calibration results, while PBIAS and RSR values close to zero are considered a good match.

3.2. Environmental Monitoring

The collection of water, sediment and ecological samples is summarised in this section. Additionally, the analyses procedures used to characterise the water quality of the basin in accordance with the WFD guidelines (Figure 3.6) are described in this section. The water and sediment analysis focused on detection of trace elements, while the ecological monitoring focused on the presence and diversity of macro-invertebrates. This work was complemented with data extracted from monitoring stations developed in the Jequetepeque basin. It should be mentioned that no previous research on sediment and ecological quality in the Jequetepeque basin was found.

The statistical analyses were performed by processing the water and sediment data to facilitate understanding of the dynamics of pollutants in the basin. The most contaminated sediment samples were examined using kinetic experiments to assess the distribution of species in the natural environment. Additionally, an ecological protocol was applied to complement the analysis of the physical and chemical properties of the soils and evaluating the magnitude of ecological pollution in the monitored samples.

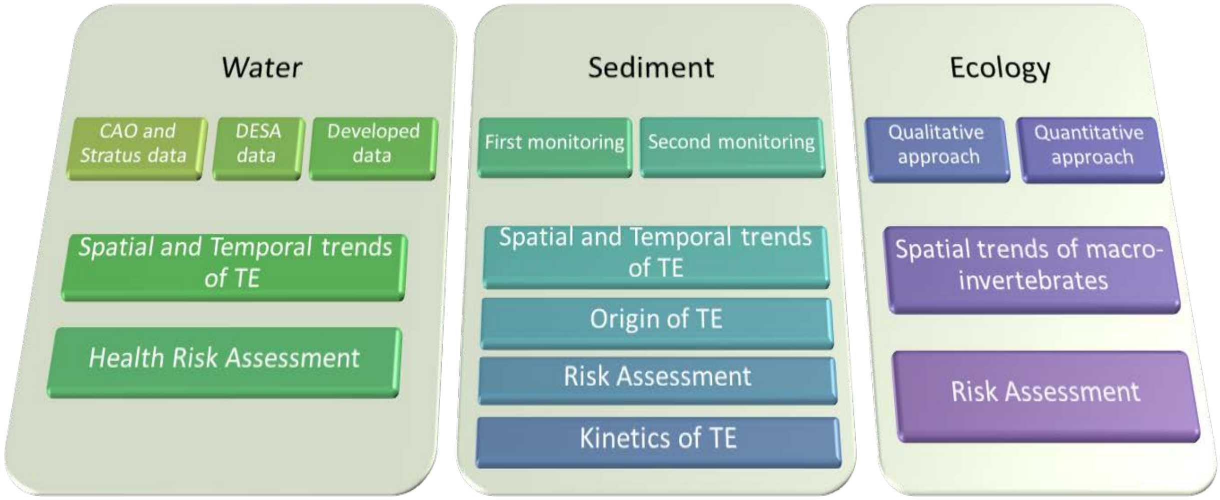


Figure 3.6: Sketch of the three components of the environmental monitoring implemented. It includes the used data and the appraisal developed for each component.

The following procedures are described in this section: (i) the water monitoring procedures, (ii) the sediment monitoring procedures, (iv) the kinetic procedures and modelling, (v) the ecological status monitoring procedure, (vi) the statistical methods, and (vii) the indicators used to identify the trace element sources and assess the associated risk.

3.2.1 Water monitoring

In this study, 4 water monitoring campaigns were designed, implemented and analysed. A special effort was made to incorporate data from previous water trace element monitoring studies performed in the Jequetepeque basin to complement the water monitoring program in this study and enhance knowledge of the magnitude of pollution and the dynamics of the pollutants. Information from three previous studies of the Jequetepeque basin was analysed in addition to the water monitoring data collected in this study.

One of these three studies involved the collection of data by the Peruvian government's "Dirección Ejecutiva de Salud Ambiental" (DESA) from 15 monitoring sites distributed within the basin in almost every month from 2003 to 2008. The other two studies were conducted by the Compliance Advisor Ombudsman (CAO) and Stratus Inc. Consulting (CAO, 2005; Stratus Inc. Consulting, 2003) and involved collecting data from 10 monitoring sites from 2002 to 2003 and 15 monitoring sites from 2004 to 2005, respectively. The monitoring sites used in these two studies were located close to the Yanacocha S.R.L. Mine site, the largest mine in the basin and the one associated with water conflicts in the region (Bebbington et al., 2007 and 2008; Panfichi and Coronel, 2011; Sosa and Zwarteveen, 2012).

The analysis of the data from these four water monitoring programs (the DESA, CAO, Stratus and the monitoring performed in this study) required three independent statistical analyses because of the disparities in the data in terms of the components, locations and sampling time periods. First, the data from the CAO and Stratus Inc. Consulting were analysed together because of the similarity of the data components and the fact that the data were collected in the same area and with the same measurement units. The monitoring conducted by DESA and the monitoring conducted in this study were executed in similar areas and with the same measurement units. Nevertheless, the remarkable differences between the monitored components, the differences in the sampling points and the gaps in the DESA data prevented the data from being combined for analysis. Therefore, the DESA data were examined separately from the monitoring data collected in this study, although the same statistical analysis techniques were used. Three different water monitoring programs conducted in the Jequetepeque basin were analysed separately to obtain better information about the concentration of trace elements in the water and the possible peaks and trends at the basin level. Further details about the three monitoring programs—the CAO and Stratus Consulting data review, the DESA data review, and the monitoring conducted in this study—are described below.

3.2.1.1. CAO and Stratus Consulting data review

Information from these two closely related studies were used in this study (CAO, 2005; Stratus Inc., 2003). Both water quality appraisals were conducted in the Rejo sub-basin of the Jequetepeque basin (Figure 3.7), with samples collected from stations located near the Yanacocha S.R.L. Mine. These two studies were performed in 2002 to 2003 by Stratus Consulting and 2004 to 2005 by the CAO in response to social conflicts that arose between the local people and the mine corporation concerning the quality and quantity of the water near the mine. It should be noted that subsistence agriculture and logging are the main activities in the sub-basin. Therefore, the presence of pesticides was neglected. The concentrations of nitrate, sulphate, and ions of Al, Ag, As, Ba, Ca, Cd, Cu, Cr, Fe, Hg, Mg, Mn, Ni, Pb, Sn, Tl, and Zn were analysed in accordance with the guidelines of the World Health Organization (WHO) and the U.S. Environmental Protection Agency (USEPA).

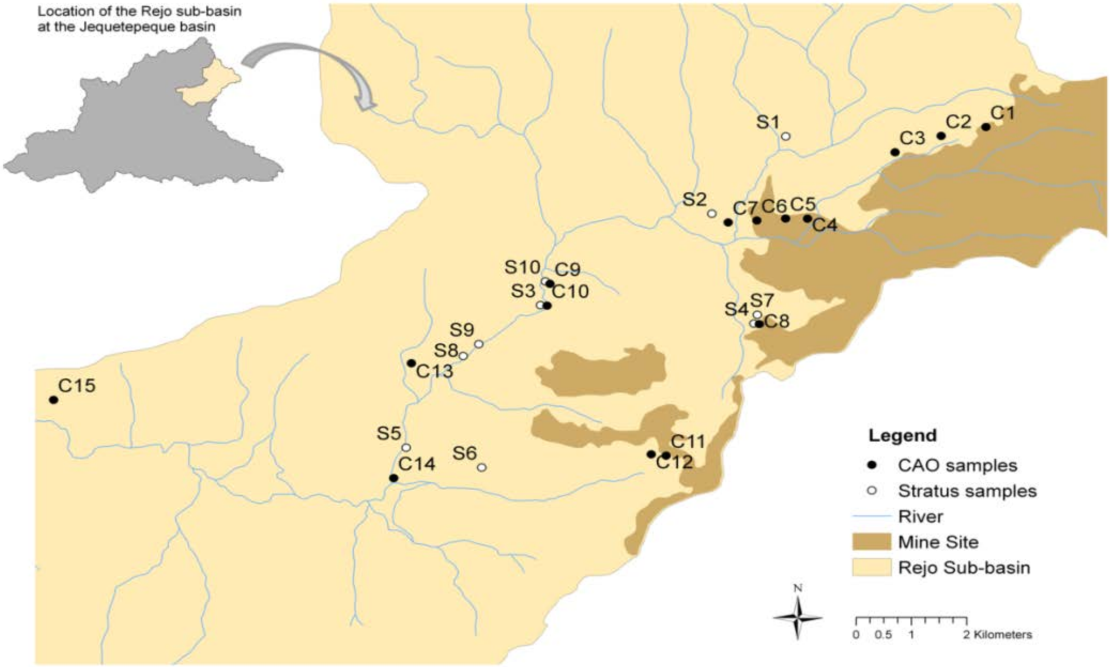


Figure 3.7: CAO and Stratus INC data monitoring sites in the Jequetepeque basin. C samples are from the CAO data, and S samples are from the Stratus Inc. data

For this survey, 10 sampling sites adding a total amount of 74 samples by Stratus (S samples) and 15 sampling points accumulating 120 points by CAO (C samples) were examined in order to evaluate the presence of water pollutants in the Rejo sub-basin from 2002 to 2005. The two studies add twenty-five sampling sites (Figure 3.7), being a few sampling points taken several times, changing the location, periodicity and frequency independently. Regarding the importance from seasons for the monitoring results (Miller et al., 2002; Cánovas et al., 2008), the data was separated between the wet season (October-March) and the dry season (April-September). In this review, the size of the analysed data set summarise 65 sample points during the wet season and 51 sample points during the dry season.

This work is based on Yacoub C., Pérez-Foguet A., Miralles N. (2011). Risk assessment and seasonal variations in southern countries: Trace element emissions in the Upper Basin Jequetepeque, Peru. It is also based on the proceedings of *IWA Watermatex,* June 201, San Sebastian, Spain. pp. 870-877.

3.2.1.2. DESA data review

The data collected by the Peruvian government's "Dirección Ejecutiva de Salud Ambiental" (DESA) were reviewed in this study. All of these data were collected at locations close to sites with high anthropogenic and industrial inputs and small cities in the Jequetepeque basin (Figure 3.8). The survey did not address organic pollutants or pesticides; only trace elements were reported.

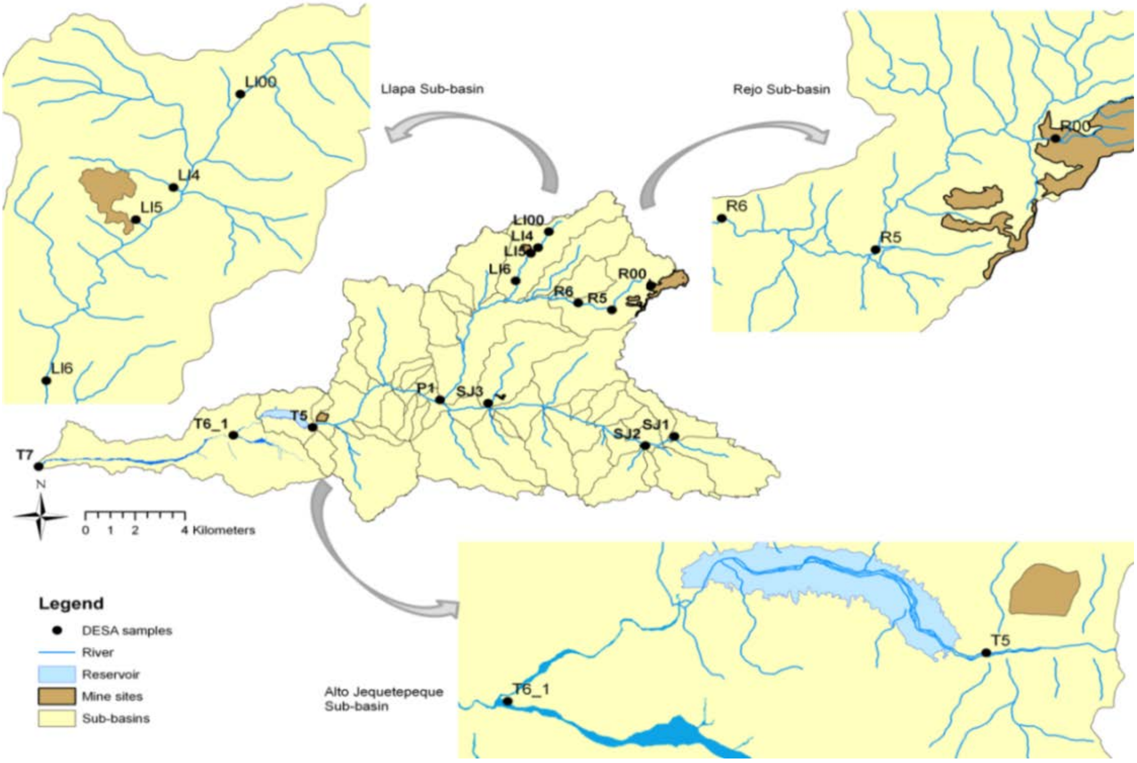


Figure 3.8: DESA data monitoring sites in the Jequetepeque basin

This survey was supported by Yacoub, C., Pérez-Foguet, A., Miralles, N. (2013). Spatial and temporal trace element distribution of a Peruvian basin: recognizing trace element sources and assessing the potential risk. J. Environ. Monit. Assess. DOI: 10.1007/s10661-013-3147-x. The final publication is available at link.springer.com.

3.2.1.3. Water monitoring for this study

The water monitoring developed in this thesis summarises four water and sediment monitoring campaigns developed from June 2008 to July 2010 in the Jequetepeque basin. The sample location of the water monitoring is the same than the sediment monitoring developed (section 3.2.2), and was developed at the same time.

The water monitoring conducted for this study involved four water and sediment monitoring campaigns in the Jequetepeque basin between June 2008 and July 2010. The sampling locations for the water monitoring were the same as those for the sediment monitoring (section 3.2.2), and the water and sediment samples were collected at the same times.

The purpose of this study was to evaluate water pollution at the basin level and thereby increase the available information about trace elements in the water in the Jequetepeque basin. Given this as the main purpose, the monitoring sites were selected on the basis of the following criteria: (i) USEPA guidelines (USEPA 1977, 1991,1994,1998,2001,2002), (ii) proximity to the main mining activities; (iii) hydrology, geology, geomorphology, erosion and topography (CAO, 2007; CARE et al., 2007; DIGESA, 2008; INRENA, 2005), (iv) previous evidence of toxicology or spillage; (v) available data from studies of water quality (CAO, 2007; DIGESA, 2008; Stratus Consulting Inc., 2003), and (vi) the feasibility of monitoring activities, particularly regarding physical access to sites and approval of local residents.

Representative sites should be selected such that sampling occurs downstream of major sources of pollution but also in integrative sinks such as reservoirs, harbours and estuaries, particularly for sediment-associated substances (EEA, 2011). In this study, samples were obtained from three sub-basins: the Llapa sub-basin (Ll samples), the Rejo sub-basin (R samples) and the Alto Jequetepeque sub-basin (T samples). The Ll samples were obtained near the Sipán S.L. Mine, the R samples were obtained near the Yanacocha S.R.L. Mine, and the T samples were obtained above and below the reservoir in the Alto Jequetepeque sub-basin (Figure 3.9).

Gold was extracted at both mines using cyanide leaching. The Yanacocha S.R.L. Mine has been active since 1993, whereas the Sipán S.L. Mine closed in 2005. The main activities in the Jequetepeque basin are agriculture, raising livestock, and mining, and there are no other activities, such as tanning or intensive farming, that produce pollution. Therefore, natural erosion and mining are presumed to be the sources of trace element pollution. Trace element release could be caused by mining activities or could simply be due to the naturally high levels of some elements in the Andes. The samples collected at the R3 monitoring site were considered to be unaffected by the mine sites because of the location of the monitoring site (Figure 3.9). Thus, R3 was considered a background sampling point.

A total of 42 samples were collected from 16 monitoring sites during three campaigns (June and November 2009 and July 2010). Ll and R samples were collected four times, twice during the dry season (June 2009 and July 2010) and twice during the wet season (November 2008 and 2009). Samples from the Alto Jequetepeque sub-basin (T samples) were collected three times, once during the wet season and twice during the dry season (June 2009, November 2009 and July 2010).

The samples were collected according to procedures established by the U.S. Environmental Protection Agency (USEPA 430/9-86-004) and the American Society for Testing and Materials (ASTM, 2000). The samples were collected in the field at a depth of 3–5 cm and stored in sterilised plastic bottles. The samples were pretreated with HNO3 to pH<2 for detection of trace elements, with H2SO4 to pH<2 for detection of ammonium, nitrates and nitrites; and with NaOH to pH>12 for detection of total and WAD cyanide. Sulphate samples were not pretreated; they were only preserved at 4 ºC. The samples were filtered through 0.45-µm membrane filters and were stored at 4 ºC until analysis.

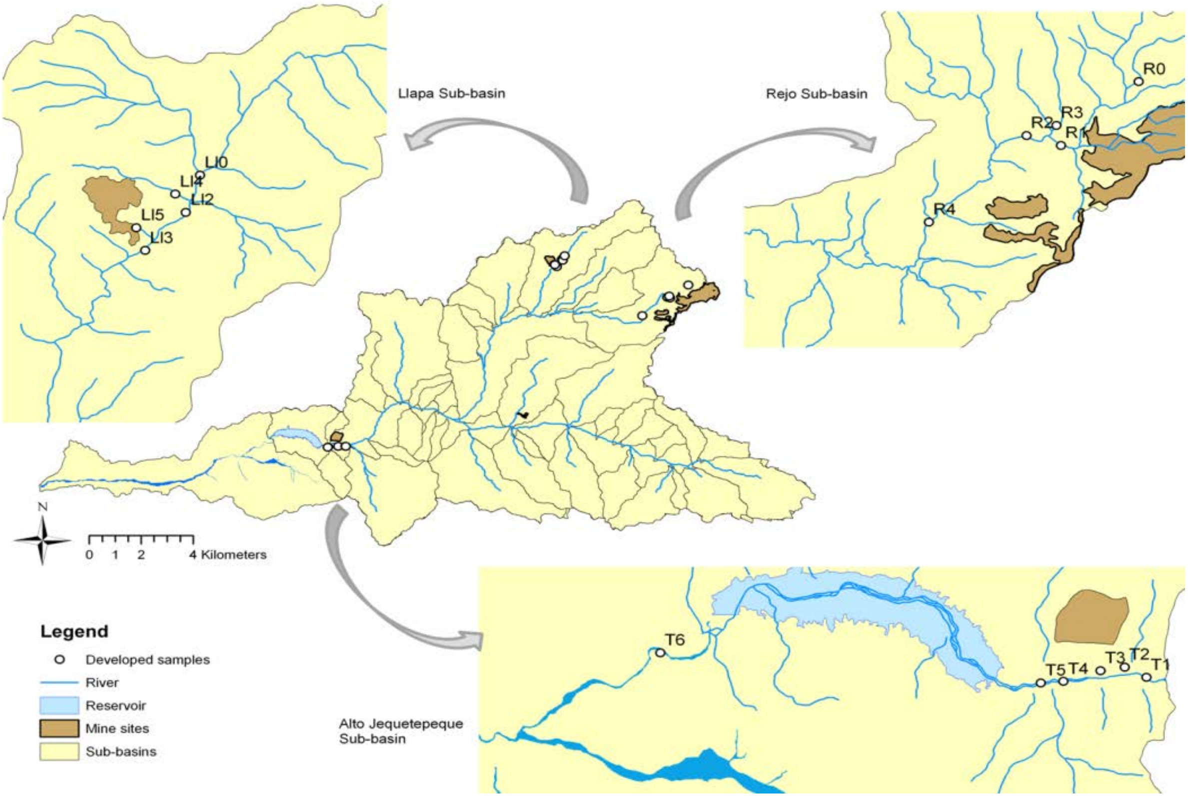


Figure 3.9: Water and Sediment monitoring sites in the Jequetepeque basin

The concentrations of TDS, TSS, chloride, weak acid dissociable (WAD) cyanide, total cyanide, nitrite and nitrate, ammonium, sulphate, Al, As, Ca, Cd, Cr, Cu, Fe, Mg, Ni, Pb, and Zn were analysed at the Corrosion and Protection Institute Laboratory of the Pontifical Catholic University of Peru in Lima, which is accredited with the Standards Council of Canada (SCC). The pH and EC of the samples were measured in the field using a Wissenschaftlich-Technische Werkstätten 340i/SET multi-parameter tool.

TDS and TSS were determined by the gravimetric method based on SM 2540 C and D, respectively. Sulphate and chloride were analysed by high-resolution liquid chromatography in accordance with EPA 300.0 rev. 2.1. Total cyanide was analysed by the titrimetric and total-cyanide-after-distillation methods, SM 4500 C and D, respectively. WAD cyanide was determined by the colorimetric method based on SM 4500 I and E. Nitrite and nitrate were analysed by spectrophotometry based on HACH 8171, and ammonium detection was based on HACH 8038. Trace element contents were determined by inductively coupled plasma optical emission spectrometry (ICP-OES model OPTIMA 3000DV - Perkin Elmer), based on EPA 200.7.

The detection limits were 1 mg/l for TSS, 4 mg/l for TDS, 0.5 mg/l for chloride, 0.001 mg/l for WAD and total cyanide, 0.013 mg/l for Al, 0.02 mg/l for Ca and ammonium, 0.01 mg/l for Fe, Mg, and nitrate and nitrite, 0.004 mg/l for Pb, 2 μg/L for Zn, 1 μg/L for As, Cd, Cr, Cu, and Ni, and 0.1 μg/L for Hg. All the reagents used were of analytical grade. The reliability of the results obtained was estimated by the relative standard deviations as being less than 10%.

This survey was supported by Yacoub, C., Pérez-Foguet, A., Miralles, N. (2013). Spatial and temporal trace element distribution of a Peruvian basin: recognizing trace element sources and assessing the potential risk. J. Environ. Monit. Asses. DOI: 10.1007/s10661-013-3147-x. The final publication is available at link.springer.com.

3.2.2. Sediment monitoring

In this section, the sediment monitoring procedure is described, including sample collection, sample pretreatment, and extraction and analysis of trace elements in the sediments. Single extraction procedures and kinetic experiments were developed to ascertain the kinetics of some selected trace elements from four sampling points and their associated mobility.

Plans for a total of 4 sediment monitoring campaigns were developed on the basis of the same criteria used for the water monitoring (section 3.2.1). The same sampling locations, periodicities and frequencies were used for the water monitoring and sediment monitoring. The locations of the sampling sites for the four campaigns were described in section 3.2.1 (Figure 3.9). The data from the first campaign, conducted in November 2008, were analysed using a slightly different procedure than the data from the other three campaigns, conducted in June 2009, November 2009 and July 2010. The BCR procedure was used for the first campaign and the BCR three-step procedure and a microwave digestion procedure were used for the other campaigns. The results of the sediment monitoring conducted in the first campaign, referred to as the first sediment monitoring (Section 3.2.2.1), were considered separately from the results of the other three campaigns (Section 3.2.2.2), referred to as the second sediment monitoring.

This section describes the first sediment monitoring, the second sediment monitoring and the kinetic procedure and modelling. The sample collection, pretreatment, extraction and analytical procedure are summarised for each.

3.2.2.1. First round of sediment monitoring

The first sediment monitoring was developed as a pilot campaign. After the results were evaluate, the procedures used were modified slightly for further monitoring. The sample collection, the BCR extraction procedure, the analytical procedure and the quality assurance and quality control process are described below.

Sampling collection

The first round of sediment monitoring was conducted in November 2008. The locations of the monitoring sites are shown in Figure 3.10. The sub-basins monitored were the Llapa and Rejo sub-basins, which were the locations from which the water monitoring samples were also obtained.

Sediment samples were collected using a core sampler and placed in plastic bottles. The samples were taken from the nearest point on the river bank, from the superficial layer (approximately 10 cm in depth) of sediments covered by approximately 20 cm of water. Three sediment subsamples were collected and mixed at each site (within 100 m of the river) to obtain a representative sample (USEPA 2001). The sub-samples were mixed in the field in a tray with a total volume of 1 L. The sediments were composed mostly of clay and silt, and the percentages of rocks varied from 0.9% to 85%, depending on the sample point, with the percentage for most cases being approximately 6%. The sediments were kept cool in the field.

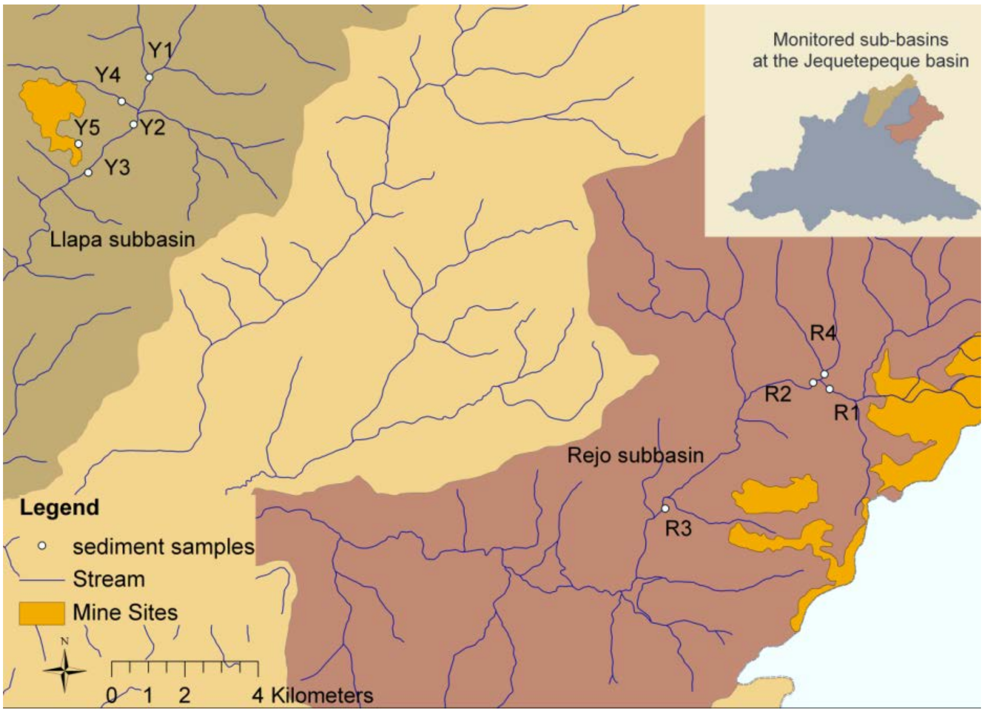


Figure 3.10: First campaign sediment monitoring sites in the Jequetepeque basin

The sediment samples were treated and analysed at the Corrosion and Protection Institute Laboratory of the Pontifical Catholic University of Peru in Lima. Electrical conductivity and pH were measured in the field. The sediment samples were dried at 60 ˚C to a constant weight (Idris, 2008) and sieved to obtain a particle size of < 63 µm (UNE Standard 7050) and retain the most trace element pollution (Arain et al., 2008; Casas et al., 2003; Fukue et al., 2006; Idris, 2008; Kartal et al., 2006; Pérez and Valiente, 2005; Prudencio et al., 2007; Varejao et al., 2009). The dried samples were stored in polyethylene bottles.

BCR extraction procedure

The BCR procedure is a standard extraction protocol for elements in soils and sediments, developed in 1987 to address the wide variation in results obtained using the sequential extraction scheme (SES) proposed by the European Community Bureau of Reference (BCR) (Ure et al., 1993), now called the Standards, Measurements and Testing Programme, SM&T, and the related lack of comparability between results (Arain 2008; Kartal et al. 2006; Pérez and Valiente, 2005; Sahuquillo et al., 1999; etc.). BCR is normally used to study trace element distribution in sediments (Nannoni et al., 2011; Pagnanelli et al., 2004; Pérez and Valiente, 2005, Routhm and Hjelmquist, 2011; Ure et al., 1993; Vareajo et al., 2011; Villalobos-Castañeda et al., 2010). This protocol was used as an initial approach in this study. The geomorphological characterisation by Mn and Fe hydro-oxy-oxides and the low organic matter content of the volcanic soils in the Jequetepeque basin warranted the application of the procedure (Mees and Stoops, 1991). The BCR procedure, together with its related phases and its respective reagents, are summarised below. Full details can be found elsewhere (Sahuquillo et al., 1999; Thomas et al., 1999; Ure et al., 1993).

Step 1 consists in extracting exchangeable water-and acid-soluble species that are weakly bound to trace elements retained on the sediment surface by relatively weak electrostatic interactions and released by changes in ionic competition or affected by minimal pH changes. These include trace elements bonded to carbonates. For each sample, 40 ml of 0.11 mol•dm-3 acetic acid is added to 1 g of sediment in a 100-ml centrifuge tube and shaken for 16 h at room temperature. The extract is separated from the solid residue by centrifugation and decantation of the supernatant liquid into a high-density polyethylene container. The container is sealed and the extract is stored at 4°C. The residue is washed by adding 20 ml of water, shaking for 15 min and finally centrifuging the resulting suspension.

Step 2 consists in extracting the reducible species contained in iron and manganese oxides, which are released because of their instability under reducing conditions. In this step, 40 ml of 0.1 mol•dm-3 hydroxylamine chloride (adjusted to pH 2 with nitric acid) is added to the residue from Step 1 in the centrifuge tube, and the extraction and wash is performed as described above.

Step 3 consists in extracting oxidable species, which are trace elements bound to various forms of organic matter and sulphides. The degradation of organic matter under oxidising conditions is responsible for releasing trace elements. Ten ml of a solution of 8.8 mol•dm-3 H2O2 (adjusted to pH 2 with nitric acid) is added carefully, in small aliquots to avoid losses due to violent reaction, to the residue from Step 2 in the centrifuge tube. The sample is digested at room temperature for 1 h with occasional manual shaking. A water coating at approximately 85˚C is then used until evaporation. When the sample is dry, the entire process is repeated. Then, 50 ml of ammonium acetate 1 mol•dm-3 is added, and the sample is shaken for 16 h at room temperature. Again, the extraction is performed as described in Step 1.

Step 4 consists in extracting residual species, which are constituent elements of the lattice mineral structure that are not easily released into water. Five ml of HCl and 15 ml of HNO3 (both trace analysis quality) were added to the sample in a sand coating in a Pyrex container and allowed to stand for 3 h at 150 ˚C. Finally, the sample is centrifuged and the supernatant is separated in a polyethylene tube and kept at 4˚C until the analyses are performed.

The trace element contents in the sample sediments are calculated as the sums of the trace element contents determined in each step, taking into account that no significant differences exist between the pseudo-total concentration of trace elements by aqua regia digestion and the sum of the extracted trace elements determined by the BCR procedure (Arain et al 2008).

Analytical procedure

The trace element contents were determined by atomic absorption spectrometry by hydride generation based on SM 3114 B-C-2005 for As, cold vapour atomic absorption spectrometry based on the EPA 245-1 method for Hg, and inductively coupled plasma optical emission spectrometry (ICP-OES model OPTIMA 3000DV - Perkin Elmer) based on EPA 200.7 for the other trace elements. The detection limits were 0.1 mg/kg for Cd, Cu, Cr, and Pb, 0.05 mg/kg for As and 0.02 mg/kg for Hg. All the reagents used were of analytical grade.

Quality assurance and quality control

The repeatability of the analysis methods was assessed by analysing three replicates. The relative standard deviations obtained varied from 5 to 11% and can be considered satisfactory, given the complex nature of and the differences between the samples of the sediment matrix.

This work was based on Yacoub, C., Pérez-Foguet, A., Miralles, N. (2012). Trace Metal content of sediments close to mine sites in the Andean region. The Scientific World Journal*,* 2012, 12 pages. doi:10.1100/2012/732519

3.2.2.2. Second round of sediment monitoring

The second round of sediment monitoring was conducted in three campaigns. In this section, the sampling collection, the microwave digestion procedure, the BCR three-step extraction procedure, the analytical procedure and the quality assurance and quality control process are described.

Sampling collection

The locations of the monitoring sites for the second round of sediment monitoring were the same as those for the water monitoring conducted for this study (Figure 3.9). The second round of sediment monitoring involved sample collection at three times: June 2008, November 2009 and July 2010.

Data treatment

The same procedure used for the first round of sediment monitoring was used for the second round of sediment monitoring (Section 3.2.2.1). The sediment samples were dried at 105 ˚C to a constant weight in accordance with ISO 5725-1:1994 and sieved to obtain two particle sizes. The coarser particles ranged in size from 1 to 0.5 mm and were used to determine the enrichment factor indicator described below. The finer particles were < 63 µm in size (UNE Standard, 7050; ISO, 3310-2; and ASTM E 323). This particle size was also performed at the first sediment monitoring (section 3.2.2.1). For the second round of monitoring, the finer particles were used for the MW digestion and BCR procedures. The dried samples were stored in polyethylene bottles.

Microwave digestion procedure

To establish the total amount of trace elements in the sediments, a microwave digestion procedure (MW digestion) was developed. The efficiency of the digestion procedure was a function of the reactive materials used, the sample matrix and the analyte of interest. There is a lack of agreement in the literature about the best combination of reactive materials to use for efficient extraction of trace elements from sediments and soils. The efficiency of the MW digestion procedure is not related only to the type of reactive materials; it is also depends on other factors such as the relative proportions of the reactive materials, the digestion time used and the pressure and temperature reached in the digestion procedure.

The MW digestion procedure has been improved over time with respect to the digestion time, the contamination of samples, the required amounts of reactive materials and samples, reduction of volatile compound losses and security. Sediment samples are difficult to digest because they are combinations of different materials (i.e., clay, silicates, etc.) (Lamble and Hill, 1998). The interferences obtained with hydrofluoric acid and hydro-boric acid were tested in the laboratory without satisfactory results. Therefore, a combination of nitric acid and hydrochloric acid was used, in accordance with the USEPA 3051 method. The MW digestion procedure chosen does not dissolve all of the sample matrix, as quartz, silicates, titanium dioxide, alumina and other oxides are not dissolved. Therefore, this digestion procedure is not considered total digestion and is referred to as pseudo-digestion.

A Berghoff MWS-2 microwave oven with a capacity of 10 PFTE, 60-ml vessels and a power of 1350 W was used. Table 3.4 give the optimised programmes for the microwave digestion of the sediment samples, as recommended by the operation manual of the apparatus and USEPA method 3052. The sample intake was 0.5 g, and 9 ml of HNO3 and 3 ml of HCl, both of analytical grade, were used as reagents (USEPA Method 3051A). No detectable contamination was found when the blank vessels processed. The final solution obtained was filtered through 0.45-µm cellulose acetate membrane filters and stored in polyethylene bottles at 4ºC until analysis.

Table 3.4: Programmes used for the MW digestion

Steps	Temperature (ºC)	Power (W)	Time (min)
1	140	80	5
2	160	80	5
3	180	80	20

BCR three-step extraction procedure

The BCR procedure is a standard extraction protocol for trace elements in soils and sediments (Ure et al., 1993) as described for the first round of sediment monitoring. The modified BCR three-step extraction procedure (BCR three-step) is a useful tool for prediction of the short- and long-term mobility of trace elements in contaminated sediments (Pérez-López et al., 2008; Oyeyiola et al., 2011). The BCR three-step protocol was used in this survey, as shown in Table 3.5.

Details of the BCR three-step protocol can be found elsewhere (Guevara-Riba et al., 2004; Margi et al., 2004; Gismera et al., 2004; Sauquillo et al., 1999; Ure et al., 1999). The solution obtained for each step was filtered through 0.45-µm cellulose acetate membrane filters and stored in polyethylene bottles at 4ºC until analysis.

Table 3.5: BCR three-step procedures and the reagents used

Step	Phases	Reagents	Procedure
F1	Soluble and exchangeable (e.g. carbonates)	20 ml of 0.11M CH_3COOH	16h at room temperature
F2	Reducible (e.g. iron/manganese oxides)	20 ml of 0.1M $HONH_2$ HCl (pH <2)	16h at room temperature
F3	Oxidable (e.g. organic matter and sulfides)	5 ml of 8.8 M H_2O_2	1h at room temperature and 1 h at 85ºC
		5 ml of 8.8 M H_2O_2	1 h at 85ºC
		25 ml of NH_4 CH_3COO (pH <2)	16h at room temperature

Analytical procedure

The trace element concentrations in the extracted dilutions at each step of the BCR and MW digestion processes were determined at the Scientific and Technological Centres of the University of Barcelona. Inductively coupled plasma mass spectrometry and optical emission spectrometry were used (ICP-MS model Elan 6000 and ICP-OES Perkin Elmer model Optima 3200RL). The following wavelengths (nm) were used to determine the analyte elements by ICP-OES: Al, 308.2; Cd, 228.8; Cr, 267.7; Cu, 324.7; Fe, 259.9; Mn, 257.6; Pb, 220.3; and Zn, 213.8. The following isotopes were used to determine the analyte elements by ICP-MS: Al, 27; As, 75; Cd, 114; Cr, 52; Cu, 63; Hg, 202; Mn, 55; Ni, 60; Pb, 208; Sb, 121; and Zn, 66.

Quality assurance and quality control

A standard reference material, CRM 320R, was used in the quality control of the analytical data to quantify the recovery of the analyte spikes due to the extracted dissolutions obtained from the BCR procedure. The uncertainty thresholds of the CRM were calculated as twice the standard deviation of the certified value. Additionally, blank determinations and replicates were performed for 25% of the samples replicated with a standard deviation less than 9%.

3.2.2.3. Kinetic procedure and modelling

The sequential extraction protocols developed in the first and second rounds of sample monitoring were performed in equilibrium conditions to obtain thermodynamic information. However, the mobility rates of trace elements were not considered in these approaches (Gismera et al., 2004). Kinetic extraction by a single reagent can be defined as a proper approach to determining the distribution of species in a natural environment, especially at different pHs and with EDTA (Fangueiro et al., 2002, 2005; Gismera et al., 2004). EDTA and acetic acid have been used as reagents to assess the bioavailable fraction in the Standards, Measurements and Testing Programme, SM&T (Ure et al., 1993). Therefore, in this study, the mobility of trace elements in the Jequetepeque river basin sediments were evaluated using two single extraction treatments, using nitric acid (at different pH levels) and EDTA. Additionally, the labile and non-labile amounts obtained with each extractant were compared.

Additionally, kinetic experiments were performed using time-based extraction experiments with EDTA as the added extractant. Different kinetic models adapted to the sediment system were used to describe the experimental data. The parameters determined by the kinetic approaches were applied to the experimental data, and the results were evaluated in mobility terms.

Sample collection

To obtain information for the points closest to the mine sites, two monitoring points were selected for each sub-basin near the mines in the basin. This is interesting from a pollution standpoint, taking into consideration the sediment flux into the basin, by which most of the fine sediments are transported along the entire length of the river until it slows down as it flows into the reservoir.

The sediment samples were extracted from the second round of sediment monitoring and were dried and sieved as described previously. The samples chosen in this study were the Ll4 and Ll5 samples obtained near the Sipán S.L. Mine in June 2009 and the R0 and R1 samples obtained close to the Yanacocha S.R.L. Mine in November 2009 and July 2010, respectively (Figure 3.9).

HNO_3 extraction experiments

In order to extract the available trace elements concentrations from the sediment samples, batch experiments at 25ºC were performed under different pH. 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. Initial pH solutions were varied from 1 to 5 in order to (i) avoid the precipitation of trace elements, and (ii) to determine the concentration at low pH values (typical from mine pollution) and which are common pHs for rivers. Suspensions were then centrifuged for 30 min at 3000 rpm before filtration in a Selecta Centronic-BL centrifuge. The equilibrium pH was verified before analysis. The samples were filtered through 0.45mm cellulose filter paper (Millipore Corporation) and the solutions were stored at 4ºC before analysis.

For each obtained sample, two replicates of the extraction procedure were made; being discarded if some precipitate appears during the extraction. The pH was recorded with a pH & Ion-Meter GLP 22 Crison. All used regents were of analytical-regent-grade and purchased from Merck and ultra-pure water Milli-Q system-Millipore.

EDTA extraction experiments

The EDTA extraction methodology was the same described in the previous section. Determining the extraction rate data of trace elements for the four sediments samples was carried out by considering the optimum operating conditions obtained in previous studies, thus, the extracting solution of 0.0125 mol·dm^{-3} of EDTA at pH 5 was used. For kinetics, extractions were stirred for different time periods varying from 5 min to 24 hr. For times less than 1 hour, the solutions were not centrifuged.

Analytical methods

The analysis was equal as the second sediment monitoring performed. The concentration of Zn, Cd, Al, Fe, Cu, Pb, As and Ni were determined by inductively coupled plasma mass spectrometry and optical emission spectrometry (ICP-MS model OPTIMA 3000DV-Perkin Elmer and ICP-OES model) based on EPA 200.7 at the Scientific and Technological Centers from the Universitat de Barcelona. All used reagents were of analytical grade.

Quality assurance and quality control

The repeatability of the analysis was assessed using two replicates. The standard deviations were less than 10%. Therefore, the results obtained from the analyses performed can be considered adequate Kinetic modelling

Different kinetic models adapted to the sediment system were used to describe the experimental data. The diffusion model assumes that the complexation reaction of trace elements 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, Yu and Klarup 1994). This model is based on Fick's second law of diffusion. Studying trace element desorption from sediments, Fangueiro et al. (2005) considered the Fickian diffusion equation for the initial stages of the desorption process. The Fickian diffusion equation that describes the diffusion in and out a cylinder can be simplified as follows:

$$\frac{M_t}{M_\infty} = q_t = k_d\sqrt{t} \qquad (3.5)$$

where M^∞ is the amount of complex ML entering or leaving the sphere after an infinite time, the total amount M_t is the complex ML (diffusive substance) entering or leaving the sphere at time t, and k_d is the intraparticle diffusion rate constant (mg g^{-1} min$^{-1/2}$). The intraparticle diffusion model developed by Weber and Morris (1963) was used as an initial approach to describing the sediment desorption processes. The mathematical dependence of uptake q_t of solids on $t^{\frac{1}{2}}$ is obtained if the desorption process is considered to be influenced by diffusion in the spherical solid and by convective diffusion in the trace element solution (Valderrama et al., 2010). The fractional approach to equilibrium changes is a function of $\left(\frac{D_t}{R^2}\right)^{\frac{1}{2}}$, where R is the particle radius and D_t is the diffusivity of a trace element within the solid at time, *t* (Senthilkumaar et al., 2006).

The model for multiple first-order reactions provides information on the real physicochemical meaning of the results and seems to fit extraction rate data well. Hence, it is assumed that there are multiple first-order reactions concurrently taking place and that their rates are independent of each other, i.e., each reaction can be described as follows:

$$\frac{dQ_i}{dt} = k_i(Q_i^0 - Q_i) \qquad (3.6)$$

where Q_i represents the quantity of a desorbed trace element from compartment *i* per gram of sediment at time *t*, Q_i^0 is the quantity of the desorbed trace element per gram of sediment in compartment i at equilibrium (t=24 h) and k_i is the rate constant of the first-order reaction for each compartment *i.* Fangueiro et al. (2005) simplified this to a model for two first-order reactions model to classify the trace elements present in the sediment into three fractions. Thus, the following equations can be applied:

$$\frac{dQ_1}{dt} = k_1(Q_1^0 - Q_1) \qquad (3.7)$$

$$\frac{dQ_2}{dt} = k_2(Q_2^0 - Q_2) \qquad (3.8)$$

It is assumed that the reactions leading to desorption of each fraction are independent. Integrating for the initial conditions $Q_i^0 = 0$ at $t = 0$ and rearranging, the following expression is obtained:

$$Q = Q_1^0(1 - e^{-\ k_1 t}) + Q_2^0(1 - e^{-\ k_2 t}) \quad (3.9)$$

It is possible to apply this equation to the trace element extraction rate to determine the three fractions, characterised as follows: Q_1^0 and Q_2^0 (mg·g^{-1}) are the fractions of the trace element that are readily extractable, associated with the rate constant k_1 and k_2 respectively, and Q_3^0 is the fraction of the trace element that is not extractable, which is obtained as the by difference between the pseudo-total concentration of the trace element in sediment Q and the concentration extracted at equilibrium ($Q_1^0 + Q_2^0$).

The Elovich model, which describes the sorption process as a group of reaction mechanisms such as diffusion in the mass of dissolution, surface diffusion and activated catalytic surfaces, can be expressed in the following form:

$$\frac{dq_t}{dt} = a\, e^{-bq_t} \qquad (3.10)$$

Integrating equation (3.10) for $q_t = 0$ at $t = 0$ and q_t at $t = t$ and subsequently linearising the integrated equation results in the following expression:

$$q_t = \frac{1}{b}\ln(ab) + \frac{1}{b}\ln(t + t_0) \qquad (3.11)$$

where a and b are the parameters of the Elovich rate equation and t_0 is equal to $\frac{1}{(ab)}$ 1. If $a, b, and\ t \geq 1$, equation (3.11) can be further simplified as follows:

$$q_t = \frac{1}{b}\ln(ab) + \frac{1}{b}\ln(t) \qquad (3.12)$$

Thus, a and b are obtained by linear regression analysis of the $q_t = F(t)$ function (Ho and McKay 1998). The statistical parameters used to assess the quality of the fitting process were the standard error of the estimate (SEE) and the coefficient of determination (r^2). A relatively high value, close to 1, of the coefficient of r^2 and a low value of SEE were used as the criteria for the best fit.

3.2.3. Statistical Analysis

Multivariate statistical analysis helps to extract information about the similarities or dissimilarities between sampling sites, identification of water and sediment quality variables responsible for spatial and temporal variations in river water quality, the hidden factors explaining the structure of the data base, and the influence of possible sources (natural and anthropogenic) (Shrestha and Kazama, 2007).

In this study, all the data were processed by principal component analysis, PCA, and hierarchical cluster analysis, HCA. PCA was performed to ascertain the spatial and temporal trends of the elements in the basin. Then, with the results obtained from the PCA analyses, HCA was used to facilitate the interpretation of the data related to the sampling sites. To maximise the data used and to minimise the error, a data treatment procedure was used. The data were checked for gaps and statistical outliers prior to statistical analysis for each monitoring program conducted in this study. 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 results. The kurtosis and skewness statistics indicated that the transformed variables were closer to a normal distribution than the original variables for almost all the analytes.

Multivariate statistical analysis of the data for each step was conducted using the SPSS v15.0 software package. The Varimax normalised algorithm was used for the rotation of PCA, which facilitates interpretation of the principal component by maximising the variance of the extracted factors and reducing the uncertainties of initial unrotated factor loading (Han et al., 2006; Joshi and Balasubramanian, 2010; Li and Zhang, 2010a, b; Passos et al., 2010; Perez and Valiente, 2005; Shrestha and Kazama, 2007). The factor loadings obtained from the PCA were the inputs to the HCA analysis. HCA is the most commonly used cluster analysis method in environmental analysis and was chosen in this study to group samples on the basis of data similarities. HCA was applied using Ward's method of agglomeration, and the squared Euclidean distance was used as the measurement of similarity (Li and Zhang, 2010b; Perez and Valiente, 2005). The most similar points were grouped in clusters, and the process was repeated until all the points belonged to one cluster (Idris 2008).

In this study, statistical analyses of the following 5 sets of data were conducted using the same methodology: (i) the CAO and Stratus water data, (ii) the DESA data (iii) the water monitoring data collected in this study, (iv) the data from the first round of sediment monitoring, and (v) the data from the second round of sediment monitoring. These data sets were analysed separately because of the disparities in the data with respect to the samples, components, locations and time periods, as described before.

3.2.3.1. CAO and Stratus water data review

Bearing in mind that the purpose of the analysis is to reveal the dynamics of the trace elements from polluted site, the multivariate statistical analysis procedure described above was applied to the CAO and Stratus Consulting data. The wet season (October–March) data and dry season (April–September) data were analysed separately to obtain information about the distributions of the pollutants (Miller et al., 2002; Cánovas et al., 2008). It was also thought that the statistical analyses might reveal different variables governing seasonal variations in water quality (Andrade et. al., 2010; Li and Zhang 2010a, b).

The data subsets consisted of 65 sample points for the wet season and 51 sample points for the dry season (Figure 3.7). The concentrations of nitrate, sulphate, and ions of Al, Ag, As, Ba, Ca, Cd, Cu, Cr, Fe, Hg, Mg, Mn, Ni, Pb, Sn, Tl, and Zn were analysed.

3.2.3.2. DESA data review

This data set consists of 199 points from 14 monitoring sites (Figure 3.8). It should be noted that for pH, EC, TDS and Cd, the gaps in the data were significant; hence, these analytes were not included in the statistical analysis. The concentrations of Cu, Cr, Fe, Mn, Pb, and Zn were determined.

3.2.3.3. Water monitoring developed for this study

A total of 50 samples from 16 monitoring sites were processed by PCA and HCA (Figure 3.9). The variables used were pH, electroconductivity, and the concentrations of TDS, TSS, chloride, WAD cyanide, total cyanide, nitrite and nitrate, ammonium, sulphate, Al, As, Ca, Cd, Cr, Cu, Fe, Mg, Ni, Pb, and Zn.

3.2.3.4. First round of sediment monitoring

Data from 9 sediment sampling sites (Figure 3.10) were analysed to determine the sediment concentrations of Al, As, Cd, Cu, Cr, Fe, Mn, Hg, Ni, Pb, Sb, Sn, and Zn. PCA and HCA were applied to the concentrations found in the 9 samples, characterised as the sums of the values obtained in each step of the SES. In this analysis, a slight modification to the other analyses was applied: a threshold value of 0.001 mg/kg was set for the Hg and Sb concentrations for results below concentration detection limits..

3.2.3.5. Second round of sediment monitoring

A total of 42 samples obtained from 15 monitoring sites were analysed using the BCR three-step procedure and MW digestion (Figure 3.9). For each sample, the concentrations of Al, As, Cd, Cu, Cr, Fe, Hg, Ni, Pb, and Zn were determined. The concentrations were evaluated separately in each step of the BCR procedure. Therefore, 3 statistical analyses of the results of the BCR three-step procedure, plus one analysis of what was referred to as the pseudo-total sediment concentration, were conducted.

3.2.4. Risk Assessment

To evaluate the environmental status of the basin and the health risks associated with the trace elements detected in the samples obtained from the Jequetepeque river basin, three indicators were used. The health risk was assessed using a hazard quotient, HQ, for all the water samples analysed in this study. An enrichment factor, EF, was used to evaluate the impact on the environment of the trace elements bonded to sediments. An environmental risk assessment was applied using the risk assessment code approach to evaluate the mobility and persistence of trace elements in sediments and their associated environmental risk.

3.2.4.1. Health Risk Assessment

To characterise risks to human health from water ingestion of trace elements, the hazard quotients (HQs) were quantified (Chen and Liu, 2006; De Miguel et al., 2007; Li and Zhang, 2010a; Marcus et al., 2010; USEPA, 1989):

$$HQ = C_c / RfD \qquad (3.13)$$

where Cc is a constituent concentration in water, defined as the maximum concentration for a chemical, and RfD is the reference dose of ingestion, which originates from a risk-based concentration table (USEPA, May 2010). Exposure and risks were estimated conservatively as the maximum concentration for a chemical in a medium within the data set (Marcus et al., 2010).

HQ values between 1 and 10 indicate little potential for adverse effects, values between 10 and 100 indicate significant potential for adverse effects, and values of 100 or more indicate that adverse effects should be expected.

This work is based on Yacoub, C., Pérez-Foguet, A., Miralles, N. (2012). Spatial and temporal trace metal distribution of a Peruvian basin: recognizing trace metal sources and assessing the potential risk. J.Environ. Monit. Asses. It is also based on the proceedings of IWA Watermatex, June 2011, San Sebastian, Spain. pp. 870-877.

3.2.4.2. Enrichment factor determination

The The purpose of determining the enrichment factor, EF, is to identify the trace element sources by distinguishing anthropogenic and natural inputs and quantifying the impact in the case of anthropogenic contributions (Chen et al., 2007; Idris, 2008; Kartal et al., 2006; Luo et al., 2012; Reimann, 2005). This assessment is a geochemical approach based on the assumption that a linear relation exists between a reference element (RE) and other elements, always under natural sedimentation conditions, which identifies and quantifies human interventions in the natural cycles of the elements (Reimann, 2005).

In this study, 15 samples from the second round of sediment monitoring were evaluated to assess the anthropogenic impact at each sampling site. The EFs were calculated according to the following equation:

$$FE = \frac{(C_M/C_{RE})_{sample}}{(C_M/C_{RE})_{reference\ material}} \qquad (3.14)$$

where the numerator is the ratio of the concentration of the element considered, CM, to that of the reference element, CRE, for the sediment sample and the denominator is the same ratio for the reference material. The reference element should have the same matrix as the samples and should be free of trace element pollution.

In this study, the EF was calculated using the concentrations determined using the MW digestion procedure. Fe was chosen as the reference element, based on the homogenised data obtained from the microwave digestion, the specific sediment matrix of the samples, and observations in the literature (Deely and Fergusson, 1994; Idris, 2008; Kartal et al., 2006). The concentration of the reference element used was based on the coarse particle size (between 0.5 and 1 mm) because it is considered to be anthropogenic pollution-free (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 previously, this monitoring site was located in the upper part of the basin and was isolated from any productive activity. Therefore, the site can be considered a better source of 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, 2005; Reimann and de Caritat, 2005).).

3.2.4.3. Environmental implications and Risk Assessment

To ascertain the environmental implications of the trace element presents in the sample sediments in the Jequetepeque basin, the 3-step BCR results from the second round of sediment monitoring were evaluated. Because the element concentrations were determined for different bonded phases, the risk should be evaluated for each step of the BCR.

First, the three fractions of the BCR were summarised as a threat to the environment. Then, a risk assessment was performed according to the risk assessment code, RAC, (Andrade et al., 2010; Villalobos-Castañeda et al., 2011). RAC 1 was obtained by evaluating the amount of each element in the exchangeable phase divided by the total amount of the element, while RAC 2 was obtained from the results of the second phase of the BCR to ascertain the risk associated with Fe and Mn oxides and hydroxides, as shown in the following equations:

$$RAC\ 1 = \frac{C_{exchangeable\ phase}}{C_{pseudo-total\ digestion}} \qquad (3.15)$$

$$RAC\ 2 = \frac{C_{exchangeable\ phase} + C_{Reducible\ phase}}{C_{pseudo-total\ digestion}} \qquad (3.16)$$

where C is the trace element concentration in the exchangeable phase, reducible phase or the pseudo-total content of the trace element in the sample ($C_{\text{exchangeable}}$, $C_{\text{reducible}}$ and $C_{\text{pseudo-total}}$, respectively).

3.2.5. Ecological monitoring

The ease of application of a biological monitoring system for assessment of aquatic ecosystems is crucial, especially to ensure the sustainable use of water resources for the benefit of the public. It is important to develop identification keys and means of characterisation of macro-invertebrate communities based on a country's biota (Haileselasie and Teferi, 2012). Additionally, ecological assessment entails the application of ecological knowledge to environmental problem-solving, given the urgent need for investigation of the aquatic biodiversity of rivers (Alkins-Koo et al., 2004). An initial approach to ecological assessment of the Jequetepeque basin was developed in this study.

An ecological campaign was performed at 22 sampling sites in July 2010, in accordance with the Ecological Status of Andean Rivers protocol, ECOSTRIAND, developed by Acosta et al. 2009. This protocol was established after an exhaustive literature review of benthonic macro-invertebrates and vegetal communities found at elevations above 2000 m.a.s.l. in the Columbian, Ecuadorian, Peruvian and Bolivian Andes (Acosta et al., 2009).

The ECOSTRIAND protocol includes the implementation of three indexes: (i) the fluvial habitat index (IHF), to assess the fluvial habitat; (ii) the quality index for riparian forests (QBR), adapted to the Andean region (QBR-And), to assess riparian forest quality; and (iii) the Andean biotic index (ABI), based on the Iberian Biological Monitoring Working Party index (IBMWP), which has been widely tested (Munné and Prat, 2009).

The selection of reference sites, sample collection and the application of the ECOSTRIAND protocol indices are described below.

3.2.5.1. Reference site selection

A total of 18 reference sites were chosen from several sub-basins in the Jequetepeque basin (Figure 3.11). All the sites were located in the upper parts of the basin. These locations were chosen to enhance the available knowledge of macro-invertebrates. The initial approach taken in this study was to determine the baseline macro-invertebrate biodiversity in the Jequetepeque basin. To achieve that goal, the reference sites chosen were far apart, approximately 6–7 km apart on average, except for the San Juan sub-basin site, located approximately 30 km from other sites (Figure 3.11). An ecological status assessment was conducted using the ECOSTRIAND indices for areas that were thought might be affected be pollution and therefore might be at risk of adverse effects on the environment.

The following criteria were defined to select the reference sites (Owen et al., 2001): no upstream alterations, pollutant-focus spills or diffuse pollution; low population and infrastructure and reduced agriculture activities in the border area; no fish stocking in the area; drainage of the community through public lands; presence of alien or invasive species; and the chosen reference sites distributed throughout the basin to better assess its the biodiversity.

The reference sites were selected taking into account the possible pressures and impacts on the ecological status at each location. The characteristics that may cause degradation of the aquatic communities were measured. Then, the risk of occurrence of degradation was assessed using the three indexes described above (IHF, QBR-And and ABI) (Acosta and Prat, 2009).

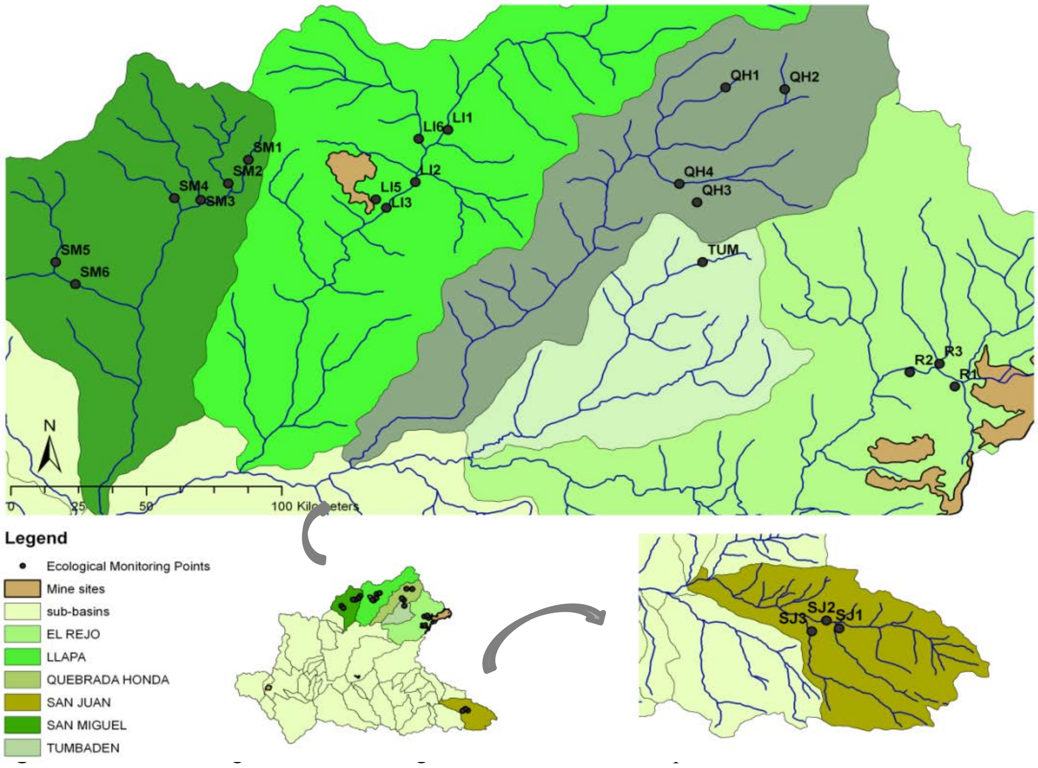


Figure 3.11: Monitoring sites of the Ecological Status River Andean protocol

The selection of the possible affected areas for ecological evaluation was based on identification of the most adversely affected locations in the water and sediment monitoring campaigns described before (Figure 3.9).

3.2.5.2. Sample collection

The sample collection procedure, including measurement of physicochemical properties in the field, the fluvial habitat monitoring, the riparian zone monitoring, macro-invertebrate monitoring, and identification procedures, is briefly summarised below. Further details can be found in the literature (Acosta et al., 2009; Pardo et al., 2002; Prat et al., 2009).

Physicochemical parameters

The physicochemical parameters measured were temperature, dissolved oxygen, electrical conductivity and pH. They were measured using a Wissenschaftlich-Technische Werkstätten 340i/SET multi-parameter tool. Additionally, the streamflow was measured by flotation to determine whether water conditions were modifying the river (Acosta et al., 2009).

Fluvial habitat monitoring

The fluvial habitat index, IHF, quantifies the heterogeneity of the fluvial habitat of a river bed. The IHF is considered a quick assessment index because the determination of the heterogeneity grade requires little time and can easily be accomplished in the field. The maximum value of the IHF is 100. Values of 75 or more are optimal, while values lower than 40 imply that a diminished presence of macro-invertebrates may be caused by the (natural or anthropogenic) poor status of the fluvial habitat (Acosta et al., 2009; Pardo et al., 2002; Prat et al., 2009). The IHF assessment is applied as shown in Table 3.6.

Table 3.6: IHF scale values. Source: Acosta et al, 2009; Pardo et al, 2002; Prat et al, 2009)

IHF	Quality Level
>75	Adequate habitat
40-75	Habitat with some constraints
<40	Habitat that could restrict the availability of some species

Riparian zone monitoring

The quality of the riparian zone was assessed using the QBR-And index (Acosta et al., 2009; Prat et al., 2008; Suarez-Alonso and Vidal-Abarca, 2000). The analysis was applied to 100 lineal meters of river bed along which the grade of the vegetal cover in the riparian zone, the vegetal cover structure, the vegetal cover quality and the natural grade of the fluvial bed were evaluated. Each section has a maximum value of 25, according to the classification shown Table 3.7.

Table 3.7: QBR-And index Quality ranges. Source: Acosta et al, 2009

QBR-And	Quality Level
≥ 96	Riparian zone without alteration, very good quality, natural status
76 - 96	Riparian zone slightly perturbed, good quality
51 - 75	Beginning of important alteration, intermediate quality
26 - 50	Strong alteration, bad quality
≤25	Extreme degradation, terrible quality

Macro-invertebrate monitoring

The applied protocol is a multi-habitat approach (Jáimez-Cuéllar P. et al., 2002) to collecting macro-invertebrate samples. All the habitats present at each sample site were evaluated, considering both the dominant habitats (sites with larger proportions of macro-invertebrates) and marginal habitats (sites with smaller proportions of macro-invertebrates). A D-net with a 300-µm mesh was used to collect the samples. The samples were preserved in plastic bottles with alcohol at 70º and fixed with formalin for posterior analysis.

After cleaning the samples, sample identification was conducted in the laboratory. A sub-sample of 200 macro-invertebrates was chosen randomly (Bonada et al., 2002). The residual sub-sample was also examined. If some taxon (group of one of more populations of organisms) was limited or was not detected before, it was included in the analysis. The taxon identification was performed at the family level, which provided enough information to assess the biodiversity and quality of the water (Bournaud et al., 1996; Rieradevall et al., 1998). The identification was conducted in collaboration with the Biology Department of the Universidad Nacional de Cajamarca. The water quality was assessed as very good, good, moderate, bad or terrible (Table 3.8).

Table 3.8: ABI quality ranges. Source: Acosta et al, 2009

ABI	Quality Level
>74	Very good
45-74	Good
27-44	Moderate
11-26	Bad
<11	Terrible

The quantity of macro-invertebrates per square meter was calculated for each monitoring site as a function of the area of the D-net used (0.04 m2) and the sampling methodology. The multi-habitat methodology applied to each point was the same: 10 points where extracted at each site, bearing in mind all the habitats present at each site, at different zones (lotic, lentic, with or without macrophytes) with roots and with different substrates (silt, clay).

3.2.5.2. ECOSTRIAND

In this study, the ecological status of the Jequetepeque river was assessed on the basis of the combination of the physicochemical properties and the three indexes described before: IHF, QBR-And and ABI. The physicochemical parameters and the IHF were determined as reference parameters for evaluating possible modified water conditions. The ecological status was determined as a function of the QBR-And and ABI results obtained. The ecological status was categorised as very good, good, regular, bad or terrible, following the classification of Table 3.9.

Table 3.9: Ecological Status classification. Source: Acosta et al, 2009

ABI	QBR-And		
	> 75	45-75	<45
> 74	Very good	Good	Regular
45-74	Good	Regular	Bad
27-44	Regular	Bad	Terrible
<27	Bad	Terrible	Terrible

4. Results and Discussion

This chapter discussed the results of this work. First of all, the hydrological modelling results were described and the hydrological characteristics of the basin were defined. Then, the data from different water monitorings was analysed and the conclusions drawn from the water quality at the basin were highlighted. After, similar analysis were performed for the data obtained for the sediment monitoring developed in order to assess the sediment quality implications to the environment. Kinetic of the trace elements from the most polluted sediment samples was also assessed. Finally, the ecological monitoring was developed to assess the quality of the ecosystem. It included a qualitative analysis of the flora and fauna, and a quantitative analysis of the macro-invertebrates.

4.1 Hydrological Modelling and uncertainty analysis

The aim of this study was to evaluate (i) the effect on the calibration process of including the terrain slope as a criterion of SWAT discretization on large mountain basins and (ii) the relative importance of the slope discretization versus the sub-basin discretization and the discretization by threshold values of definition. Therefore, 10 discretization examples were analysed, summarising a total of 30 cases evaluated in order to analyse the slope effects on the model applied to the Jequetepeque River Basin. This basin was considered a large mountain basin representative in terms of slope variations and size (with 80% of slope variation in more than 4,000 km^2), with existing data required for modelling.

4.1.1 Influence of the slope discretization criterion in the calibration process

In order to assess the influence of the slope discretization in calibration, two analyses were performed and verified: case 1 coarse and fine discretizations, C1C and C1F respectively (Table 3.2).

4.1.1.1 Parameter identification

After applying the LH-OAT method, 14 parameters out of a total of 28 were chosen for the parameter estimation; their sensitivity rank was given in Table 4.1. Ranks 1 to 6 were categorized as ‘important’, while ranks 7 to 20 as ‘slightly important’.

The meaning of each parameter was described briefly below. The base flow alpha factor (*Alpha_Bf*) is the direct index of groundwater flow response to changes in recharge (Smedema and Rycroft, 1983).

Average slope steepness (*Slope*) is a parameter related to topographic characteristics defined by the GIS topographic information. SWAT users frequently vary this value by soil type and land cover. Saturated hydraulic conductivity (*Soil_K*) relates the flux density to the hydraulic gradient and is a measure of the ease of water movement through the soil, while *Soil_Z* is the depth from soil surface to bottom of layer. *Esco* is the soil evaporation compensation factor and is related to the erosion processes. This factor allows

SWAT users to fit the depth distribution to the soil evaporative demand by capillary action, crusting and cracks.

CN_K2 is the effective hydraulic conductivity in the main channel alluvium while *CN_H2* is the Manning's *n* number for the main channel.

Cn2 is the runoff curve number for moisture condition II, calculated by the soil conservation service (SCS) runoff equation and adjusted soil moisture before a precipitation event. The runoff curve number is a function of the permeability of soils, land use, and antecedent soil water conditions. SWAT default values are appropriate for a 5% slope and are the typical curve numbers from moisture condition II for various lands and soil types (SCS Engineering Division, 1986).

Surlag is the surface runoff lag coefficient. SWAT incorporates a surface runoff storage feature to lag a portion of the surface runoff release to the main channel. The *Surlag* parameter controls the total available water that will be allowed to enter the main channel on any one day.

Canmax is the maximum canopy storage and is related to the land cover characteristics of the basin. Drops of rainfall may cause erosion, and the erosion reduction due to the plant cover and its morphology can be evaluated in SWAT by this parameter. *Epco* is the plant uptake compensation factor.

Gwqmn is the threshold depth of water in the shallow aquifer required for return flow to occur while *Revapmn* is the threshold depth of water in the shallow aquifer for evaporation and diffusion upward and for percolation to the deep aquifer to occur. The water movement from the shallow aquifer into the overlying unsaturated zone only occurs if the volume of water in the shallow aquifer is equal or greater than this factor (Neitsch et al., 2001a, 2001b).

Table 4.1: List of parameters chosen with sensitivity analysis (SA) and output analysis (OA) rank result, for two discretization cases (C1C and C1F).

Parameter	C1C		C1F	
	SA	OA	SA	OA
Alpha_Bf	4	2	4	2
Canmx	12	10	11	10
Ch_K2	1	3	1	3
Ch_N2	3	12	3	12
Cn2	2	1	2	1
Epco	16	14	15	14
Esco	5	4	5	4
Gwqmn	15	15	14	15
Revapmn	27	27	27	27
Slope	11	6	12	6
Sol_Awc	9	9	9	9
Sol_K	10	5	10	5
Sol_Z	7	8	6	7
Surlag	6	11	7	11

Despite having the lowest sensitivity, the *Canmx*, *Epco, Gwqmn, Revapmn*, and *Soil_Awc* parameters were included in the parameter estimation, because they are highlighted in the literature (Van Griensven et al., 2006) and in a previous work made for this basin (Yacoub C. and Pérez-Foguet A., 2010. Assessing slope influence in ArcSWAT model of Andean watersheds. In the proceedings of XVIII International Conference of Computational Methods in Water Resources, June 2010, Barcelona, Spain)

Similar parameters were chosen for calibration in basins with comparable characteristics (Fadil et al., 2011; Hörmann et al., 2009; Setegn, 2010; Yang et al., 2008). Since differences between coarse and fine discretizations were small (Table 4.1), the same 14 parameters were chosen for the parameter estimation. This result illustrated that the relevance of parameters do not depend significantly on including terrain slope as a discretization criterion.

4.1.1.2. Parameter estimation

Similar results were obtained for both discretizations. This match was not surprising, as there is the same selected space of the algorithm for the two discretizations, since the set of parameters were the same and the values of the objective function were similar. Additionally, the total number of runs was similar for the two approximations. No significant differences between either case were present, except for the computational cost (the cost of fine discretization approximately twice that of coarse).

Table 4.2 gave the obtained parameter values for three instances: the fine discretization and the coarse discretization. In order to appraise the differences on the achieved values, the significance of each obtained parameter values and its sensitivity were discussed below. Extremely small differences were presented in the most sensitive parameters, *Cn2*, *CH_N2*, *CH_K2* and *Esco*. Indeed, minimal differences of these parameters were found when comparing the C1C and C1F cases.

Table 4.2: Parameter estimation for C1C and C1F discretizations

Parameter	C1C	C1F
Alpha_Bf	0.206	0.976
Canmx	0.215	2.923
Ch_K2	148.55	100.62
Ch_N2	0.203	0.229
Cn2	1.235	1.189
Epco	0.406	0.359
Esco	0.976	0.831
Gwqmn	933	44.186
Revapmn	72.725	478.86
Slope	1.223	1.231
Sol_Awc	1.164	0.974
Sol_K	1.074	1.035
Sol_Z	0.817	1.083
Surlag	0.259	0.026

However, it should be pointed out that these values showed better simulation results for the coarse discretization, except for the most sensitive, the *CH_K2*, which had a better adjustment for the fine discretization. This may be due to the meaning of the parameters, with *CH_K2* being the one most influenced of the size area of the HRU. Note that the calculations of the effective hydraulic conductivity in the main channel are described in each HRU. Hence, a better match was obtained since the HRUs were more realistic in the fine discretization than in the coarse. Additionally, the sensitive *Surlag* parameter presented a difference of one order of magnitude between the two cases. The low *Surlag* values were predicted because of the basin characteristics: water was first stored and then slowly drained out. The two cases agreed with each other in this point, but an extremely minor and unrealistic value was obtained for the fine discretization case.

On the other hand, a significant difference was found for another important parameter: *Alpha_Bf*. It varied from one extreme of the interval that exhibits a land with slow hydrological response values (for the coarse discretization) to the other extreme, with fast hydrological response values (for the fine discretization). The high values obtained for the fine case can be considered unrealistic as the basin has a slow hydrological response due to the Páramo soils located at the upper part (Molina et al., 2007). The disparity in this value could reflect model and/or experimental error (Green and Van Griensven, 2008). As mentioned earlier, these differences appeared to not effect on the response of the basin, but coarse discretization seemed to be closer to the natural behaviour of the basin. Last, *Epco*, with also small sensitivity, presented no changes between the two discretizations.

4.1.1.3. Verification

Figures 4.1 and 4.2 showed hydrographs for coarse and fine discretizations simulated with the respective best parameter set obtained in the automatic calibration. Figure 4.1 showed the calibration period and Figure 4.2 showed the validation period. The obtained calibration gave very good hydrographs for both.

Differences in calibration between the two cases showed a rapid response at the beginning of the rainy season (mainly in October and November) for the fine discretization case, whereas the coarse discretization case showed an increased drainage at the end of the rainy season (between May and April) (Figure 4.1). Therefore, better minor adjustments were obtained for the fine discretization case than for the coarse. Additionally, the discretization including slope as a criterion for HRU (the fine one), gave better validation than not include it. It is also considering the end of the rainy season (Figure 4.2). Based on these findings, the model was able to simulate a reliable scenario with both discretizations using its corresponding set of parameters.

Table 4.3 showed the quantitative statistics obtained for calibration and validation for coarse and fine discretizations from C1. According to Moriasi et al. (2007), results showed “very good” values for all statistics in all cases of discretization with calibration and validation simulation results, excluding the

PBIAS from fine discretization (defined as a “good” result). Moreover, comparing the obtained values with values from the literature of the SWAT model gave very good values in most of the cases for all the assessed statistics (Bonuma et al., 2011; Fadil et al., 2011; Huang et al., 2008; Moriasi et al., 2007; Muleta et al., 2007; Sulis et al., 2009; Vazquez and Engel, 2008).

The best NSE and RSR calibration values were achieved for the fine discretization C1F, although at the same time, the worse PBIAS was obtained by comparing with C1C. On the other hand, for the validation period, the results showed slighter differences between coarse and fine discretizations than for calibration, with less sensitivity to the slope variations.

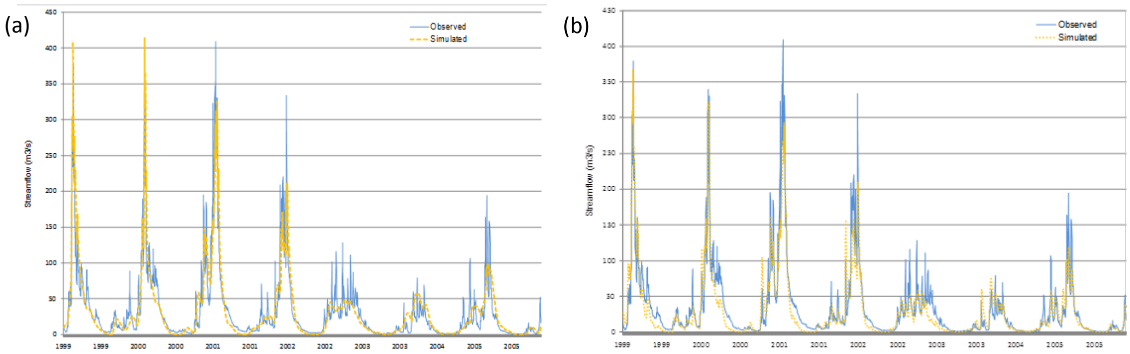


Figure 4.1: Comparison of measured and simulated daily streamflow (m^3/s) from 1999 to 2005 for (a) coarse discretization case and (b) fine discretization case

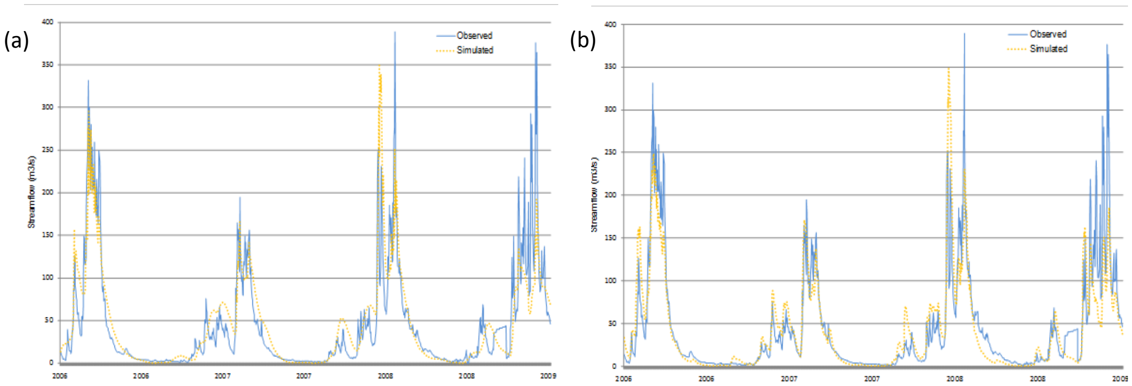


Figure 4.2: Comparison of measured and simulated daily streamflow (m^3/s) from 2006 to 2009 for (a) coarse discretization case and (b) fine discretization case

As discussed in the last section, the set of parameters from the coarse discretization was considered to be better than the fine one. This is in agreement with some findings showed in Table 4.3 and Figures 4.1 and 4.2. Hydrographs and PBIAS statistics showed improved values for the calibrated set of parameters obtained for the coarse discretization as compared to those of the fine one, taking into account the very good defined values for calibration and validation of the SWAT model (Moriasi et al., 2007).

Considering this, it can be concluded that the automatic calibrations were better for a coarse mesh, and that the finest discretization due to slope criterion did not imply a better automatic calibration. Some authors have reported the relatively insensitivity of streamflow predictions to different discretizations (Gassman et al., 2007; Merz et al., 2009; Migliaccio and Chaubey, 2008; Muleta et al., 2007, Setegn, 2010). The present study results agreed with this, emphasizing perhaps that a slightly better improvement is obtained for coarse discretization. The better results for coarse discretizations were also suggested in a similar size basin (2010 km^2) by Gong et al. (2010).

Table 4.3: Statistic values for calibrated and validated streamflow for C1C and C1F with its respective set of parameters

		nº Sub-basins	nº HRUs	NSE	RSR	PBIAS
Calibration	C1C – best p-val.	28	94	0.819	0.425	0.024
	C1C – median of good p-values	28	94	0.824	0.420	0.020
	C1F – best p-val.	28	436	0.857	0.379	0.128
Validation	C1C – best p-val.	28	94	0.705	0.543	-0.031
	C1C – median of good p-values	28	94	0.717	0.532	-0.033
	C1F - best p-val.	28	436	0.739	0.511	0.054

4.1.2 Influence of the slope discretization criterion compared to other discretization criteria

In order to assess the influences of sub-basin discretization and threshold implication on model simulation, five cases were discussed below. The evaluation was performed three times, applying (i) the coarse set of parameters obtained from the coarse discretization calibration, to the CnC cases, (ii) the fine set of parameters obtained from the fine discretization calibration to the CnF cases, and (iii) the coarse set of parameters obtained from the coarse discretization calibration to the CnF cases, given in Table 4.4.

4.1.2.1. The set of parameters of C1C calibration to CnC discretizations

The statistics for the calibration and validation periods are given in Table 4.4. The statistics showed that decreasing the number of HRUs resulted in worse simulation results than the default discretization, while increasing it did not necessarily improve the simulation results. They only slightly improved for the validation period. Taking into account that the sub-basins increased the number of HRUs by more than 4:1, this improvement was considered to be minor, while the automatic sub-basin structure represented a better enhancement. Additionally, the implications of changing the threshold values to increase the number of HRUs (C5), which means increasing by two-fold the number of HRUs respective to the default values, only presented better adjustment for PBIAS in the validated periods, so that we concluded that the default threshold values were more appropriate.

4.1.2.2. The set of parameters of C1F calibration to CnF discretizations

The results obtained were summarised in Table 4.4. Comparing the results from the two sets of parameter, better simulation results were obtained without considering the slope to be a criterion for a number of sub-basins equal or less than to the default sub-basin discretization. However, spreading the number of discretizations up to 28 resulted in the opposite behaviour: better simulation results were obtained for the fine discretization case than for the coarse one. This may be due to the fact that the increase in the number of sub-basins fitted better with more slope-detailed values.

Table 4.4: Statistic values obtained for all the cases, with different set of parameters from different discretizations for calibrated and validated streamflow

Set of parameters	Discret. Case	nº Sub-basins	nº HRUs	Calibration		
				NSE	RSR	PBIAS
C1C-best	C1C	28	94	0.824	0.420	0.020
	C2C	12	44	0.714	0.535	-0.152
	C3C	19	62	0.758	0.491	0.491
	C4C	35	119	0.826	0.417	0.067
	C5C	28	188	0.817	0.428	0.054
C1F -best	C1F	28	436	0.859	0.376	0.124
	C2F	12	208	0.828	0.415	-0.105
	C3F	19	293	0.840	0.400	-0.028
	C4F	35	538	0.852	0.385	0.158
	C5F	28	859	0.848	0.390	0.149
C1C-best	C1F	28	436	0.820	0.424	0.035
	C2F	12	208	0.703	0.545	-0.154
	C3F	19	293	0.737	0.512	-0.129
	C4F	35	538	0.830	0.412	0.066
	C5F	28	859	0.821	0.424	0.052

Set of parameters	Discret. Case	nº Sub-basins	nº HRUs	Validation		
				NSE	RSR	PBIAS
C1C-best	C1C	28	94	0.705	0.543	-0.031
	C2C	12	44	0.645	0.595	-0.102
	C3C	19	62	0.690	0.557	-0.069
	C4C	35	119	0.717	0.532	0.024
	C5C	28	188	0.703	0.545	0.004
C1F -best	C1F	28	436	0.741	0.509	0.060
	C2F	12	208	0.729	0.521	-0.183
	C3F	19	293	0.736	0.514	-0.110
	C4F	35	538	0.743	0.506	0.091
	C5F	28	859	0.719	0.530	0.088
C1C-best	C1F	28	436	0.711	0.538	-0.020
	C2F	12	208	0.636	0.604	-0.106
	C3F	19	293	0.678	0.568	-0.078
	C4F	35	538	0.692	0.555	0.106
	C5F	28	859	0.695	0.552	0.002

4.1.2.3. The set of parameters of C1C calibration to CnF discretizations

As observed earlier, the set of the parameters obtained from the fine case was unrealistic. For that reason, the set of parameters from the C1-coarse discretization, C1C, was applied to the fine discretization (Table

4.4). For calibration and validation periods, the statistic values were close to the values obtained with the coarse discretization and coarse set of parameters, while the obtained values were slightly better for the fine discretization than for the coarse (for the coarse set of parameters). Once a good parameter set was chosen, the slope discretization obtained best results.

In general, it can be concluded that, despite the slope discretization, increasing the number of HRUs improved the NSE, RSR, and PBIAS values for calibration and validation, and therefore enhanced the modelation. Nevertheless, increasing the number of HRUs could be a concern due to the (i) the spread of the number of sub-basins, or (ii) the modification of the threshold values (C4 and C5 respectively), which showed slightly better NSE and RSE values in calibration, but slightly worse values for validation, than case 1. Therefore, the included information (increasing the number of soil types and land uses) in these slight percentages was not a determining factor for achieving better results. This is in agreement with findings in the literature (Haverkampt et al., 2002), which define that for streamflow simulations, increasing the number of sub-basins was more sensitive than characterizing the basin with the land use and soil criteria.

Additionally, the default sub-basin discretization was considered to be the best option, taking into consideration the slight improvements on the above mentioned indicators and the number of increased HRUs (approximately 25% more for the C4, and almost twice for the C5), and therefore the computational time needed. Hence, to include terrain slope in discretization, criteria were less critical that choosing an adequate number of sub-basins.

4.1.3 Conclusions

The results presented here showed that distributed hydrologic models as a complex as SWAT, in large catchments (3,564.8 km^2) and without large amounts of data (11 years), can successfully be automatically calibrated and validated. Calibration was applied for (i) coarse spatial discretization (without the slope in the discretization criterion) and (ii) fine spatial discretization (with the slope in the discretization criterion). The performed sensitivity analysis showed that parameters slightly depend on slope inclusion, and emphasized the importance of considering output values in parameter specification.

The simulations presented different behaviour: a fast response was obtained for the fine discretization case, and a slow one for the coarse discretization. Hence, the set of calibrated parameters for the coarse spatial discretization seemed to be more realistic than the fine one. Thus, including slope as a discretization criterion was not a determining factor for obtaining better calibrations. This is significant, considering that the computational cost (CPU time) of the fine discretization was slightly more than twice that of the coarse one.

Five different cases of sub-basin discretization were evaluated with and without the slope criterion, resulting in very good hydrographs and statistics for all cases. As a result, the influence of slope in run-off simulations was a less determining factor than the sub-basin discretization. Best results were obtained with the default sub-basin discretization, the same one used in calibration. On the other hand, increasing the number of HRUs by decreasing the threshold values did not ensure better results with the default sub-basin discretizations.

The inclusion of slope led to a significant improvement of simulation results when discretizations with a reduced number of sub-basins (less than the default discretization) were used. In these cases, including slope enhanced the simulation results. A minimum precision of spatial discretization is needed for simulation. It can be provided when sub-basins are delineated or, later, when HRUs are defined. In this case, the inclusion of slope as a criterion did not offer an advantage with respect to fixing the other thresholds with a lower value. Variability of land uses and soil types cannot be supplied by large requirements of proper slope representation.

4.2 Water monitoring

In this work, 4 campaigns of water samples were designed, implemented and analysed. A special effort was made to compile the existent water trace element analyses performed in the Jequetepeque basin. Then, three independent statistical analyses were developed (i) CAO and Stratus Consulting data review, (ii) DESA data review, and (iii) the water monitoring carried out in this survey as described previously (Section 3.2.1.).

First, the data from the CAO and the Stratus Inc. Consulting was analysed together because of they have applied similar components, in the same area and with the same detection ranges. On the other hand, DESA data was examined separately from the specific monitoring program developed because of the remarkable differences between the monitored components, the difference in the sampling points and the existent gaps present the DESA.

Multivariate statistical techniques such principal component analysis (PCA) and hierarchical cluster analysis (HCA), are useful in large data matrix to gain knowledge about the distribution of pollutants and its sources. In order to detect the similarities and differences between the data, the PCA (Bengraine and Marhaba, 2003; Joshi and Balasubramanian, 2010; Kartal et al., 2006; Li and Zhang, 2010a; Passos et al., 2010; Shrestha and Kazama, 2007), and HCA were carried out (Han et al., 2006; Li and Zhang, 2010b; Perez and Valiente, 2005).

In order to reveal the sources and the spatial distribution, PCA was applied to 443 water samples in the Jequetepeque basin as described in Section 3.2.3. Then, the trace elements sources and spatial and temporal distributions were assessed at the basin level to ascertain the possible risk of pollution. Finally, the hazard quotient (HQ) was developed for the three cases to evaluate the risk associated with the water ingestion.

4.2.1 CAO and Stratus data review

The data from monitorings performed in the Rejo sub-basin from CAO and Stratus studies, were analysed to identify seasonal water quality variables (Section 3.2.1.1). Differences of trace element concentration between the seasons were not as great as expected (Table 4.5).

Table 4.5: Analysis of variance for trace element concentrations (in µg/l) for each season in the Rejo sub-basin

	Dry season				Wet season			
	Mean	S.D.	Min	Max	Mean	S.D.	Min	Max
Nitrate	456.9	989	4	4080	155.3	252.1	0	1000
Sulphate	65169	103403	6000	472000	53876	88507	1280	410000
Chloride	-	-	-	-	2156	5562	147	4770
Ca	29259	47065	3.3	166000	28458	48686	2.3	170000
Mg	2362	6468	0.3	28400	1254	4265	0.3	26600
Ag	0.9	1.67	0	5	0.76	1.59	0	7
Al	205.4	514.7	0	2870	246.1	527.1	10.7	3430
As	6.8	9.6	0	40.7	6.35	4.86	0.4	20.2
Ba	50.2	32.3	18	167	49.62	29.72	18.6	161
Cd	1.1	1.66	0	5	1.58	1.72	0	5
Cr	2.1	3.39	0	10	1.72	3.05	0	10
Cu	5.9	8.32	0.19	42	10.79	12.54	0	57
Fe	389.5	539.2	0	2460	265.6	453	25	2830
Hg	0.1	0.13	0	0.4	0.1	0.14	0	0.5
Mn	201.9	306.4	4.86	1550	150.1	185.3	12	902
Ni	3.4	3.41	0.23	10	4.62	3.73	0	13
Pb	6.8	10.3	0	56	10.42	9.52	0	42.7
Se	1	0.97	0	3.7	0.88	1.6	0	10
Tl	2.7	4.06	0.02	10	4.94	5.53	0.02	25
Zn	33.1	34.4	1.87	138	49.58	52.6	1.34	225

The dry season includes April to September; the wet season includes October to March.
MCLG: maximum contaminant level goal. MCL: maximum contaminant level.

PCA was applied to assist in the identification of sources of pollutants by using the software package SPSS 15.0. Tables 4.6 and 4.7 gave the factor loadings, eigenvalues and cumulative percentages of variances with a Varimax rotation during the wet and the dry season respectively. PCA of the dataset evolved 4 and 5 PCs both with eigenvalues >1, explaining about 83% and 85% of the total variances during the wet season and the dry season respectively.

There were high correlations among the elements on each factor, which means that the sources were different for each group of elements. During the wet season, the first factor was dominated by As, Pb, Tl, Ca and Mg, accounting for 31.4% of the total variance. The dry season presented the same factor explaining the 24.7% of the total variance. This factor could be attributed to anthropogenic activities, due to mineral deposit contains elevated concentration of As and Pb (MWH Americas Inc., 2006).

Table 4.6: Rotated component matrix during the wet season data (n= 65). Values below 0.3 are not shown

Element	Principal Components				Communalities
	1	2	3	4	
As	**0.93**				0.91
Ba				**0.92**	0.88
Cd	0.58	**0.70**			0.86
Cu		**0.88**			0.86
Pb	**0.84**				0.81
Ni	0.63	**0.65**			0.87
Tl	**0.78**		0.41		0.81
Zn		**0.86**			0.77
Ca	**0.88**	0.37			0.96
Fe			0.41	**0.83**	0.87
Mg	**0.90**	0.31			0.96
Mn		**0.84**		0.30	0.86
Al			**0.87**		0.84
Cl		0.35	-0.66		0.60
Sulphate		**0.72**	-0.33		0.69
Eigenvalues	4.70	4.12	1.93	1.79	
Cumulative %	31.36	58.85	71.73	83.66	

PCA loadings > 0.65 are shown in bold

Table 4.7: Rotated component matrix during the dry season data (n=51). Values below 0.3 are not shown

Element	Principal Components					Communalities
	1	2	3	4	5	
As	**0.90**					0.87
Ba				**0.86**		0.79
Cd					**0.93**	0.91
Cu		0.58	0.54		0.46	0.87
Pb	**0.80**		0.44			0.89
Ni	0.48		0.33	0.39	0.63	0.89
Tl	**0.79**		0.52			0.91
Zn	0.34	0.47	0.63	0.34		0.84
Ca	**0.70**	0.55		0.32		0.93
Fe	0.37			**0.76**		0.75
Mg	**0.71**	0.50		0.38		0.93
Mn		**0.69**		0.58		0.86
Al			**0.81**			0.80
Cl		**0.88**				0.81
Sulphate		**0.85**				0.78
Eigenvalues	3.70	3.17	1.98	2.33	1.66	
Cumulative %	24.68	45.80	59.03	74.55	85.59	

PCA loadings > 0.65 are shown in bold

The second factor was loaded primarily by sulphate, Mn, Cu, and Zn. Significant differences were obtained between two seasons. The dry season presented weaker loadings of Cu and Zn and stronger loadings of chloride than the wet season. Additionally, moderate loadings of Ca and Mg appeared during the dry season. It may be due to the management of the water treatment plant, which uses $FeCl_3$ and lime.

The third factor showed strong positive loadings for Al, while Ba and Fe reported strong loadings for PC4, explaining around 15 - 11 % of the total variance for both seasons respectively. Al is most abundant in earth crust, and Ba and Fe primarily derives from geology, suggesting possibly different soil sources (Romero et. al., 2006; Li et. al., 2010a, b).

The fifth factor was given only during the dry season, accounting about 11% of the total variance mainly contributed by Cd, while during the wet season Cd is related to factor 2. It could suggest a difference source of Cd between seasons, or could be related to the easy Cd release from sediments.

Relationship between individual samples and each loading classifies samples with similar pollutant trends. There was a separation between the samples in two main groups. First group included four samples from CAO study near the mine sites (C1, C2, C11 and C12 samples; see Figure 3.7). In this group, most contaminated samples of all the data were present with strong loadings of factors 1 and 3. It presented a common feature: all the samples come from mine drainages with lime treatment. Therefore, As, Pb, Tl, Ca and Mg were predominantly originating by mining.

It should be noted that this group only showed sample points located near Cerro Negro open pit, which began its operation in 2003, just at the same year that CAO monitoring was carried out. For that reason, we assume sample points from Stratus INC study were not included in this group. As an exception, there was an outlier sample (S8), located around 8km downstream of the mine sites, which reported strongest correlation with factor 3. Thus, elevated concentrations of Al were present for that point in both seasons. Taking it into account, great amounts of Al can be considered released due to their predominant presence in mineral deposits as alunites (MWH Americas Inc. 2002, 2006).

The other group of samples was concerned with drainages from water treatment plant and leach PADs. For each season, six samples located downstream of the mine sites (C3, C4, C5, C6, C7 and S8) presented high sulphate, Mn, Ba and Fe contents, being the main variables contributing to factors 2 and 4 (Figure 4.3).

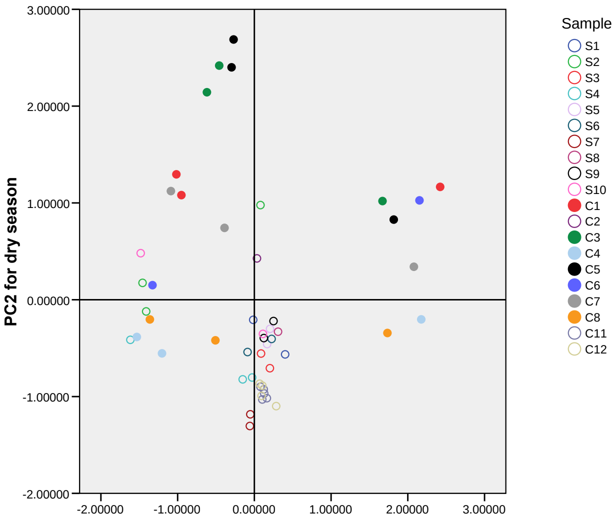


Figure 4.3: Plot of loadings of the PC2 and PC5 during the dry season

Ba and Fe were predominantly obtained during the wet season originating from pedogenic process and mineral weathering (Romero et. al., 2006; Li et. al., 2010b). Specifically, three samples (C4, C6 and S8) reported higher Ba and Fe content than the other samples; it may suggest mixed sources in the area (geogenic origins and mining) for these points.

On the other hand, this group showed significant differences between two seasons for factor 2. The wet season included Cd, Ni, Cu and Zn with high correlations for two sampling points near the mine site (C3 and C5), while sampling points from Stratus INC study (S8, S9, S10) and some outliers carried out in November were characterized by moderate contents. As mentioned before, the dry season included chloride, Cu, Ca and Mg mainly for two sampling points near mine site (C3 and C5). Specifically, samples carried out in August and September reported strong correlations with factor 2 (C1, C6, C7 and S2).

Finally, Ni and Cd presented different behaviour, showing high contents for samples taken in August from CAO study, except for two points near Cerro Negro open pit (C11 and C12). Ni and Cd may be originating from the mine operations due to samples come from drainage leaching pads.

4.2.2 DESA data review

Mean concentrations and standard deviations of each monitoring site collected by DESA from 2004 to 2008 were given in Table 4.8. Considering that low concentrations with homogeneous distribution across the site and therefore lower standard deviations indicate a major natural source or lithogenic character, whereas high pollutant concentrations accompanied by high standard deviations suggest anthropogenic sources (Pérez and Valiente, 2005), some highlights were extracted from Table 4.8.

The highest concentrations and standard deviations were found in Ll5 and in a lesser extent, to Ll4, SJ1 and R00 indicating an anthropogenic source, while homogeneous distributions were obtained for the other monitoring sites. Highest mean values and standard deviations of pH, EC TDS, and Cd were present in Ll5, while considerable EC values were also obtained for R00 and P1 monitoring sites. The two first sites are located nearby mine areas, whereas P1 is located downstream, highlighting a peak of concentration related to anthropogenic sources.

The factor scores of the 6 available trace element concentrations the loadings of the principal components and the cumulative percentages for the rotated matrix were given in Table 4.9. The 4 components accounted for more than 90% of the total variance. All four contributed to a similar extent to the overall variance, being the first one the principal contribution. The communalities values were over 0.7, supporting the decision to use the four factors.

Table 4.8: Mean and standard deviation for the number of samples obtained in each sampling point (nº) for the concentrations of the DESA water samples, from 2003 to 2008. All the analytes are in mg/l except for EC (in µS/cm) and pH

	pH	EC	TDS	Cd	Cr	Cu	Fe	Mn	Pb	Zn
Llapa sub-basin samples										
Ll00	7.85 ± 0.89 (6)	118 ± 36 (5)	75 (1)	<0.01 (3)	<0.05 (8)	0.41± 1.13 (8)	10.7 ± 23.7 (8)	0.4 ± 1.02 (8)	<0.025 (8)	0.05± 0.037 (8)
Ll4	6.77± 1.53 (16)	437 ± 317 (14)	199 ± 133 (9)	<0.01 (11)	<0.05 (18)	0.35 ± 0.85 (18)	6.6 ± 16.2 (18)	0.55 ± 0.64 (18)	0.026 ± 0.003 (18)	0.46 ± 0.93 (18)
Ll5	5.02 ± 1.80 (9)	1810 ± 753 (7)	976 ± 378 (3)	0.05 ± 0.08 (6)	0.05 ± 0.005 (19)	9.53 ± 17.1 (19)	455 ± 1476 (19)	5.39 ± 6.93 (19)	0.1 ± 0.166 (19)	0.9± 0.79 (19)
Ll6	7.39 ± 0.61 (16)	159 ± 37 (15)	83 ± 19 (11)	<0.01 (11)	0.05 ± 0.01 (19)	0.41 ± 0.93 (19)	3.2± 3.78 (19)	0.16 ± 0.13 (19)	<0.025 (19)	0.1 ± 0.14 (19)
Rejo sub-basin samples										
R00	7.37 ± 0.55 (19)	366 ± 156 (16)	209 ± 75 (11)	<0.01 (13)	0.048 ± 0.01 (20)	0.22 ± 0.85 (20)	1.5 ± 4.2 (20)	0.49 ± 1.29 (20)	0.028 ± 0.011 (20)	0.074 ± 0.04 (20)
R5	7.6 ± 0.56 (16)	83 ± 37 (13)	42 ± 22 (9)	<0.01 (11)	<0.05 (17)	<0.01 (17)	0.36 ± 0.16 (17)	0.03 ± 0.01 (17)	0.025 ± 0.001 (17)	0.039 ± 0.004 (17)
R6	7.7 ± 0.74 (14)	72 ± 26 (11)	38 ±13 (7)	<0.01 (10)	<0.05 (15)	0.008 ± 0.01 (15)	0.56 ± 0.31 (15)	0.09 ± 0.12 (15)	<0.025 (15)	0.049 ± 0.026 (15)
San Juan sub-basin samples										
SJ1	7.9 ± 0.65 (10)	255 ± 66 (8)	129 ± 34 (8)	<0.01 (10)	<0.05 (13)	0.007± 0.004 (13)	2.22 ± 4.31 (13)	0.96 ± 3.36 (13)	<0.025 (13)	1.33 ± 4.64 (13)
SJ2	8.18 ± 0.53 (7)	335 ± 88 (7)	169 ± 45 (6)	<0.01 (6)	<0.05 (9)	0.007 ± 0.005 (9)	1.75 ± 1.69 (9)	0.05 ± 0.046 (9)	0.027 ± 0.004 (9)	0.056 ± 0.028 (9)
SJ3	7.96 ± 0.45 (9)	333 ± 137 (6)	166 ± 68 (6)	<0.01 (9)	<0.05 (11)	0.014 ± 0.022 (11)	4.78 ± 9.04 (11)	0.16 ± 0.23 (11)	0.03 ± 0.01 (11)	0.129 ± 0.18 (11)
Puclush river sample										
P1	7.73 ± 0.71 (18)	206 ± 111 (16)	108 ±61 (10)	<0.01 (13)	0.052 ± 0.02 (20)	0.041 ± 0.057 (20)	2.09 ± 2.1 (20)	0.081 ± 0.06 (20)	0.025 ± 0.001 (20)	0.056 ±0.06 (20)
Alto Jequetepeque sub-basin samples										
T5	8.26 ± 0.4 (9)	294 ± 60 (7)	152 ± 29 (6)	<0.01 (6)	0.042 ± 0.02 (11)	0.041 ± 0.087 (11)	6.36 ± 9.2 (11)	0.33 ± 0.43 (11)	0.028 ± 0.008 (11)	0.158 ± 0.269 (11)
T6	8.25 ± 0.4 (6)	249 ± 26 (5)	125 ± 13 (5)	<0.01 (5)	<0.05 (7)	0.011 ± 0.01 (7)	0.33± 0.17 (7)	0.028 ± 0.005 (7)	<0.025 (7)	0.048 ± 0.026 (7)
T7	7.92 ± 0.39 (11)	563 ± 242 (8)	283 ± 124 (8)	<0.01 (8)	0.043 ± 0.02 (12)	0.011 ± 0.02 (12)	0.21 ± 0.16 (12)	0.24 ± 0.56 (12)	0.03 ± 0.018 (12)	0.043± 0.017 (12)

The first factor, F1, explained 28.6% of the total variance and was heavily correlated on Zn, and weakly on Mn and Fe. The second factor, F2, was highly dominated by Cu, and in a lesser extent by Fe and Mn, accounting for 27.3% of the total variance. The third factor, F3, was dominated to Pb and accounts for 17.9% of the total variance. The fourth factor, F4, strongly depended on Cr with a total variance of 16.8%.

Table 4.9: Varimax rotated values for water samples of the DESA data (*n* = 199). Values below 0.3 are not shown

	Principal Components				
Elements	1	2	3	4	Communalities
Cu		**0.923**			0.921
Cr				**0.997**	0.997
Fe	0.548	0.617			0.746
Mn	**0.681**	0.560			0.846
Pb			**0.944**		0.997
Zn	**0.918**				0.923
Eigenvalues	1.71	1.63	1.07	1.01	
Cumulative Variance (%)	28.55	55.78	73.67	90.52	

PCA loadings > 0.65 are shown in bold

HCA was performed with the factor loadings obtained from the PCA (Han et al., 2006; Li and Zhang, 2010b; Perez and Valiente, 2005); suggesting a total number of 5 groups. Score plots can illustrate the relationships between all the samples, being a satisfactory manner to obtain the polluted areas (Han et al., 2006; Kartal et al., 2006). In this sense, the obtained clusters were plotted according to the factors (Figure 4.4) highlighting some insights.

The higher peaks of Zn, Fe and Mn (F1) were presented mainly in Ll4, Ll5 and SJ1 as highlight cluster 5. Concerning to Zn, the highest concentration was obtained in SJ1, located near the principal road, being similar to the concentrations attributed to traffic pollution in the literature (Joshi and Balasubramanian, 2010). Fe and Mn also showed high values in SJ2 and SJ3, being all the samples from the San Juan sub-basin higher for these trace elements than the other samples. Therefore, this factor associated with this area, may be related to a mixed source of traffic pollution and natural sources of weathering of parent material and subsequent pedogenesis (Joshi and Balasubramanian, 2010; Kartal et al., 2006; Li and Zhang, 2010a, b; Romero et al., 2006).

The presence of Cu, Fe and Mn (F2) and Pb (F3) was highlighted for Ll5, R00, SJ3, T5 and T7 as underline cluster 3, showing the high mean values and standard deviations of all the samples taken. Cluster 4 also underlined the presence of these trace elements for Ll00, Ll4, Ll5, Ll6, T5, SJ3 and P1 samples, with slighter concentrations than in cluster 3. Cluster 2 emphasized the same trend for the same points that cluster 3 and 4, but only for samples taken during the dry season. Therefore, these factors were mainly associated with anthropogenic inputs such as mining. Their strong correlations and their elevated values in intense mine areas at the upper part of the basin reflected this (Table 4.8, Figure 3.8).

Trace elements from the mines located at the upper parts of the basin are transported (in sediment form) to the lower parts, where the slow flow causes the accumulation of the fine grains of sediments in the river banks that could be released to the water column (Macklin et al., 2006; Miller et al., 2002). Then, the source of T5 and T7 samples (located at the lower part) may be the same than clusters 2 to 4 underlined due to the dynamics of the basin.

Cr was related to F4 and may be attributed to a combination of natural and industrial sources; high concentrations with high standard deviations were obtained close to the Sipán S.L. Mine site, and significant concentrations were also showed downstream. Additionally, cluster 4 links the Cr peak observed in P1 with the Ll00, Ll4, Ll5, Ll6, T5, and SJ3 samples, supporting the assumption that a combination of natural erosion and mining is the pollution source. Cluster 1 presented weak loadings on all the factors for all the samples, supporting the difference between the samples taken and the suggested sources of pollution for the monitoring points in the other samples.

Findings in the literature consider seasonality as an important factor (Li and Zhang, 2010a, b; Luis et al., 2010). Only cluster 2 reflected the seasonality, showing the peaks on July 2003 and 2005. Specifically, Cu, Fe, and Mn concentrations were related to the dry season obtained for cluster 2 samples (located in sub-basins without the mentioned facilities) that could be due to a combination of natural erosion and release of acid mining drainage (AMD). The outstanding points for the other clusters did not rely on the sample season, supporting the findings of the analysis of the data from the CAO and Stratus studies (section 4.2.1). The particularities on mine processing and water treatment facilities located at the upper parts of the basin could interfere in the natural hydrology of the basin at these points due to the management of the mine dam located upstream and the management operation of their treatment plants. These facts could explain the independence from season of most of the analysed trace elements in the water samples.

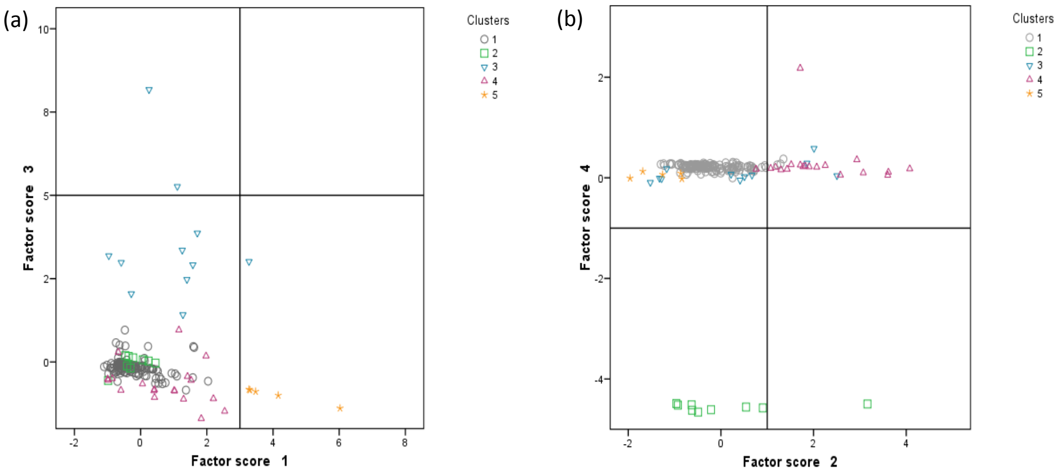


Figure 4.4: Score plot of the 5 clusters obtained for the DESA data (from 2003 to 2008) between factor score 1 and 3 (a) and factor score 2 and 4 (b).

4.2.3 Monitoring performed for this study

Mean concentrations and standard deviations of the data collected from 2008 to 2010 are given in Table 4.10. Overall, the standard deviations from this monitoring were lower than those from the analysis of the DESA data, suggesting a decrease in the contributing sources. Nevertheless, the standard deviations obtained from this monitoring are not homogeneous for all the sites.

The loadings of the principal components, the cumulative percentages for the rotated matrix, and the factor scores of the concentrations are shown in Table 4.11. There are a total of seven components with eigenvalues >1, which account for the 89% of the total variance and the communalities values obtained were over 0.78, sustaining the decision to obtain seven components.

Table 4.10: Mean and standard deviation of the water samples performed in this work from 2008 to 2011. Units in mg/l except for EC (in µS/cm) and pH.

	nº	pH	EC	TSS	TDS	SO_4^{2-}	Cl^-	$NO_3^- + NO_2^-$	NH_4^+	CN_{WAD}	$CN_{Tot.}$
Llapa sub-basin samples											
Ll1	4	7.84 ± 0.34	72.5 ± 40	2.5 ± 2	40 ± 35	1.95 ± 1.31	0.788 ± 0.9	0.048 ± 0.056	0.033 ± 0.027	<0.001	0.0508 ± 0.1
Ll2	4	8.01 ± 0.32	105.8 ± 10.6	2.75 ± 2.06	60.75 ± 42	8.41 ± 2.53	0.37 ± 0.23	0.078 ± 0.084	0.043 ± 0.032	<0.001	<0.001
Ll3	4	7.92 ± 0.27	135 ± 25.7	6.5 ± 4.93	90 ± 32	21.72 ± 10.35	0.37 ± 0.23	0.77 ± 1.35	0.085 ± 0.077	<0.001	<0.001
Ll4	4	6.02 ± 2.68	404.75 ± 220	4.75 ± 4.79	153 ± 109	88 ± 59	0.96 ± 1.25	0.58 ±0.39	0.0325 ± 0.02	<0.001	<0.001
Ll5	4	6.47 ± 3.12	1130 ± 634	40 ± 27	871 ± 667	633 ± 442	0.44 ± 0.3	0.17 ± 0.14	0.125 ± 0.09	<0.001	<0.001
Rejo sub-basins samples											
R0	1	5.69	1229	42	601	692	5.4	1.10	0.92	<0.001	<0.001
R1	4	7.46 ± 0.06	394 ± 229	17 ± 15	249 ± 164	139 ± 87	6.74 ± 10	1.59 ± 1.62	0.81 ± 1.24	0.001± 0.001	0.002 ± 0.003
R2	4	7.38 ± 0.17	298 ± 196	11.75 ±11.8	178 ± 136	101 ± 64	4.24 ± 6	1.12 ± 1.36	0.56 ± 0.9	0.001± 0.001	0.002 ± 0.002
R3	4	7.62 ±0.15	85 ± 65	6 ± 6	55 ± 27	18 ± 29	0.5 ± 0.4	0.26 ± 0.28	0.05 ± 0.045	<0.001	<0.001
R4	1	7.37	101	14	98	28	1.3	0.80	0.10	<0.001	<0.001
Alto-Jequetepeque sub-basin samples											
T1	3	8.34 ± 0.07	398 ± 31	11.34 ± 8	189 ± 18	68 ± 12	9.58 ± 1.9	0.77 ± 0.21	0.03 ± 0.02	<0.001	<0.001
T2	3	8.496 ± 0.16	389 ± 25	11.3 ± 11.6	185 ± 14	70 ± 11	9.79 ± 1.8	0.7 ± 0.26	0.05 ± 0.02	<0.001	<0.001
T3	3	8.46 ± 0.08	395± 21	14.8 ± 6.6	186 ± 14	68 ± 5.8	9.68 ± 1.5	0.72 ± 0.22	0.07 ± 0.05	<0.001	<0.001
T4	3	8.41 ± 0.07	406 ± 35	10.3 ± 10.1	193 ± 20	68 ± 17	10.08 ± 3.3	0.67± 0.31	0.06 ± 0.04	<0.001	<0.001
T5	3	8.39 ± 0.09	410 ± 36	13.6 ± 14.2	196 ± 19	54 ± 33	6.69 ± 5.7	0.59 ± 0.41	0.097 ± 0.03	<0.001	<0.001
T6	1	8.22	260	4	119	31	3.4	0.22	0.01	<0.001	<0.001

	nº	Al	As	Ca	Cd	Cr	Cu	Fe	Mg	Ni	Pb	Zn
Llapa sub-basin samples												
Ll1	4	0.207 ± 0.19	<0.001	10.44 ± 8.2	<0.001	<0.001	0.003 ± 0.0023	0.223 ± 0.134	1.11 ± 0.38	0.006 ± 0.009	<0.004	0.005 ± 0.003
Ll2	4	0.38 ± 0.45	<0.001	14.89 ± 2.57	<0.001	<0.001	0.004 ± 0.0024	0.36 ± 0.35	1.475 ± 0.08	<0.001	<0.004	0.0095 ± 0.006
Ll3	4	0.33 ± 0.27	0.005± 0.006	16.94 ± 9.76	<0.001	<0.001	0.014 ± 0.012	0.358 ± 0.23	1.385 ± 0.43	0.006± 0.009	<0.004	0.76275 ± 1.51
Ll4	4	0.71 ±0.48	<0.001	66 ± 46	<0.001	0.53 ± 1.05	0.13 ± 0.14	0.33 ± 0.1	4.37 ± 0.9	0.009 ±0.008	<0.004	0.11 ± 0.1
Ll5	4	8.796 ± 6.44	0.029 ± 0.048	305 ± 88	0.013 ± 0.005	0.0023 ± 0.002	0.812 ± 0.511	9.43725 ± 12.4	7.78 ± 3.5	0.039 ± 0.028	<0.004	0.396 ± 0.19
Rejo sub-basins samples												
R0	1	1.76	0.010	266	0.004	<0.001	0.171	2.1	4.6	0.004	0.025	0.29
R1	4	0.60 ± 0.52	0.007 ± 0.005	64 ± 39	<0.001*	<0.001*	0.015 ±0.005	0.72 ± 0.5	1.91 ± 0.6	0.01 ± 0.014	0.012 ± 0.01	0.03 ± 0.01
R2	4	0.36 ± 0.26	0.004 ± 0.003	48 ± 31	<0.001*	<0.001*	0.011 ±0.003	0.46 ± 0.23	1.5 ± 0.5	0.002 ± 0.001	<0.004	0.02 ± 0.01
R3	4	0.063 ± 0.034	0.002 ±0.0005	6.8 ± 0.54	<0.001*	<0.001*	0.002 ± 0.001	0.07 ± 0.06	0.54 ± 0.1	<0.001	<0.004	0.006 ± 0.003
R4	1	0.40	0.005	17	<0.002	<0.002	0.008	0.4	1.0	0.002	0.018	0.01
Alto-Jequetepeque sub-basin samples												
T1	3	0.37 ± 0.26	0.003	55.5 ± 2.8	<0.001	<0.001	0.002 ± 0.0015	0.397± 0.27	8.1 ± 0.45	<0.001	<0.004	0.021± 0.02
T2	3	0.24 ± 0.15	0.004 ± 0.002	53.2 ± 2.3	<0.001	<0.001	0.003 ± 0.0026	0.25 ± 0.14	7.9 ± 0.44	0.002	<0.004	0.014 ± 0.009
T3	3	0.35 ± 0.24	0.002 ± 0.001	55.5 ± 7.2	<0.001	0.004**	0.002 ± 0.0009	0.46 ± 0.18	8.1 ± 0.3	<0.001	<0.004	0.09 ± 0.11
T4	3	0.22 ± 0.17	0.002 ± 0.0005	55.5 ± 7.2	<0.001	<0.001	0.005 ± 0.0055	0.24 ± 0.21	8.1 ± 0.14	0.0017 ± 0.0012	<0.004	0.012 ± 0.006
T5	3	0.34 ± 0.31	0.003 ± 0.0015	58.3 ± 5.8	<0.001	<0.001	0.002 ± 0.001	0.376 ± 0.379	8.28 ± 0.1	<0.001	<0.004	0.012 ± 0.005
T6	1	0.12	<0.001	35	<0.001	<0.001	0.002	0.0	4.5	<0.001	<0.004	0.01

*The first campaign was given a detection limit of 0.002 mg/l for Cr and Cd
**The third campaign presents a peak of Cr, while the other campaigns were under the detection limit

Table 4.11 gives the eigenvalues and percentage of the cumulative variance for each component, and the factor scores for the related elements. It should be noted that the similarities between the factors loadings obtained from the results from the DESA data and the of the two factors were associated with mining are similar with F1 from this study related to F1 and F2 from the DESA data, and F4 from this work parallel to F3 and F4 from the DESA data.

Table 4.11: Varimax rotated values for water samples performed in this work (*n* = 51). Values below 0.3 are not shown

	Principal Components							
Elements	1	2	3	4	5	6	7	Communalities
pH	-0.445		0.405	-0.647				0.912
EC	0.382	**0.795**						0.924
TSS			**0.868**					0.91
TDS		0.364	0.643	-0.417			-0.308	0.91
Chloride	-0.311	0.636	0.372			0.406		0.914
WAD CN					**0.923**			0.909
Total CN					0.302		**0.895**	0.923
N+N		0.307	**0.777**					0.826
Ammonium			0.637		0.606			0.884
Sulphate		0.41		-0.425	0.303	0.448	-0.458	0.898
Al	**0.87**							0.925
As	0.472					**0.764**		0.849
Ca	0.569	**0.747**						0.94
Cd	**0.902**							0.843
Cr				**0.915**				0.953
Cu	**0.916**							0.932
Fe	**0.84**					0.321		0.87
Mg		**0.943**						0.951
Ni	**0.866**							0.849
Pb	0.376	-0.325		0.489		0.49		0.802
Zn	**0.73**	0.309						0.784
Eigenvalues	5.77	3.20	2.81	2.08	1.81	1.59	1.46	
Cumulative Variance (%)	27.48	42.72	56.08	65.99	74.60	82.16	89.10	

PCA loadings > 0.65 are shown in bold

In order to obtain the relationships between all the samples (n = 50) HCA and score plots were used (Figure 4.5). Taking into account the lack of industrial activities in the region, and comparing the mean concentrations of all the points with huge concentrations near mine sites and their standard deviations, the source of Cu, Cd, Ni, Al, Fe, Zn, and Cr (related to F1 and F4) can be associated with mining (Table 4.10, Figure 3.9).

These findings were in agreement with the clusters 2 and 3 obtained. Cluster 2 was related to Ll5 samples which presented the highest levels of the basin for all the trace elements described, while cluster 3 also reported peaks of Cu, Ni, Al, Fe, and Zn mainly on R0, R1, R2, R4, and Ll3. It should be noted that Cd peaks only appeared on Ll5, located just downstream of the Sipán S.L. Mine site. Additionally, Cr was observed mainly in Ll4 with lower levels in Ll5, suggesting the same source.

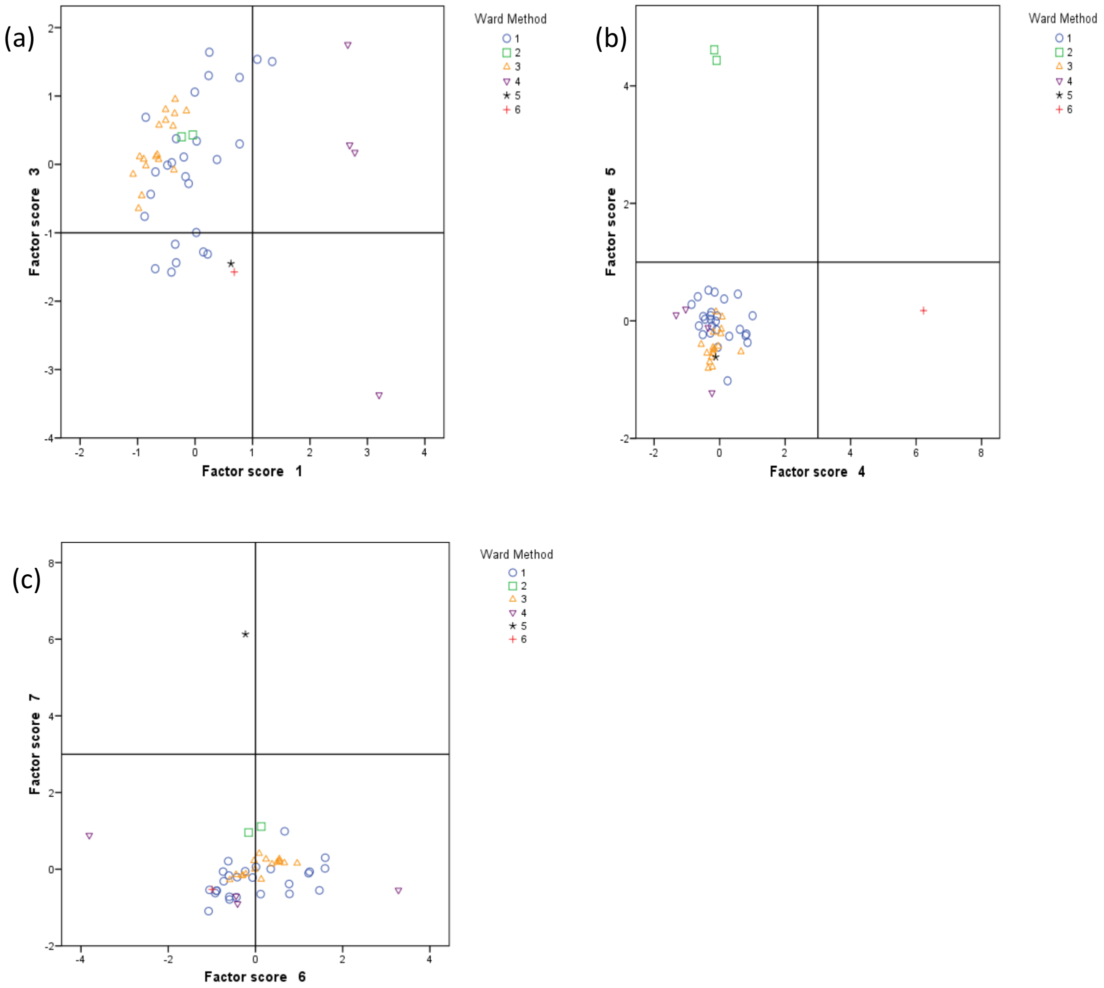


Figure 4.5: Score plot of the 7 clusters obtained for the water monitoring developed in this work (from 2008 to 2010) between factor score 1 and 3 (a), factor score 4 and 5 (b) and factor score 6 and 7 (c)

High values of EC and concentrations of Ca, Mg, chloride and sulphates (F2) were present at November 2008 for Ll4 (cluster 4) and at all the T samples (cluster 1). This can be attributed to anthropogenic activities, such as fertilizers and pesticides from agriculture, which is the main activity in the lower part of the basin (Wana and Okieimen, 2011).

TDS, TSS, nitrite and nitrate, and ammonium (F3) were mainly present in Ll5 (associated with cluster 2) and also in R0, R1, R2, R4 and Ll3 (linked to cluster 3) during the wet season. Importantly, during the wet season, the water treatment plants of mine operate significantly more than during the dry season because of the strong rainfalls. Therefore, the volumes of treated water introduced into the river are higher than during the dry season. Therefore, the source appeared to be attributed to anthropogenic activities as flocculants from the treatment plants; this is in agreement with the research at these sites on the CAO and Stratus data.

Peaks from WAD cyanide (F5) were related to R1 and R2 highlighted in cluster 5, while total cyanide (F7) was linked to cluster 2, 5 and 6. These parameters appeared in the closest points downstream of the mine sites, so an anthropogenic source was related to these factors; here, spillage is the most plausible explanation.

Higher As and Pb concentrations (connected to F6) appeared during the wet season for samples present in cluster 2 and 3, where mineral deposit contained elevated concentration of As and Pb (MWH Inc., 2006). These trace elements are known to be associated with jarosites. This is in agreement with findings in the literature; with a lag time for time discharges of trace elements observed, especially for Pb (Lin et al., 2007). Therefore, the source of pollution of As and Pb at R0, R1, R2, and R4, and adding Ll3 and Ll5 monitoring sites for As, can be attributed to mining.

4.2.4 Spatial and temporal distribution of trace elements

4.2.4.1 Spatial distribution

From the results found in the statistical analysis reported in sections 4.3.1 to 4.3.3, the effect of each sub-basin was considered and discussed below. In order to compare the rivers of the world with similar impacts, the maximum and mean of trace elements concentrations in some rivers affected by mine pollution was showed in Table 4.12. From the results found in the statistical analysis discussed in sections 4.2.2 and 4.2.2, how each sub-basin is affected is considered below.

Llapa sub-basin

Taking into account the locations of the sample points, the Llapa sub-basin was considered to be the most polluted area of the Jequetepeque River Basin, with mining the contributing source of pollution. The biggest concentration peaks of trace element were located at Ll5, although Ll4 was also considered relevant, especially for Cr contributions. These points were located downstream of the Sipán S.L. Mine site.

Cu and Mn peaks obtained at Ll5 had maximum values of 59.5 and 22.5 mg/L, respectively. These values are higher at the Jequetepeque basin than those obtained from rivers located near mine sites worldwide, such as the Andean region, Asia, or Europe (Miller et al., 2004; Lin et al., 2007; Parra et al., 2011; Tarras Wahlberg and Nguyen, 2008; Sarmiento et al., 2011) and similar to values obtained at rivers affected by Rio Tinto Mine in Spain.

Fe presented an extraordinary peak of 6508 mg/L, which is higher than any value reported in the literature (Table 4.12). Mean concentrations of Cu (3.5 mg/L) were higher than the concentrations found in Bolivia, Chile, or Portugal rivers near mine sites (Miller et al 2004; Parra et al., 2011; Luis et al 2010), and higher than the concentrations found 16 km downstream of the mine sites in China rivers (Lin et al., 2007; Ma et al., 2011).

Table 4.12: Mean and maximum values for rivers affected by mine pollution. All the analytes are measured mg/L except for EC (in µS/cm) and pH.

Source		Measure	pH(a)	EC	SO_4^{2-}	Al	As	Ca	Cd	Cr	Cu	Fe	Mg	Mn	Ni	Pb	Zn
DESA Data (entire basin)		Mean	7.4	415	-	-	-	-	<0.01	<0.05	1.0	45	-	0.8	-	0.03	0.27
		Max.	1.91	2660	-	-	-	-	0.21	0.128	59.5	6508	-	22.5	-	0.74	16.8
Llapa sub-basin		Mean	6.7	524	-	-	-	-	0.02	<0.05	3.1	162	-	1.8	-	0.04	0.35
		Max.	1.91	2660	-	-	-	-	0.21	0.051	59.5	6508	-	22.5	-	0.74	3.7
Rejo sub-basin		Mean	7.6	193	-	-	-	-	0.01	<0.05	0.08	0.86	-	0.2	-	0.03	0.06
		Max.	5.6	578	-	-	-	-	0.02	<0.05	3.8	19.3	-	5.9	-	0.07	0.18
San Juan sub-basin		Mean	7.99	304	-	-	-	-	<0.01	<0.05	0.009	2.9	-	0.4	-	0.03	0.58
		Max.	7.1	509	-	-	-	-	<0.01	<0.05	0.014	4.8	-	12.4	-	0.06	16.8
Alto Jequetepeque and Puclush sub-basins		Mean	7.96	308	-	-	-	-	<0.01	<0.05	0.03	2.3	-	0.2	-	0.03	0.08
		Max.	7.3	1100	-	-	-	-	<0.01	0.128	0.3	32	-	2	-	0.03	0.16
Developed Monitoring (entire basin)		Mean	7.7	363	131	1.0	0.005	70	0.002	0.03	0.07	1.0	4.3	-	0.01	0.01	0.12
		Max.	5.7	1644	692	8.8	0.029	377	0.013	2.1	1.54	28	8.5	-	0.04	0.03	3.02
Llapa sub-basin		Mean	7.1	375	151	1.9	0.007	80	0.003	0.17	0.19	1.8	3.4	-	0.01	0.01	0.26
		Max.	3.5	1644	633	8.8	0.029	377	0.013	2.1	1.54	28	12.3	-	0.04	0.01	3.02
Rejo sub-basin		Mean	7.1	421	195	0.6	0.005	80	0.002	0.001	0.02	0.5	1.5	-	0.00	0.01	0.07
		Max.	5.7	1229	692	1.8	0.010	266	0.004	0.002	0.17	2.1	4.6	-	0.01	0.03	0.29
Alto Jeque. sub-basin		Mean	8.4	377	60	0.3	0.002	52	0.001	0.001	0.003	0.3	7.5	-	0.00	0.00	0.03
		Max.	8.3	410	70	0.4	0.004	58	0.001	0.002	0.005	0.8	8.5	-	0.00	0.00	0.09
Canovas et al 2009		Mean	2.7	3870	3583	192	0.32	86	0.27	0.06	55	489	184	25	0.49	0.51	55
		Max.	3.6	8080	9474	483	0.88	184	0.74	0.18	148	1385	463	56	1.28	1.6	145
Gozzard et al 2011		Mean	6.7	459	81	0.15	-	70	-	-	-	-	14	0.09	-	-	4.3
		Max.	7.2	582	105	0.15	-	88	-	-	-	-	19	0.09	-	-	5.6
Lin et al 2007	3.5 KM	Mean	2.6	-	-	64	0.03	-	36.7	-	4.11	49.6	-	17.5	72	3.01	23.3
	3.5 KM	Max.	2.7	-	-	64	0.04	-	110	-	4.87	78.9	-	25.6	216	7.15	32.5
	16 KM	Mean	4.6	-	-	0.8	0.003	-	0.01	-	0.39	3	-	1.3	0.002	0.14	1.3
	16 KM	Max.	6	-	-	1.5	0.004	-	0.01	-	0.8	9	-	2	0.004	0.22	2.1
Lin et al 2007	25 KM	Mean	6.1	-	-	0.5	0.008	-	0.003	-	0.1	2.7	-	0.5	0	0.05	0.9
	25 KM	Max.	6.4	-	-	0.9	0.008	-	0.005	-	0.19	5.4	-	1.1	0	0.09	1.1
Luis et al 2010		Mean	4.5	3481	2747	53	0.01	230	0.11	-	2.9	121	400.68	61	0.82	0.12	48
		Max.	2	9230	8124	178	0.02	577	0.31	-	9.1	562	1151	175	2.22	1	134
Ma et al 2011	10 KM	Mean	2.8	1492	-	65	-	-	0.087	-	2.33	91	-	28	-	1.2	31
	10 KM	Max.	2.3	347	-	98	-	-	0.171	-	4.87	271	-	50	-	11	67
	16 KM	Mean	4.9	322	-	3.9	-	-	0.007	-	0.32	2.2	-	2.4	-	0.13	3.5
	16 KM	Max.	6.7	566	-	13	-	-	0.022	-	1.15	19	-	6.2	-	2.97	39
	25 KM	Mean	5.6	239	-	0.56	-	-	0.005	-	0.13	2.6	-	2	-	0.06	2.4
	25 KM	Max.	6.8	398	-	2.4	-	-	0.011	-	0.49	17	-	8.1	-	1.02	19
	29KM	Mean	7.1	96	-	0.08	-	-	0.003	-	0.02	0.36	-	0.9	-	0	0.76
	29 KM	Max.	7.2	107	-	0.16	-	-	0.007	-	0.03	0.56	-	1.2	-	0	0.9
	56 KM	Mean	7.2	77	-	0.39	-	-	0.001	-	0.01	0.25	-	0.16	-	0	0.15
	56 KM	Max.	7.3	91	-	0.67	-	-	0.002	-	0.02	0.33		0.32		0	0.23
Miller et al 2004		Mean	-	-	-	-	0.009	-	0.006	-	0.009	-	-	-	-	0.009	1.2
		Max.	-	-	-	-	0.02	-	0.03	-	0.02	-	-	-	-	0.024	3.6
Palmer et al 2011		Mean	4.8	4000	1074	121	-	132	0.67	2.87	-	30	79	2334	-	24	-
		Max.	1.9	10000	3076	345	-	303	3.6	7.96	-	97	151	7462	-	75	-
Parra et al 2011		Mean	7.8	429	101	15	0.01	-	-	-	0.08	0.9	115	-	-	-	-
		Max.	8.3	1073	378	25	0.01	-	-	-	0.47	1.6	188	-	-	-	-
Tarras-Walberg and Nguyen 2008		Mean (b)	-	-	-	0.008	0.112	-	0.001	0.00002	0.0004	-	-	0.001	0.11	0.001	0.000
		Mean (c)	-	-	-	3.9	0.003	-	0.003	0.009	0.156	-	-	2.7	0.12	0.002	0.1
		Mean (d)	-	-	-	3.1	0.001	-	0.001	0.004	0.038	-	-	0.04	0.004	0.06	5.0
		Mean (e)	-	-	-	1.4	0.001	-	0.002	0.001	0.017	-	-	0.08	0.001	0.27	2.4
Sarmiento et al 2011		Mean	4.6	-	4452	45	1.29	-	0.06	0.008	9.8	-	-	19	0.46	0.16	36
		Max.	2.9	-	8460	80	3.76	-	0.12	0.014	20	-	-	37	0.90	0.72	72

(a)minimum values for pH; (b) Background values; (c) Samples affected by drainage from the new tailings deposits; (d)Samples affected by drainage from the waste rock deposits; (e)Samples from the open pits

The peak of concentration of Pb (0.74 mg/L) at Ll5 was similar to concentrations reported in Asian rivers. Mean Pb concentrations at Ll5 were similar to rivers affected by drainage of waste rocks in Vietnam (Tarras Wahlberg and Nguyen, 2008) and at 16 km downstream of the mine sites in China (Ma et al., 2011; Lin et al., 2011). Additionally, Zn concentrations were similar to concentrations reported in rivers located 16 km downstream of a mine site (Lin et al., 2007) at rivers affected by drainage tailings (Tarras Wahlberg and Nguyen, 2008) and at the Pilcomayo river in Bolivia (Miller et al., 2004).

Of all the sampling points in the Jequetepeque basin, Cd peaks only appeared in Ll5, with a highest peak of 0.21 mg/L, which is higher than concentrations reported in several studies of rivers affected by mine sites (Lin et al., 2007; Miller et al., 2004; Tarras Wahlberg and Nguyen, 2008).

As mentioned before, Cr concentrations were higher at Ll4, with mean concentrations of 0.53 mg/L and a peak of 2.1 mg/L. The Cr concentrations from mining contributions can be considered important as findings in literature reported (Cánovas et al., 2009; Tarras-Wahlberg and Nguyen, 2008; Sarmiento et al., 2011). Additionally, the EC values and Ca concentrations at Ll5 showed peaks of 1644 µS/cm and 376.7 mg/L, respectively, while Ll4 presented peaks of 734 µS/cm and 135.5 mg/L, respectively. Those values are similar to values reported in rivers from the Andean region, Europe, or Asia with mining activities (Parra et al., 2011; Gozzard et al., 2011; Ma et al., 2011 for EC; and Luis et al.; 2011; Palmer et al., 2011).

Ll4 and Ll5 were located at the upper part of the basin where no other activities were developed. Thus, the source of these can be attributed to mining activities, which supports the findings obtained in the chapter 4, section 2.

Rejo sub-basin

The highest concentrations of ammonium, chloride, nitrate and nitrite, sulphate and WAD cyanide in the entire basin were present in the Rejo sub-basin (Table 4.8). Ca mean concentrations (around 80 mg/L) at Jequetepeque were similar to those reported for rivers with mining impacts in Spain and UK (Canovas et al., 2008; Gozzard et al., 2011). Considering the peaks at R0 (266 mg/L), similar values were found in rivers in Portugal and Indonesia (Luis et al., 2011; Palmer et al., 2011). Two peaks of sulphate were found at R0 and R1 (692 mg/L and 248 mg/L respectively), these values are higher than some findings in UK and Chile rivers affected by mine impacts (Gozzard et al., 2011; Parra et al., 2011).

Additionally, the Rejo sub-basin contributed significantly to the peaks of Al, As, Fe, Cu, Ni, and Pb in nearby mine areas, but a dilution effect was observed downstream (Table 4.8). These findings were similar to some studies at the Andean region. As Table 4.12 gave, similar values were found to Chile for Cu and Fe (Parra et al., 2011), and in Bolivia for Al, As, Fe, Cu, Ni, and Pb (Miller et al., 2004). Specifically, Al, As, Cu, and Ni presented similar values to rivers affected by waste rocks and open pits, while Pb concentrations were similar only to points affected by open pits in Vietnam (Tarras-Wahlberg and Nguyen, 2008). This is in agreement with the findings obtained in previous sections of 4.2, where the contributing source of these trace elements was attributed to mining activities.

San Juan sub-basin

Lower concentrations were observed at the rest of the sub-basins, except for one peak of Zn of 16.8 mg/L in the San Juan sub-basin. As shown in Table 4.12, this peak of Zn was higher than those reported for rivers with mining activities in Bolivia (Miller et al., 2004), UK (Gozzard et al., 2011), or Vietnam (Tarras-Wahlberg and Nguyen, 2008). Nevertheless the mean concentrations obtained were significantly lower than the mean concentrations found in the literature mentioned above (Table 4.12); thus, the Zn presence in the entire basin can be considered slight. As mentioned in section 4.2.2, the source of Zn may be related to a mixed source of pollution (e.g. natural sources, traffic pollution, etc.), taking into account the findings in the literature.

Alto Jequetepeque sub-basin

Puclush and Alto Jequetepeque sub-basins samples are located downstream to the other sub-basins, explaining the homogeneity of the concentrations observed in almost all the components. High concentrations were observed for Ca, Mg, and sulphates, with means of 52 mg/L, 7.5 mg/L, and 60 mg/L, respectively (Table 4.12).

Concentrations of Ca, nitrates and nitrites, and sulphates were one order of magnitude smaller than the concentrations obtained at the Rejo sub-basin, while Mg values were higher at T samples (Table 4.8). Significant concentrations of chloride were found comparing with the other sub-basins, ranging from 6.6 to 12 mg/L (Table 4). Nevertheless, chloride concentrations found in rivers near mine sites reported concentrations one or two orders of magnitude higher (Ma et al., 2011; Luis et al., 2010).

Due to the hydrodynamics of the basin, mixed sources were expected at the lower part of the basin. The difference between the analytes can indicate mixed sources of pollution. It support the findings underlined in section 4.2.3, where the source of the concentrations can be attributed to a mixed source of agriculture and mining activities.

We should point out that greater concentrations were obtained in T5, just before the river flows into the reservoir. This fact is hardly surprising, since higher concentrations at that point were expected because of the hydrodynamics of the basin (Canovas et al., 2008; Macklin et al., 2006; Miller et al., 2002).

Note that, at the Jequetepeque basin, values obtained near mine sites are similar to those obtained at the Andean region, while lower values were reported from the UK mine sites, and the highest values were reported in places such as China or Spain.

4.2.4.2 Temporal distribution

Differences between the seasons (wet and dry) were not as great as expected as the analysis of the CAO and Stratus data showed (Table 4.5and 4.6). This was in agreement with the results of the DESA data and the monitoring developed in this work. Some insights were obtained from the difference between seasons performed in the CAO and Stratus review. Several differences were observed considering peaks from each season, where concentrations are high for nitrate, As, Mn, and Pb during the dry season and for Ag, Cu, Hg, Ni, Se, Tl, and Zn during the wet season.

Peak loads can be considered relevant because of extremely variations of the total concentrations depending on the sampling time (Figure 4.6). Peak loads were calculated as the sum of all trace elements for each monitoring period. Major peaks were shown in the study of CAO (sampling in 2004 and 2005) than in the study of Stratus Inc. (sampling in 2002 and 2003), where almost all peaks were found during the wet season. When initial rainfalls occur, extremely high peaks were present (September, November) for all sampling data, whereas significant peaks appeared in February and May in 2005. The period between seasons occurs most of the water discharge, dissolved contaminant, and suspended matter transport (Cánovas et. al., 2008). Then, these peaks reported at the first rains, were expected.

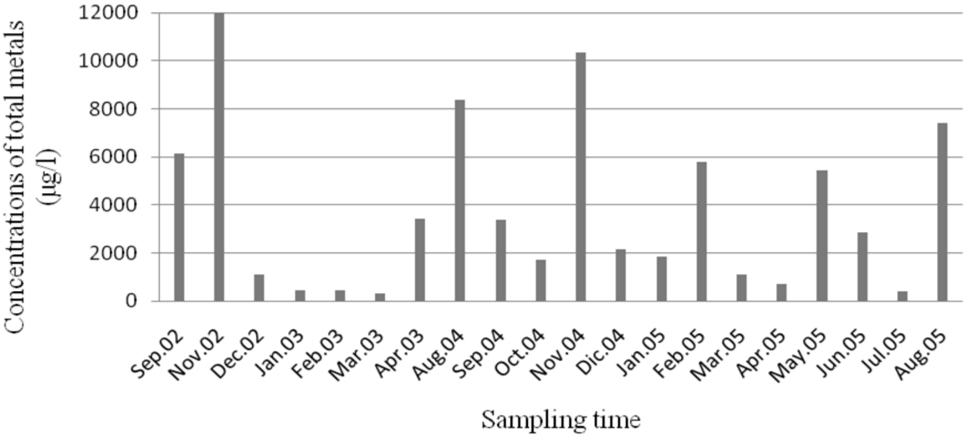


Figure 4.6: Total concentrations (in µg/l) of 15 elements (Ca, Mg, sulphate and nitrate were excluded) for different time

Nevertheless, August was the second month for all sampling data with large peaks. Differences in the (flow and concentration) peaks between the months of sampling did not seem to follow any trend. During the dry seasons, high concentrations were expected in the upper parts of the basin (Miller et al., 2002), but just a peak in August was surprising.

In addition, extremely low concentrations of all sampling points for the rainy season of 2003 were particularly unexpected. It could be due to mining operations, where dams and water treatment plants can alter the hydrologic response of the basin. Taking into account the increased flow in rainy season, the total load of trace elements was extremely high for samples S1, S4, S8 and C7, which are located downstream the dam of the mine. It should be noted that the major peaks meant that the total load of trace elements was much higher for that points. It may be due also by punctual events due to mining operations, independent of the monitoring period.

Seasonal variations were not found from CAO and Stratus data review, and the same occurred for the DESA samples and the monitoring program developed. Nevertheless, a trend was observed over the time; in which the concentrations of Cu and Fe were extremely higher for samples taken before 2008 than for those taken later. Since these elements are related to the mine sources, a plausible explanation for this could be that the Sipán S.L. Mine closed in the Llapa sub-basin in 2005, and that mine extraction in the Rejo sub-basin ended in 2005 (S.A.C., 2010).

On the other hand, some trends were observed for the monitoring developed which show the highest concentrations for the 2008 wet season with respect to the other seasons. Additionally, for both studies (the DESA data and the developed in this work), the presence of Cu can be considered significant as compared to the findings in the literature (Cánovas et al., 2008; Li and Zhang, 2010a, b; Lin et al., 2007; Miller et al., 2002; Parra et al., 2011; Tarras-Wahlberg and Nguyen, 2008). Additionally, pH, CE, TDS, Cd, Pb, and Zn did not show differences over time, suggesting that the mines located in the upper part that are still active are sources of pollution that place the basin population at risk.

4.2.5 Risk assessment

The hazard quotient was estimated in order to obtain the possible effects of the trace elements on human health by water ingestion (Table 4.13). If the HQ is between 1 and 10 indicates a small potential for adverse effects, between 10 and 100 indicates significant potential, and equal to or greater than 100 indicates adverse effects should be expected (Marcus et al., 2010).

Table 4.13: Hazard Quotient, HQ, for the (a) CAO and Stratus data, (b) DESA data and (c) monitoring developed. HQ is calculated for each case by the maximum water concentration, Cc, and the Reference ingestion Dose (in mg/l)

	Cc $^{(a)}$	Cc $^{(b)}$	Cc $^{(c)}$	RfD ingestion	HQ $^{(a)}$	HQ $^{(b)}$	HQ $^{(c)}$
Al	3.4	18	-	1	3.4	-	18
As	0.041	2.67	-	0.0003	136	-	8900
Ba	0.167	-	-	0.2	0.8	-	-
Cd	0.005	0.02	0.08	0.0005	10	160	40
Cr	0.01	2.67	0.128	0.003	3.3	43	890
Cu	0.057	1.535	59.5	0.04	1.4	1488	38
Fe	2.83	28.04	6508	0.7	4	9297	40
Hg	0.0005	-	-	0.0003	1.7	-	-
Mn	1.55	-	22.5	0.025	62	900	-
Ni	0.013	0.08	-	0.02	0.7	-	4
Pb	0.056	0.1	0.255	0.0014	40	182	71
Se	0.01	-	-	0.005	2	-	-
Zn	0.225	3.02	16.77	0.3	0.8	56	10

The maximum concentration exceeded the threshold effects for almost all the trace elements developed for all the studies, except for Ba, Ni and Zn from the CAO and Stratus data. Taking into consideration the CAO and Stratus data (where minor concentrations were found), adverse effects for As were expected for oral intake. Besides, significant potential for Cd, Mn, and Pb and small potential for Al, Cr, Cu, Fe, Hg, and Se were presented.

The data from the DESA monitoring reported the highest concentrations, therefore, higher HQ were expected. Indeed, the HQs obtained for DESA data were much higher than 100 or higher than 10. As a result, adverse effects on health due to Cd, Cu, Fe, Mn, and Pb, and significant effects due to Cr and Zn, can be expected to present an outstanding risk if the water is ingested. Considering the lack of water facilities and trace element remedial in the region, this poses a serious health concern for the population of these areas.

The samples monitored in this work showed HQs higher than 100 for As and Cr, indicating adverse health effects for ingestion. Al, Cd, Cu, Fe, and Pb quotients were above 10, implying significant effects on human health whereas Ni and Zn values were above 1, which can be considered to have a small effect for the population health. This was in agreement with the findings about the temporal trends discussed in the last section, with only the potential Cr affect to human health worse for the samples monitored in this work than for the DESA samples. Therefore, the presence of trace elements determined at the basin can be considered harmful to human health.

4.2.6 Conclusions

Water samples along the Jequetepeque basin were analysed by principal component analysis and hierarchical cluster analysis to investigate the distribution of trace elements and their sources. Major peaks were observed mainly near to the mine areas. The most polluted area of the basin was located downstream the Sipán S.L. Mine, with mining presenting the contributing source of TDS, TSS, sulphate, Al, As, Ca, Cd, Cu, Cr, Fe, Mg, Ni, and Zn. The Rejo sub-basin also contributed significantly, with peaks of Al, As, Fe, Cu, Ni, and Pb near to the Yanacocha S.R.L. Mine. Samples obtained from the middle part, near the reservoir, reported homogeneous values, indicating a natural source. Ca, Mg, chloride, TDS, TSS, nitrite and nitrate, ammonium, and sulphate peaks were mainly located at the Rejo sub-basin and at the middle of the basin, these are likely connected to a mixed source of anthropogenic activities, such as fertilizers and flocculants from the mine treatment plants.

Concentrations of dissolved trace elements in water samples from the CAO and Stratus study at the Rejo sub-basin were elevated, especially for As, Mn, Pb, and nitrate, during the dry season and for Ag, Cu, Hg, Ni, Se, Tl, and Zn during the wet season. Differences in peaks between the months of sampling did not seem to follow any trend. The highest peaks of all the data were reported in November and in August. It may be due to mining operations, where dams and water treatment plants may alter the hydrologic response of the basin. Correlation analysis demonstrated that no seasonal trends were observed in the Rejo sub-basin.

Taking into account that, the concentrations of the DESA data were higher than the concentrations from the study developed in this work, and they were also higher than the CAO and Stratus concentrations. The temporal trends showed the highest concentrations for samples taken before 2005, especially for the Cu and Fe concentrations. The closure of the Sipán S.L. Mine in the Llapa sub-basin and the ending of the mine extraction in the Rejo sub-basin in 2005 provide a plausible explanation for this.

The implications on human health by water ingestion in the region decreased after 2005. Nonetheless, the levels of Cr and As still pose adverse effects and of Al, Cd, Cu, Fe, and Pb significant effects for human health, creating an outstanding risk for the populations of these areas. Considering the lack of water facilities and trace element remedial in the region, special attention should be paid in the regulatory policy, and further efforts in the mine remedial processes needed to be taken.

The pollutant distribution assessment is critical to understand the dynamics of pollutants and risk assessments in basins with anthropogenic activities as mining. Correlation analyses separated by season for different data sets assisted that purpose, and identified sources of pollutants. Despite of the different trends between seasons were not as significant as expected, this methodology contributes to identifying and tackling environmental problems leading to more accurate treatment and monitoring programs.

4.3 Sediment Monitoring

This chapter was divided in 3 sections. First the results from the first sediment monitoring were reported and discussed by the statistical analysis. Then, the second sediment monitoring results for the three campaigns developed (June 2009, November 2009 and July 2010) were discussed in terms of trace element concentration and partition, and the obtained indicators were developed evaluating their associated risk for the Jequetepeque basin. The last section highlighted the results from the kinetics and modelling developed for four of the sediment samples from the second sediment monitoring.

4.3.1 First sediment monitoring

The first sediment monitoring was developed in this work as a pilot campaign in November 2009. A specific monitoring campaign was designed based on the guidelines provided by the United States Environmental Protection Agency (U.S. EPA 1977, 1987, 1991, 1994, 1998, 2001, 2002). It was carried out summarising a total of nine points at two sub-basins of the Jequetepeque basin (Rejo and Llapa sub-basin), both close to the mine sites (Figure 3.10). The sediment concentrations of Al, As, Cd, Cu, Cr, Fe, Hg, Ni, Pb, Sb, Sn, and Zn were analysed for the four fractions of the BCR analysis. It was used to identify chemically-active forms in the sediment samples (Ure et al., 1993), following considerations from the literature (Pérez-López et al., 2008; Sahuquillo et al., 1999) as described in section 3.2.3.4.

Additionally, a comparative study of trace element concentrations was made based on sediments collected from the mainstream and tributaries of two sub-basins (Yang et al 2009). The ecological risk for the aquatic life was determined by comparison of the sediment trace element concentrations with the concentrations established in the Canadian Sediment Quality Guidelines for the Protection of Aquatic Life (CCME, 202).

Finally, the sediment analysis data was processed using principal component analysis (PCA) and hierarchical cluster analysis (HCA), which identify similarities and differences between the data, to obtain more information about the pollution sources and their distribution patterns.

The results obtained from the first sediment monitoring were discussed in this section, summarised as follows: evaluating (i) the trace element concentrations reported in the river sediments, (ii) the ecological risk of the aquatic life associated with the presence of the trace elements in the river sediments, (iii) the trace element partitioning and its implication to the environment, and (iv) the spatial distribution.

4.3.1.1 Trace element concentration

The results obtained from the First sediment monitoring developed in November 2008, were discussed below. Different trends were observed between both sub-basins. First, the concentration range, median, mean, standard deviation (SD), and skew of trace element in sediment samples from the mainstream (Ll1, Ll2, Ll3) and tributaries (Ll4, Ll5) at the Llapa sub-basin was reported in Table 4.14. In this area, tributary sampling points were located in streams flowing directly from the mine site (Figure 3.10).

Table 4.14: Trace element concentration (mg/kg) from first sediment monitoring at the Llapa Sub-basin with median, mean, standard deviation and skew for Ll1, Ll2 and Ll3 (mainstream points); threshold effect level (TEL) and probable below level (PEL).

	Ll1	Ll2	Ll3	Ll4	Ll5	Median[a]	Mean[a]	SD[a]	Skew[a]	TEL	PEL
pH	7.30	7.60	7.68	-[c]	3.44	7.60	7.53	0.2	-1.4	-	-
EC[b]	31.00	35.00	38.00	734.0	212.0	35.0	34.7	3.5	-0.4	-	-
Al	13687	19379	12649	24523	15266	13687	15238	3623	1.6	-	-
As	5.3	2.5	53.9	22.7	350.7	5.3	20.6	28.9	1.7	5.9	17
Cd	2.4	4	3.1	3.7	11.3	3.10	3.17	0.8	0.4	0.6	3.5
Cr	5.4	6.8	4.3	5.7	5.5	5.40	5.50	1.3	0.4	37.3	90
Cu	10.3	133.1	63.4	502	446	63.40	68.93	61.6	0.4	35.7	197
Fe	12397	13930	14478	17810	24884	13930	13602	1079	-1.2	-	-
Hg	n.d.[d]	1.02	n.d.	n.d.	1.26	0.00	0.34	0.6	1.7	0.17	0.49
Mn	749	1206	958	934	373	958	971	229	0.3	-	-
Ni	5.9	9.4	8.4	10.5	11.6	8.40	7.90	1.8	-1.2	-	-
Pb	8.1	20	8.9	9.5	35	8.90	12.33	6.7	1.7	35	91
Sb	0.9	1.2	1.2	1.2	4.75	1.20	1.10	0.2	-1.7	-	-
Sn	64.7	93.3	71.1	65.5	85.4	71.10	76.37	15.0	1.4	-	-
Zn	45	90.6	76	126.1	114.65	76.00	70.53	23.3	-1.0	123	315

[a] Calculated for mainstream samples (Ll1, Ll2, Ll3) [b] Ohms*1000 [c] no available [d] no detectable (n.d.)

In the Llapa sub-basin (Table 4.14), concentrations of Cr, Ni and Sn did not differ significantly between samples, but differences were observed in the values of Al, Fe and Zn. These findings are in agreement with the literature (Doaa and Gahada, 2011; Passos et al., 2010). Slightly high values were found in Ll2, located at the mainstream, and in Ll4 and Ll5, located at tributaries. Mainstream and the tributary point Ll5 concentrations showed comparatively greater differences of the remaining elements (As, Cd, Cu, Pb and Sb). As was more than sixteen times higher in tributaries than in the mainstream, and Cu, for which a ratio of over 8:1 was obtained.

Table 4.15 reported the concentration range, median, mean, standard deviation (SD), and skew of trace element in sediment samples for the mainstream (R1, R2 and R3) and tributary (R4) monitoring points at the Rejo Sub-basin. In this case, R4 was located in a stream that does not come into contact with mine drainage and can therefore be considered non-polluted. In the Rejo sub-basin, concentrations of Al, As, Cr, Fe, Sb, and Sn were similar at all sampling points and minor differences were found for Hg, Ni and Pb. In contrast, considerable differences were found for Cu, Cd, and Zn showing comparatively higher concentrations in R1. Lowest trace element concentrations of the whole data set for almost all of the trace elements were obtained in the R4 tributary.

Table 4.15: Trace element concentration (mg/kg) in sediment samples with grain size <63 µm for tributaries of the Rejo Sub-basin with median, mean, standard deviation and skew for R1, R2 and R3 (mainstream points), threshold effect level (TEL) and probable below level, (PEL).

	R1	R2	R3	R4	Median[a]	Mean[a]	SD[a]	Skew[a]	TEL	PEL
pH	-[c]	-	-	-	-	-	-	-	-	-
EC[b]	37	-	32	-	34.5	34.5	-		-	-
Al	15605	13575	9602	14330	13575	12927	3054	-0.9	-	-
As	55.9	63.3	48.8	56.8	55.9	56	7.3	0.0	5.9	17
Cd	12.3	4.5	5.4	3.1	5.4	7.4	4.3	1.6	0.6	3.5
Cr	3.3	7.6	4.8	6.7	4.8	5.2	2.2	0.9	37.3	90
Cu	198	34.4	42.8	16.6	42.8	91.7	92.1	1.7	35.7	197
Fe	15360	16810	15261	14732	15360	15810	867	1.7	-	-
Hg	0.1	0.17	0.1	0.09	0.1	0.12	0.0	1.7	0.17	0.49
Mn	3712	879	932	350	932	1841	1621	1.7	-	-
Ni	12	11.8	7	6.4	11.8	10.3	2.8	-1.7	-	-
Pb	92.6	54.7	40.5	47.9	54.7	62.6	26.9	1.2	35	91
Sb	n.d.[d]	n.d.	n.d.	n.d.	-	-	-	-	-	-
Sn	76.3	79.7	62.8	87.5	76.3	72.9	8.9	-1.5	-	-
Zn	453	122	150	55	150	242	183	1.7	123	315

[a] Calculated for mainstream samples (R1, R2, R3) [b] Ohms*1000 [c] no available [d] no detectable (n.d.)

Trace element concentrations from monitoring points near mine sites exceed the levels present in unpolluted areas, such as the tributaries or mainstream. Homogeneous distribution across the site (R4 in the Rejo sub-basin and Ll1, Ll2 and Ll3 in the Llapa sub-basin) confirmed this concern, especially in the Llapa sub-basin with lower standard deviations. Therefore, mine pollution was present in the Llapa sub-basin for As Cd, Cu, Pb and Sb and in the Rejo sub-basin for Cu, Cd and Zn.

4.3.1.2. Ecological Risk Assessment

The potential toxicological effect of sediment trace element content was assessed in this section. For this purpose, the sediment concentrations were compared with the concentrations established in the Canadian Sediment Quality Guidelines for the Protection of Aquatic Life (CCME, 2002). Two levels of ecological risk were defined for sediment samples: the threshold effect level (TEL) below which adverse biological effects are expected to occur rarely, and the probable effect level (PEL) above which adverse effects are expected to occur frequently.

Concentrations of Cd and Cu in the Llapa sub-basin were above the PEL in all tributary samples and concentrations of Pb and Zn were above the TEL in 33% of the tributary samples (Table 4.14). In addition, Hg concentrations were above the PEL in approximately 33% of both mainstream and tributary samples. As gave values far above PEL for Ll5 and downstream from this tributary (Ll3) values were also above PEL.

Table 4.15 showed that concentrations of As in the Rejo sub-basin were above the PEL in all samples (mainstream and tributary) while Cd was above PEL only in mainstream samples. This is congruent with other findings present in the literature (Doaa and Gahada, 2011). Concentrations of Cu, Pb and Zn were above the PEL in 33% of the mainstream samples.

In conclusion, according to Canadian guidelines, there is a risk of toxicity on the aquatic life by As, Cd, Cu, Hg, Pb and Zn in the studied area. This was particularly frequent for As, Cd and Cu in the Llapa sub-basin, whereas considerable toxicological effects caused by Pb and Zn were expected in the Rejo sub-basin. These results were consistent with the total content of trace elements in sediments nearby mine sites, suggesting that mining not only cause pollution, but also effect on the aquatic life.

4.3.1.3. Trace element partitioning

The concentrations of trace elements in all monitoring points for each sequential extraction step (acid-extractable, reducible, oxidable and residual) were presented from the mainstream and tributaries of the Llapa (Figure 4.7a) and the Rejo sub-basins (Figure 4.7b). It should be noted that almost the entire content sum of Sn and Sb was present in the residual fraction in all samples of the Llapa and the Rejo sub-basins, respectively.

The results for Step 1 reported that Zn was the most important in this fraction due to its high percentage value in samples R1, R3, Ll4 and Ll5 (40%). Similar trends were found in a previous work in regions with this type of pollution (Kartal et al., 2006; Pérez and Valiente, 2005; Yang et al., 2009). Additionally, high contents of Ni, Cu and Cd were also relevant (above 20%) increasing the potential risk of pollution. Therefore, contamination by Zn, Ni, Cu and Cd can be attributed to mining in its immediate area.

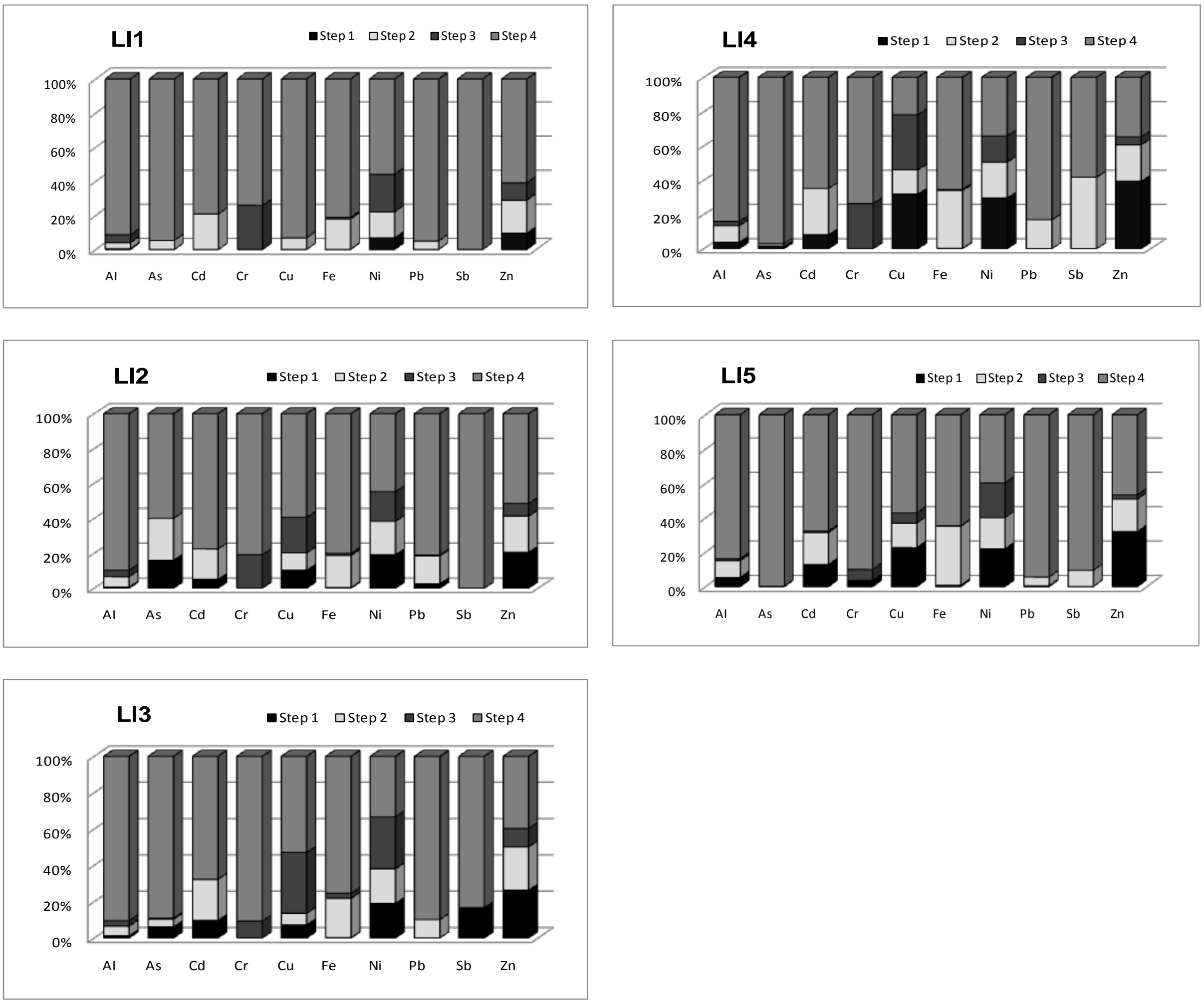


Figure 4.7a: BCR results from the mainstream (Ll1, Ll2, and Ll3) and tributaries (Ll4 and Ll5) points in the Llapa sub-basin

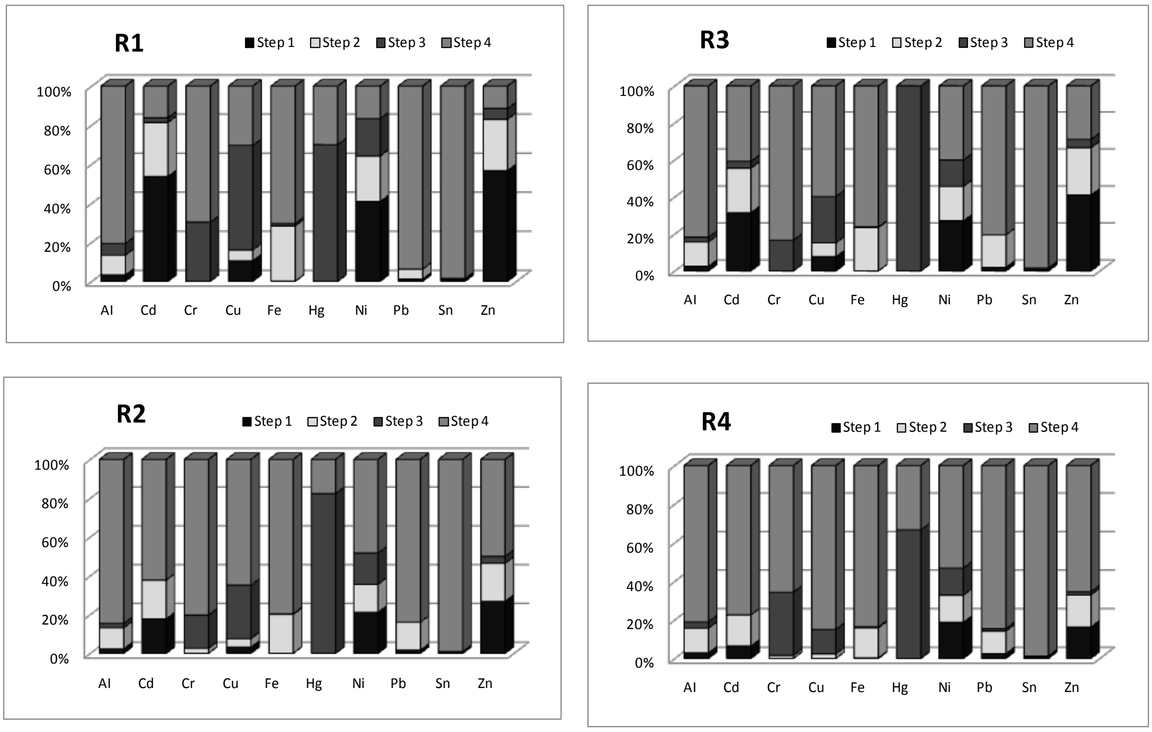


Figure 4.7b: BCR results from the mainstream (R1, R2, and R3) and tributary (R4) points in the Rejo sub-basin.

Fe, Zn, Cd and Ni account 20% of the total content in Step 2 for all the samples. Zn and Cd were primarily due to anthropogenic sources according to sediment trace element content analysis and Step 1. These findings were consistent with contaminated sediments and soils in the literature (Galan et al., 2003; Kraus and Windegand, 2006; Pueyo et al., 2008). The presence in this step could be as a result of continuous input of these trace elements from mining. Concerning Fe and Ni distribution, the highest contents were found at sample points close to the mine sites, indicating that this may be attributed to lithogenic and anthropogenic activities. These findings were in agreement with the literature (Mendici et al., 2011; Passos et al., 2010; Pérez and Valiente 2005).

Approximately 20% of As was bounded to Fe in Ll2 probably adsorbed onto Fe oxy-hydroxides (Galan et al 2003). Approximately 40% of the total concentration of Fe and Sb was present in the second fraction, for the specific case of point Ll4, and Ll5 in a lesser extent, similar to findings from a contaminated zone due to a mine spill (Kraus and Windegand, 2006). Downstream from these points, approximately 20% of Sb was found in the first fraction. Sb was mainly detected in the residual fraction or bound to oxy-hydroxides because of its low solubility; therefore it is surprising to find a considerable amount of Sb in Step 1. However, low concentrations of Sb were present in this sample, meaning that it did not present an environmental risk.

Considerable percentage of Hg was related to the oxidable fraction (23%) for all samples from the Rejo sub-basin, being a significant threat to the environment due to the high toxicity of Hg. Additionally, Cr and Cu were reported at this fraction. It should be noted that Hg and Cr were found in low and homogeneous concentrations for all samples; therefore lithogenic origins may be related to this fraction. The presence of Cu in the third fraction was only related to the Llapa sub-basin and R1. Similar to Fe and Ni distribution in the reducible fraction, the presence of Cu in all the Llapa samples may be related to lithogenic origins while in R1 may be primarily related to anthropogenic inputs. Differences between samples for Cu in this fraction are in agreement with a previous work (Galan et al., 2003; Mendici et al., 2011; Yang et al., 2009).

The order of relative abundance within the mobile fraction in all the samples (considering the percentage of trace elements extracted as the sum of the three first fractions), was: Zn (69%) >Ni (61%)> Cu (58%)> Cd (47%)> Fe (26%) > Hg (23%) >Cr (21%)> Al (15%) > Sb (12%) = Pb (12%) >As (2%) = Sn (2%). Elevated concentrations of trace elements in residual fractions (low percentage of mobile fraction) indicated that the sediments are relatively unpolluted, then lithogenic origins can be related to Al, Sb, Pb, As and Sn (Andrade et al., 2010).

Summarising, Zn, Ni, Cu and Cd showed the greatest amounts of trace elements in the bio-available fractions being a significant threat to the environment. The risk was particularly higher for the Rejo than the Llapa sub-basin where high and available concentrations of Cd, Cu and Hg -and to a lesser extent Pb and Zn- were found in sediment samples close to the mine sites (Table 4.14 and 4.15). The Llapa study area illustrated different behaviour at specific points for As, Fe and Sb taking into account the main results outlined above (Figure 4.7a). However, content of As, Fe and Sb in these related samples were low (Table 4.14), therefore their presence in movable fractions did not represent an environmental risk. Despite low values given for Cr and Hg, their availability can be considered also as a potential risk effect on the environment due to its their specific toxicity, so subsequent studies must be carried out in order to evaluate their environmental risk, especially in the Rejo Sub-basin.

4.3.1.4. Spatial distribution of trace elements

A statistical analysis by PCA and HCA was carried out in order to obtain the spatial distribution of the trace elements at the basin level, and its possible relationship with anthropogenic activities. Table 4.16 presented loadings of trace elements on the principal components with the cumulative percentages in each case. Four eigenvalues, greater than one, were taken into account being approximately 90% of the total variance. The corresponding rotated factors were obtained by Kaiser's Varimax rotation. Table 4.16 showed the factor scores in terms of 13 trace element concentrations for all sediment samples. Communalities were over 0.8, which confirms the decision to use four factors.

Table 4.16: Varimax rotated for all sediment samples of the Jequetepeque River Basin (*n* = 13). Values below 0.3 are not shown

	Principal Components				
Elements	1	2	3	4	Communalities
Zn	**0.932**				0.981
Mn	**0.922**	-0.342			0.976
Cr	**-0.702**		0.520		0.813
Ni	0.541	0.448	0.364	0.465	0.842
As		**0.922**			0.927
Fe		**0.910**		0.316	0.979
Cd	0.633	**0.648**	0.321		0.924
Sn			**0.877**		0.825
Hg			**0.873**		0.870
Pb	0.442	0.307	**0.655**	-0.508	0.976
Al				**0.880**	0.836
Sb	-0.336		-0.308	**0.787**	0.832
Cu	0.435	0.502		**0.705**	0.946
Eigenvalues	3.446	2.990	2.683	2.608	
Cumulative%	26.504	49.506	70.148	90.208	

PCA loadings > 0.65 are shown in bold

HCA was applied to the nine samples, expressed in terms of the four factors. The dendrogram was shown in Figure 4.8. The largest jump in rescaled distance cluster was found from the values 7 to 18 (Figure 4.8). The members of the five clusters were as follows: cluster 1 is formed by R2, R4 and R3; cluster 2 by Ll5; cluster 3 by Ll2; cluster 4 by R1; and cluster 5 by Ll1, Ll3 and Ll4. Note that cluster 1 only contained sampling points from the Rejo sub-basin and Cluster 5 only contains points from the Llapa sub-basin.

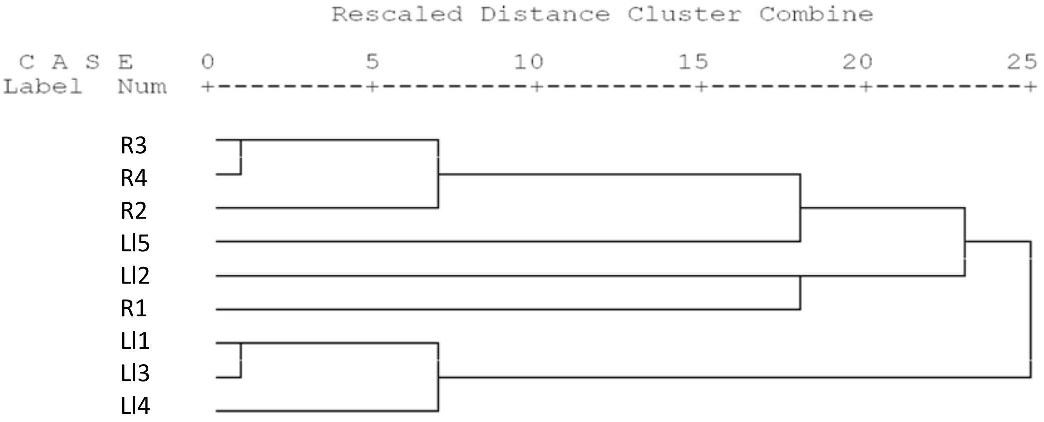


Figure 4.8: Dendrogram representing the results of the HCA analysis of sediment samples

Clusters 2, 3 and 4 were characterized by high values of certain trace elements (each cluster is related to different factors), whereas the second set of clusters was characterized by low values of almost all trace elements. This interpretation of the HCA results suggested that cluster 1 may represent a characteristic natural profile of trace element content in the Rejo sub-basin (with relatively low values for most trace elements, particularly those in Factor 4, with the exception of those in Factor 3), and cluster 5 a characteristic natural profile of the Llapa sub-basin (with relatively low values for most trace elements, particularly those in Factor 3, with the exception of those in Factor 4).

In contrast, the configuration of clusters 2, 3 and 4 may be related to different sources of pollution in the sub-basins (leading to a different relative importance of Factors 1, 3 and 4). The Rejo sub-basin may be characterized by relatively low natural concentrations of Al, Sb, Cu, and Ni, and the Llapa sub-basin by relatively low natural concentrations of Hg, Pb, and Cr, which appears to be consistent with the results in Tables 4.14 and 4.15.

Pollution may be expected in the mainstream of the Rejo sub-basin and would increase in areas closer to the source of mine drainage, leading to high concentrations of Cd, Cu, Ni, Pb, and Zn. Two pollution profiles were found in the Llapa sub-basin. Very high concentrations of As, Cd, Cu, Fe, Ni, and Sb were recorded in a tributary at the sampling point closest to the mine. High concentrations of Al, Cu, Cr, Hg, Ni, Pb, and Sn were obtained in the mainstream located downstream of the tributaries carrying mine drainage. Cu and Pb were found in the polluted areas of the Rejo sub-basin though they did not form part of its expected natural profile. The PCA analysis produced similar results to the previous assessments: low values were recorded at point Ll1 in the Llapa sub-basin, which is in the mainstream located upstream of the contact with mine drainage, and at point R4 in the Rejo sub-basin.

4.3.1.5. Conclusions

Sediment samples from the Llapa sub-basin showed considerable differences in the concentrations of As, Sb, Cd, Cu, Pb, and Hg between the mainstream and the tributary point Ll5 (the closest to the mine). In the Rejo sub-basin, considerable differences in the concentrations of Cd, Cu, and Zn were found between mainstream (downstream of flow from the mine site) and tributary samples.

Toxicity exposure on the aquatic life was frequently caused by sediment contamination with As, Cd, Cu, Hg, Pb, and Zn. As, Cd, and Cu concentrations were particularly high in the Llapa sub-basin whereas Pb and Zn were high in the Rejo sub-basin.

Mobility of the trace elements, assessed by SES analysis, was: Zn (69%) >Ni (61%)> Cu (58%)> Cd (47%)> Fe (26%) > Hg (23%) >Cr (21%)> Al (15%) > Sb (12%) = Pb (12%) >As (2%) = Sn (2%). Therefore, Zn, Ni, Cu, and Cd can be considered as a significant threat to the environment in all the monitoring points. In addition, relevant percentages of Cr and Hg were available in some points of the Rejo, and As, and Sb in the Llapa sub-basin. The risk was particularly high in the Rejo compared with the Llapa sub-basin, where high and available concentrations of Cd, Cu and Hg (and to a lesser extent Pb and Zn) were found.

Principal component and cluster analyses provided a plausible characterization of the natural (non-polluted) trace element content profiles of the basin. Besides, sets of trace elements characteristic of different pollution sources were identified in the two sub-basins: (i) Pollution can be expected in the mainstream of the Rejo sub-basin, particularly at the closest point to the mine drainage, where high concentrations of Zn, Cr, Ni, Cd, Cu, and Pb were found, (ii) Two pollution profiles were identified in the Llapa sub-basin: one in a tributary at the closest sampling point to the mine, which showed very high concentrations of As, Cd, Fe, Ni, and Cu; and the other in the mainstream located downstream of the tributaries affected by mine drainage, where high concentrations of Al, Cu, Cr, Hg, Ni, Pb, Sb, and Sn were recorded.

4.3.2 Second sediment monitoring

This section reported and discussed the results from the three campaigns of sediment monitoring performed in June and November 2009 and July 2010 in the Jequetepeque sub-basin (Figure 3.9). The following terms were argued below: the quality assurance and quality control obtained at the analytical procedure, the trace element concentration, the source of trace elements, its environmental implications, and the spatial and temporal distribution of trace elements.

4.3.2.1. Quality Assurance and Quality Control

The efficiency of the digestion procedure was considered suitable when obtained recoveries varied between 70-130% (Kartal et al., 2006; Martínez, 2008). Table 4.17 shows the recoveries for all the trace elements analysed, being all within this range. Therefore the results were considered valid. Cr was the exception, giving only 61% recovery. Low recoveries for Cr were found in the literature (Pérez-López et al., 2008) and could be due to difficulties in the total release of the Cr reported in the sample, mainly related to aluminium-silicates and its slow kinetics.

Table 4.17: Obtained recoveries for CRM 320R. Units in mg/kg

	CRM 320R	Uncertainty	Measured value	S. D.	Recovery (%)
Fe	25700	1300	21659	742.1	84
Zn	319	20	290.5	8.4	91
Cu	46.3	2.9	36	6.3	78
Cr	59	4	36.9	0.8	63
Cd	2.6	0.2	2.4	0.2	91
Hg	0.9	0.1	0.7	0.1	81
As	21.7	2	19.2	1	89
Ni	27.1	2	22.3	1.8	83

It should be noted that no results in the literature were obtained for the BCR three-step extraction procedure performed for CRM 320R. In this work, three samples of CRM 320R were included in the BCR three-step extraction scheme carried out to obtain data from CRM 320R at the extraction procedure. The results were given in Table 4.18. Good results were achieved considering the standard deviation and cumulative variance obtained for each trace element.

Table 4.18: The mean, standard deviation (S.D.) and cumulative variance (C.V.) for the CRM 320R samples obtained from the BCR three-stage procedure (n=3). Units in mg/kg.

	Exchangeable phase			Reducible phase			Oxidable phase		
	Mean	S.D.	C.V. (%)	Mean	S.D.	C.V. (%)	Mean	S.D.	C.V. (%)
Al	27.80	1.15	4	677.67	14.01	2	2457.14	78.54	3
Zn	132.43	1.17	1	90.26	0.28	0.3	38.38	3.64	9
Cu	0.72	0.10	14	5.34	0.13	2	28.22	0.64	2
Pb	1.04	0.02	2	39.54	0.10	0.3	23.81	0.32	1
Ni	3.03	0.07	2	4.38	0.06	1	11.32	1.55	14
Cr	0.25	0.02	8	1.31	0.02	1	15.92	0.46	3
As	1.89	0.03	1	7.70	0.07	1	6.50	0.09	1
Cd	0.82	0.00	1	1.20	0.01	1	0.23	0.07	29

4.3.2.2. Trace element concentration

The pseudo-total trace element contents of all the samples collected along the basin and analysed by MW digestion are summarised in Table 4.19. The results are given as a mean of the three campaigns and its standard deviation.

Table 4.19: Trace element mean concentrations and standard deviations for the second sediment monitoring (n=3). Samples R0, T6 and T7 were analysed in one campaign (n=1).Units in mg/kg, except for Al and Fe in g/kg (^{a}).

	Llapa Sub-basin					Rejo Sub-basin			
	Ll1	Ll2	Ll3	Ll4	Ll5	R0	R1	R2	R3
Al ^{a}	61 ± 1.1	60 ± 5.5	43.8 ± 9.6	61 ± 2.9	33 ± 3.8	11	56 ± 18	39 ± 4	40 ± 1.1
Fe ^{a}	37 ± 3.3	37 ± 3	44 ± 6.4	41.8 ± 2.8	57 ± 1.2	35	37 ± 5.7	33 ± 4.3	30 ± 2
As	7.2 ± 2.3	11 ± 4.1	86 ± 65	40 ± 16	188 ± 40	582	116 ± 31	61 ± 31	45 ± 34
Cd	0.2 ± 0.02	0.36 ± 0.03	1.3 ± 0.5	0.5 ± 0.17	1.1 ± 0.65	1.64	10 ± 1.62	2.6 ± 1.5	0.5 ± 0.25
Cr	14 ± 2.4	14 ± 1.3	13 ± 4.7	15 ± 1.02	9.7 ± 1.4	5.73	17 ± 3.6	12 ± 1.5	12 ± 1.9
Cu	24 ± 4.1	144 ± 86	233 ± 99	790 ± 62	395 ± 148	681	574 ± 243	112 ± 102	17 ± 6
Hg	0.06 ± 0.02	0.1 ± 0.07	0.7 ± 0.19	0.2 ± 0.01	0.9 ± 0.26	6.72	1.2 ± 0.5	0.2 ± 0.16	0.05 ± 0.04
Ni	10 ± 1.8	12 ± 1.9	16 ± 3.06	18 ± 2.7	12.8 ± 4.7	3.42	18 ± 3.7	11 ± 3.1	11 ± 4
Pb	16 ± 3.1	17 ± 3.3	25 ± 11	17.2 ± 3.3	41 ± 4.7	1026	183 ± 71	52 ± 17	36 ± 18
Zn	87 ± 6.7	115 ± 6.8	144 ± 22	198 ± 4.7	114 ± 43	156	459 ± 86	160 ± 59	104 ± 33

	Alto Jequetepeque Sub-basin						
	T1	T2	T3	T4	T5	T6	T7
Al ^{a}	29 ± 11	35 ± 6	30 ± 4.9	30 ± 5.3	28 ± 3.7	26	29
Fe ^{a}	40 ± 17	29 ± 4.6	29 ± 5.7	28 ± 5.7	28 ± 6.7	37	32
As	34 ± 19	23 ± 2.9	22 ± 4.3	22 ± 6.3	23 ± 6.7	17	24
Cd	0.8 ± 0.2	1 ± 0.29	0.8 ± 0.19	0.8 ± 0.3	0.9 ± 0.37	0.71	0.59
Cr	21 ± 5	16 ± 5.3	15 ± 2.6	14 ± 4.2	14 ± 3.5	35	18
Cu	19 ± 5	27 ± 4.9	21 ± 4.2	22 ± 3.7	23 ± 2.4	22	20
Hg	0.1 ± 0.11	0.09 ± 0.03	0.07 ± 0.02	0.08 ± 0.02	0.2 ± 0.07	0.10	0.67
Ni	13 ± 2.6	13 ± 3.2	11 ± 2.3	11 ± 3	11 ± 2.7	24	12
Pb	33 ± 11	29 ± 6.9	26 ± 4	27 ± 6	24 ± 14	22	30
Zn	108 ± 12	116 ± 26	101 ± 19	104 ± 24	114 ± 46	91	88

Al and Fe were significantly more abundant (40,399 and 36,135 mg/kg on average respectively) 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 showed were considerably different depending on the sub-basin while Fe concentrations were more homogeneous along the basin.

Ni and Cr concentrations also showed minor variations between the samples developed in this study (Table 4.19). The concentrations of Cr in the Jequetepeque basin were in agreement with the small differences obtained and were significantly lower than the concentrations found in the literature (Coynel et al., 2009; Goldhaber et al., 2009; Mendici et al., 2011). The Ni concentrations found in the literature were similar (Coynel et al., 2009) or lower (Goldhaber et al., 2009; Mendici et al., 2011) than the results obtained.

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

The higher variations obtained for the As and Hg concentrations, 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 obtained values in a French basin affected by mining (Coynel et al., 2009).

The contents of Cu differed significantly from 10.7 to 861 mg/kg, resulting in an average of approximately 189 mg/kg. This concentration is 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).

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

The Cd contents on the sediment samples ranged considerably from 0.2 to 11.4 mg/kg, with an average of 1.5 mg/kg. The mean concentration was in agreement with findings in the literature, showing similar mean concentrations in the anthropogenic affected areas in France, Italy and Bolivia (Coynel et al 2009, Mendici et al 2011, Salvarredy-Aranguren et al 2008). However, the major peaks of Cd observed for each study in the literature are higher than those obtained for this survey. On the other hand, the average values are lower and the peaks were higher than the European and United States soils and sediment values (Goldhaber et al., 2009).

It should be noted that a previous sediment monitoring (section 4.3.1) was carried out in the upper parts of the basin in November 2008, where the concentrations were similar than the obtained in this monitoring. The trace elements were within the range of variation reported at the second sediment monitoring; Ll5 and R1 being the most polluted monitoring sites for Ad, Cd, Cu, Hg, Pb, and Zn. As, Hg, Pb, Cd, Zn and Cu (in decreasing order) reported exposure on the aquatic life to toxicity, following the Canadian Guidelines (CCME, 2002; Burton, 2002). In can be concluded that, the toxicity due to As, Hg, Pb, Cd Zn and Cu on the aquatic life is relevant from November 08 to July 2010 for the monitored points near mine sites in the Jequetepeque basin.

4.3.2.3. Identification of trace elements sources

In this survey, 15 sampling points from the three sub-basins (Ll1-Ll5, R1-R3 and T1-T5) were evaluated by the enrichment factor (EF), to assess the anthropogenic impact at each sampling site. A total of 12 points were evaluated from the first campaign developed in June 2009 from the three sub-basins (Ll1-Ll5, R1-R3 and T1-T4) of the Jequetepeque basin, as observed in Figure 3.9. Once the EF was calculated, the range defines the pollution grade of the monitoring sites, using the scale suggested by Birth (Table 4.20).

Table 4.20: Enrichment factor scale

EF	Enrichment grade
< 1	No enrichment
1-3	Minor enrichment
3-5	Moderate enrichment
5-10	Moderately severe enrichment
10 -25	Severe enrichment
25-50	Very severe enrichment
> 50	Extremely severe enrichment

The results indicated that Cd showed the highest enrichments of all the samples from the Jequetepeque basin (Table 4.21). The sub-basin with the highest enrichment was the Rejo sub-basin, where very severe enrichment was found in the R1 monitoring site and moderately severe enrichment for the R2 monitoring site (located downstream of R1). Additionally, all the T samples showed moderately severe enrichments. In the Llapa sub-basin, moderately severe enrichments were found for the Cd in Ll3, and moderately enrichments were obtained in Ll5 for As and Cd, suggesting that the presence of As and Cd at these points is due to anthropogenic activities.

The Pb concentrations also showed severe enrichment in R1 and decreased approximately four times the enrichment in R1 for the other R samples, suggesting that the severe Pb enrichments found in R1 were mainly due to mining activities. Additionally, moderate enrichment was determined for As and Zn at R1. The highest enrichments for Cd, Cu, Ni, Pb and Zn were obtained at this site, indicating that the pollution grade of this site was the worst of the sub-basin. For most of the other samples, minor enrichments were obtained.

Taking into account the location of the samples and the determined EF, the anthropogenic source for Cd, Pb and Zn was due to mining activities, mainly from the Yanacocha Mine. Furthermore, As and Cu enrichments were higher near the Sipán Mine, suggesting that this is the main pollution source in the Jequetepeque basin. The EF for Al, Fe, Cr and Ni showed no enrichments or minor enrichments according to the Birth scale. Therefore, these concentrations were considered to be primarily from natural sources.

Table 4.21: Enrichment factors obtained for all the monitoring sites in 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

4.3.2.4. Trace element partitioning

Figure 4.9 presented the relative percentages of the trace element partitioning with respect to the pseudo total concentration at these points. The residual fraction was calculated as the result of subtract the sum of the three steps to the pseudo-total concentration of the digestion procedure, considering it a better approach (Butler, 2011; Luo et al., 2012; Martínez, 2008; Mester et al., 1998; Oyeyiola et al., 2011).

According to Figure 4.9, the Al partitioning was in this order: residual (90%) >> oxidable (6%)> reducible (3%)> exchangeable (1%). Fe was mainly associated with the residual fraction, accounting for 76% to 94% on Fe total (88% on average). Fe related to the reducible phase was the second form present in the sediment samples from the Jequetepeque basin, differing between 2% and 20% of the total concentration. Higher concentrations bounded to the extractable fractions (the sum of the three first fractions) were obtained in samples monitored near mine sites (Figure 3.9 and 4.9). The partitioning order on average was: residual (89%)>> reducible (8%)> oxidable (4%)> exchangeable (0.3%). This fractionation was similar that the one reported in Grande River mouth, Mexico (Villalobos-Castañeda et al., 2010) and in Danube River sediments (Relic et al., 2005).

The concentrations of Cr were principally in the residual fraction, summarising on average for 81% of the total content. Secondly, the Cr contents were bounded to the oxidable fraction by an 11% while reducible and exchangeable steps each accounting 4%. There was a peak in the R0 sample, where the oxidable fraction was the 43.4%. Similar values were observed in the sediments from the Po River, one of the most polluted basins from Italy (Malferrari et al., 2009).

Similar to the Cr partitioning, the Ni fractionation order in sediment samples from Jequetepeque was: residual (63%)>> oxidable (19%)> reducible (9%) ≈ exchangeable (9%). Additionally, the highest mobile concentration was present in R0 sample (accounting for 99%), suggesting that it can be attributed to a contaminated place. As the Cr percentages, the Ni partitioning was similar than the observed in the contaminated Po River (Malferrari et al., 2009), and was in agreement to findings in the literature from the mine polluted areas in Spain (Galan et al., 2003).

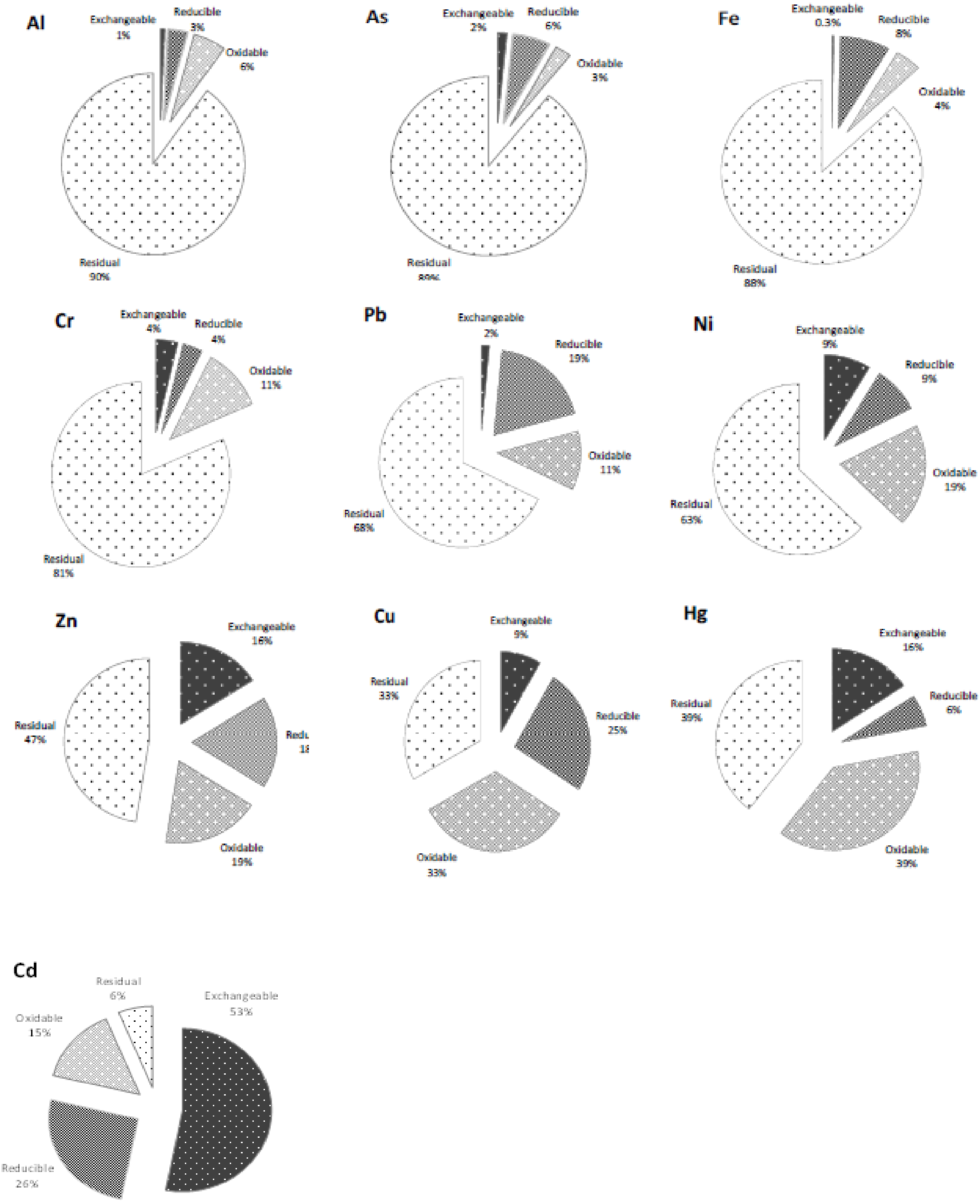


Figure 4.9: Percentages of each phase of the BCR three-step for all the samples and elements obtained

The As residual fraction varied depending on the sample from 76% to 99% of its total amount. The remaining concentrations were mainly in the reducible fraction, being 6% on average and varying between 0.1% and 17% of the total content. The partitioning profile was: residual (89%)>> reducible (6%)> oxidable (3%)> exchangeable (2%). As gives Figure 4.10, 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). Similar As values were obtained in polluted sediments in India (Routh and Hjelmquist, 2011) and in rivers in Kosovo affected by mine sites (Nannoni et al., 2011).

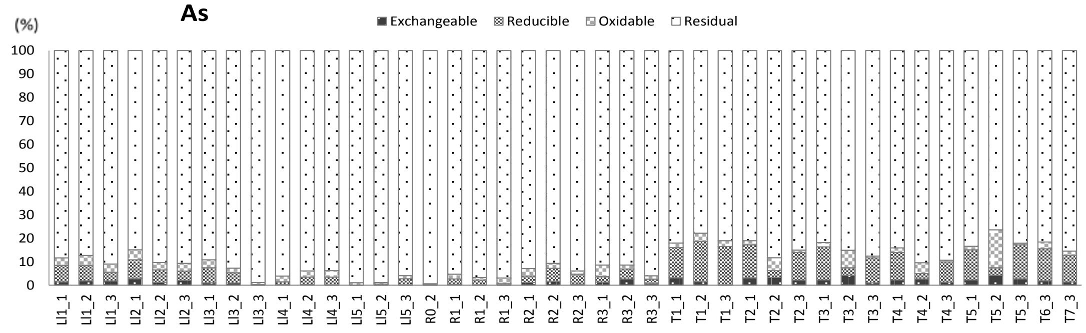


Figure 4.10: As mobility for all the samples of the second sediment monitoring.

The Pb fractionation order was: residual (68%)>> reducible (19%)> oxidable (11%)> exchangeable (2%). This partitioning illustrated the same pattern as the one obtained for As in the same places, as shown in Figure 4.10. Similar to the As case, this trend was also observed in mining areas in Kosovo (Nanoni et al., 2011), and comparable percentages were also found in an Italian contaminated basin (Malferrari et al., 2009).

The fractionation of Hg in surface sediments showed a wide range of variation as Figure 4.11 reported. The residual and oxidable phases were on average 39% one of the total amount of Hg, whereas the exchangeable phase accounted the 16% and the reducible phase reported 6% of the total amount of Hg on average.

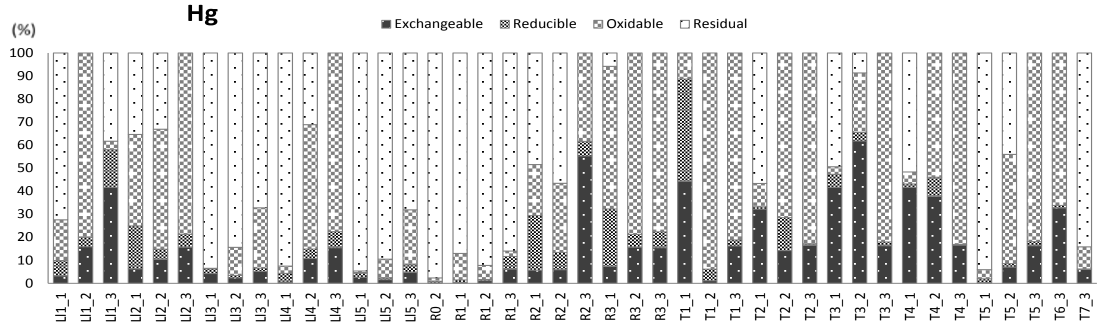


Figure 4.11: Hg mobility for all the samples of the second sediment monitoring

The partitioning of Cu was higher for the mobile fractions than for the residual fraction. Specifically: residual (33%) ≈ oxidable (33%)> reducible (25%)>> exchangeable (9%). The mobile fractions ranged widely depending on the sediment samples. The oxidable and residual fractions varied from 1% to 99%, whereas fewer differences were obtained for the exchangeable fraction, which ranged from 0 to 24%. Findings in the literature showed this heterogeneity for Cu partitioning (Galan et al., 2003, Passos et al., 2010).

Almost half of the concentration of Zn was present in the residual phase, and the rest was present in the mobile fractions in similar proportions: 19% in the oxidable phase, 18% in the reducible phase and 16% in the exchangeable phase. According to Figure 4.12, the exchangeable phase was higher for the R1 samples, suggesting an anthropogenic source. This is in agreement with the results obtained in the Po River (Malferrari et al., 2009).

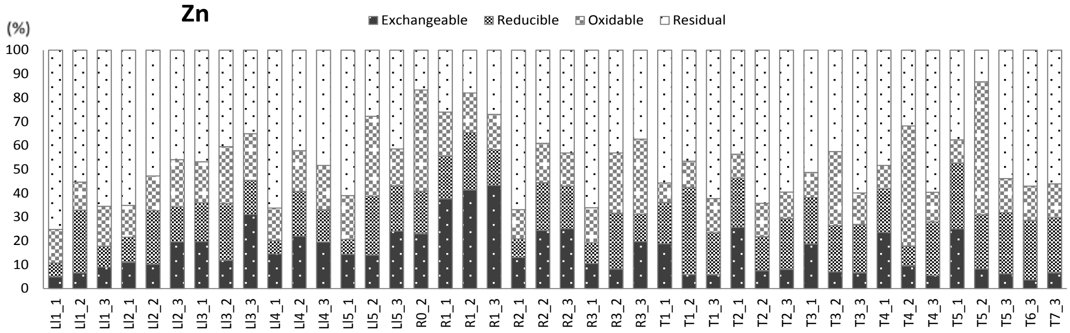


Figure 4.12: Zn mobility for all the samples of the second sediment monitoring

Cd was the most mobile element, mainly in the exchangeable phase (53% on average), ranging from 34% to 72% depending on the sample. The fractionation profile of Cd was as follows: exchangeable (53%)>> reducible (26%)> oxidable (15%)> residual (6%). Similar trends of Cd partitioning were found in the street sediments in Turkey, in Spanish sediments affected by mining and in Italian sediment from polluted rivers (Kartal et al., 2008; Margui et al., 2004; Malferrari et al., 2009; Medici et al., 2011).

4.3.2.5. Environmental implications

The first three extracted sediment phases were defined as the bioavailable fraction that may be released to the water column depending on environmental conditions. This approximation was a conservative approach to assess the environmental implications of the element partitioning in the Jequetepeque sediment samples. Taking the pollution into consideration, 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 mobility of the Cd, Cu, Hg and Zn releases were a serious concern for the environment in almost all the monitoring points 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 was also developed. The RAC evaluates the potential risk of the trace element on the environment as described in Table 4.22 (Villalobos-Castañeda et al., 2011). Figure 4.13 shows the average values obtained for each trace element. The RAC 1, which evaluates the risk associated with the exchangeable trace elements from the sediments, highlighted the risk for Cd, Hg and Zn. Additionally, the RAC 2, which considered also the trace elements associated with the reducible phase, reported high or very high risk for almost all the trace elements in the Jequetepeque basin.

Table 4.22: Risk assessment code, RAC, ranges

% Values	RAC
> 50	Very high risk
31 - 50	High risk
11 -30	Medium risk
1 - 10	Low risk
<1	No risk

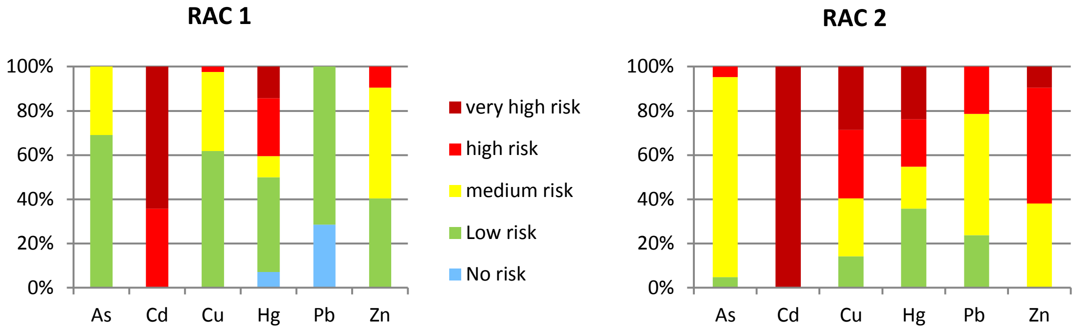


Figure 4.13: Risk Assessment Code 1 and 2, RAC 1 and RAC 2, for As, Cd, Cu, Hg, Pb and Zn evaluated as the sum of all the 42 samples monitored (16 points in three campaigns).

According to Table 4.23, the RAC1 showed a very high risk for Cd in all the samples carried out in the Ll4, Ll5, R1 and R2 monitoring points, which are the points closest to the mine sites.

Furthermore, Hg showed a very high risk, with extremely high values for the samples taken during the wet season in R3 and during the dry season in R2 and T1. The samples from R1were also obtained a high risk for the environment because of the concentration of Zn in all the samples and for Cu concentrations of the samples taken during the wet season.

Including the second easiest mobile phase and the reducible phase in the RAC2 code, Cd and Zn increased the environmental risk to high or very high for almost all the samples monitored. On the other hand, Hg only increased the risk for the samples highlighted in RAC1. It should be noted that the Cu concentrations also increased from low or medium risk to very high values during the wet season in Ll1, R3, T1, T3 and T5.

Similar trends were observed for the Pb case, where RAC2 exposed a high risk for samples taken during the dry season in the Alto Jequetepeque basin (T samples). The importance of the reducible phase and its effect on the environment was highlighted for Cu during the wet season and Pb during the dry season. The increases of Cu during the wet season (winter) and of Pb during the dry season (summer) were also reported in an Italian basin characterised by metalworking industries and handicraft factories (Medici et al., 2011).

Table 4.23: RAC1 and RAC2 results for elements that present some risk for all the second sediment monitoring samples

		As		Pb		Hg		Cu		Zn		Cd	
		RAC 1	RAC 2	RAC 1	RAC 2	RAC 1	RAC 2	RAC 1	RAC 2	RAC 1	RAC 2	RAC 1	RAC 2
Ll1	jun-09	2	6	1.3	20	3	10	4	7	5	11	42	72
	nov-09	4	12	1.4	20	40	51	2	672	7	33	45	86
	jul-10	4	8	1.3	9	42	58	1	3	9	18	42	80
Ll2	jun-09	5	14	1.5	18	6	25	8	16	11	22	41	71
	nov-09	5	15	1.1	20	10	15	12	103	10	33	79	137
	jul-10	8	16	1.7	12	39	52	12	15	20	34	53	87
Ll3	jun-09	12	26	0.9	16	4	6	15	33	20	36	45	74
	nov-09	8	19	0.6	13	2	3	10	116	12	36	39	72
	jul-10	16	26	0.7	3	5	7	18	27	31	45	61	77
Ll4	jun-09	6	11	1.6	11	1	4	17	23	15	20	60	74
	nov-09	12	23	1.5	18	11	15	24	63	22	41	68	90
	jul-10	8	19	1.1	19	20	28	20	48	20	33	66	86
Ll5	jun-09	7	15	1.0	11	3	5	17	28	14	21	59	71
	nov-09	11	18	0.8	7	2	2	16	80	14	39	56	74
	jul-10	14	31	0.4	12	5	8	13	43	24	43	59	80
R0	nov-09	12	22	1.2	8	0.1	1	29	63	23	41	41	52
R1	jun-09	11	23	0.6	8	0.5	2	24	50	38	56	72	92
	nov-09	22	44	0.2	6	1	2	32	69	41	65	71	93
	jul-10	14	23	0.5	2	6	12	18	24	43	58	64	86
R2	jun-09	8	15	1.3	12	6	29	5	11	13	21	53	82
	nov-09	10	20	1.3	16	6	13	18	112	24	44	67	93
	jul-10	11	23	0.9	29	124	138	6	42	25	43	56	85
R3	jun-09	8	17	1.2	13	7	32	4	9	11	19	47	86
	nov-09	10	21	0.9	19	186	251	2	659	8	32	48	84
	jul-10	16	25	1.9	16	42	60	3	6	20	31	57	82
T1	jun-09	7	17	3.8	22	250	499	9	17	19	36	67	87
	nov-09	6	15	0.4	48	1	8	4	576	6	42	50	84
	jul-10	3	9	0.4	54	18	21	4	39	6	23	43	72
T2	jun-09	8	16	4.6	29	32	33	9	31	26	46	71	90
	nov-09	10	12	0.7	1	16	33	4	6	8	22	52	83
	jul-10	6	16	1.9	47	42	43	5	38	8	29	55	87
T3	jun-09	6	14	3.5	30	42	47	9	18	19	38	58	78
	nov-09	10	13	0.8	2	62	66	5	274	7	26	40	74
	jul-10	6	14	2.2	49	54	59	4	37	7	27	52	72
T4	jun-09	6	13	3.4	18	42	43	10	20	24	42	67	84
	nov-09	13	14	0.6	1	80	98	5	6	10	18	41	70
	jul-10	7	18	1.1	49	42	42	3	35	6	28	51	79
T5	jun-09	5	13	7.8	46	0.3	2	8	28	25	53	69	88
	nov-09	13	15	1	1	7	9	12	543	8	31	34	65
	jul-10	8	18	1.4	46	42	46	4	40	6	32	51	79
T6	jul-10	4	13	1.5	46	42	43	3	31	4	29	45	78
T7	jul-10	7	17	2	50	6	6	5	44	7	30	53	75

4.3.2.6. Spatial and temporal distribution of TE along the basin

Statistical Analysis

To ascertain the spatial and temporal distribution and the partitioning distribution of the trace elements in the Jequetepeque basin PCA and HCA were carried out for each sample obtained by the BCR three-step procedure and MW digestion. The loadings of the principal components, the cumulative percentages for the 4 rotated matrices and the factor scores of steps 1, 2, 3 and pseudo-total concentrations are shown in Table 4.24. There were different components, 4 or 5 depending on the case, accounting from 83 to 90% of the total variance. The communalities values obtained were over 0.73, sustaining the used components for each case.

Table 4.24: PCA results for each BCR phase and the pseudo-total digestion of all the samples performed

Element	Acid exchangeable phase					Reducible phase				
	Principal components					Principal components				
	1	2	3	4	h^2	1	2	3	4	h^2
Al	0.52	0.62	-0.44		0.89	**0.96**				0.96
Fe		**0.72**			0.62	**0.87**				0.84
Zn	**0.91**	0.32			0.94	0.34	**0.75**		0.47	0.92
Cu	**0.76**		-0.35		0.79				**0.94**	0.93
Cr		**-0.79**			0.73	-	-	-	-	-
Pb		0.52	0.71		0.88	**0.83**				0.80
Cd	**0.87**				0.85		**0.93**			0.91
Hg				**0.96**	0.94			**0.94**		0.90
As			**0.91**		0.86	0.52	0.52	-0.50		0.82
Ni	**0.87**			0.34	0.90	**0.85**				0.84
Eigenvalues	3.35	2.04	1.76	1.24		3.49	1.89	1.29	1.24	
Cumulative %	33.49	53.91	71.52	83.92		38.75	59.78	74.16	87.93	

	Oxidable Phase						Pseudo-total concentration				
	Principal components					h^2	Principal components				h^2
	1	2	3	4	5		1	2	3	4	
Al		0.33	**0.83**			0.91				**0.94**	0.94
Fe	0.52	0.57				0.75		**0.91**			0.91
Zn	**0.83**		0.36			0.91	**0.86**			0.33	0.95
Cu	**0.69**		0.59			0.88	0.49	**0.69**		0.41	0.92
Cr					**0.97**	0.97			**0.95**		0.93
Pb		**-0.93**				0.92	**0.79**			-0.42	0.88
Cd	**0.89**					0.86	**0.94**				0.90
Hg				**0.97**		0.95	0.49	**0.67**			0.78
As	**0.88**					0.88	0.61	0.64		-0.32	0.90
Ni	0.55	0.43	0.41		0.31	0.78			**0.85**	0.34	0.93
Eigen values	3.32	1.61	1.47	1.22	1.20		3.12	2.36	1.96	1.60	
Cum.%	33.18	49.25	63.92	76.14	88.17		31.24	54.87	74.44	90.39	

HCA was performed with the factor loadings reported from the PCA of each step of the BCR and the pseudo-total content of trace elements from the samples of the second sediment monitoring (Han et al., 2006; Perez and Valiente, 2005). Four dendrograms were obtained, one for each analysis (Figure 4.14). The group of the samples was chosen according to data similarities (clusters) found between 10 and 15 values of the distance for the four cases (Figure 4.14). Groups of 5 clusters were reported for each case, except for the oxidable phase of the BCR case, which reported 6 groups of clusters.

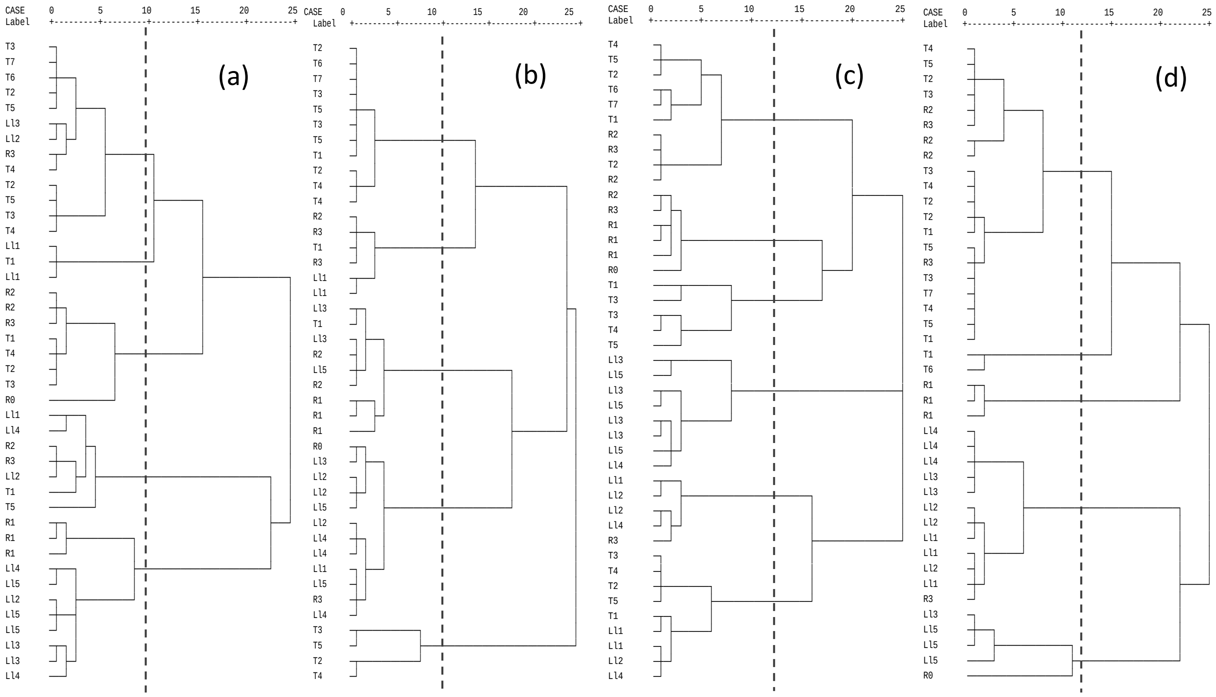
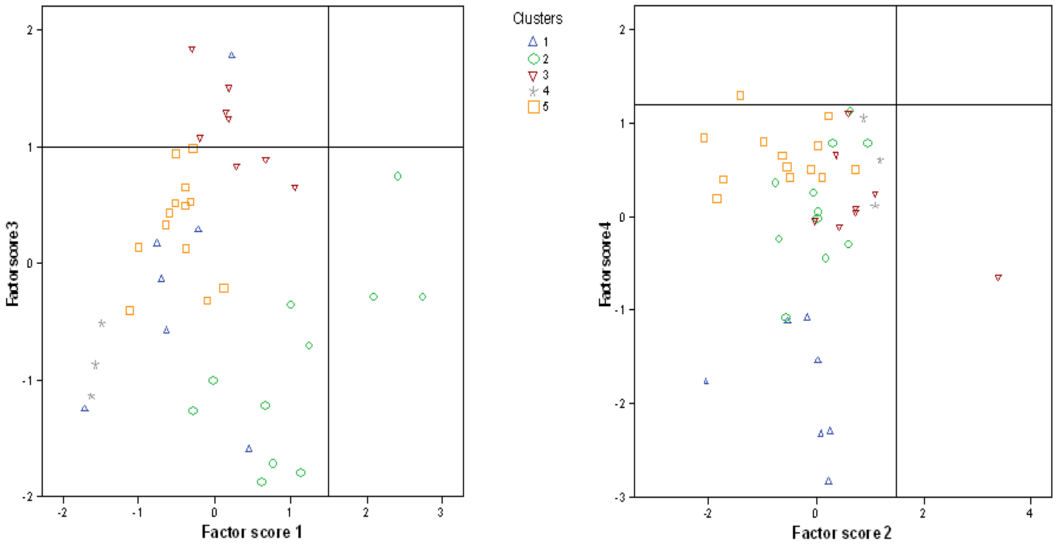


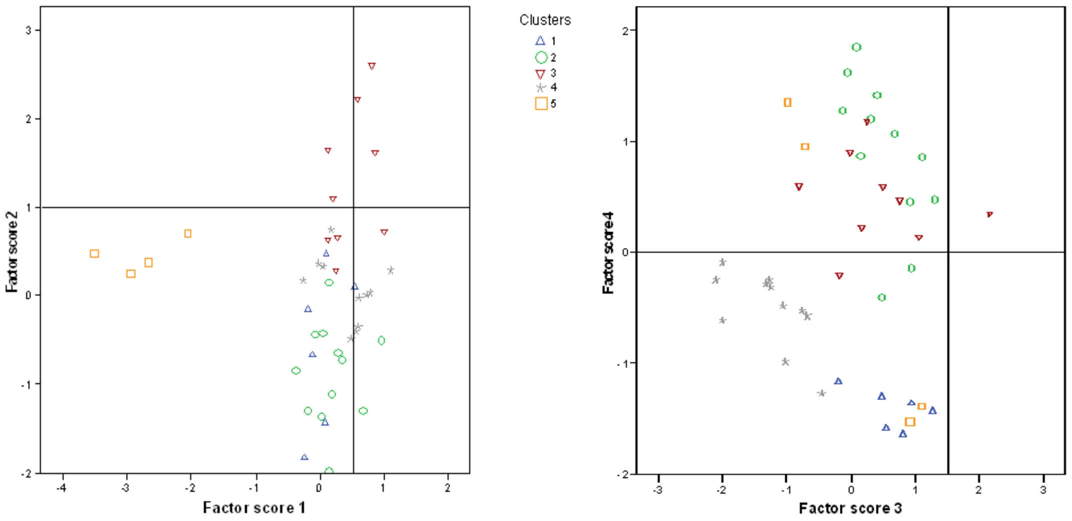
Figure 4.14: Dendrogram using Ward Method and mean of Euclidean distance for the exchangeable, reducible and oxidable phases of the BCR (a, b and c respectively) and the pseudo-total content (d)

The groups of clusters obtained from the HCA were plotted according to the factor loadings of the PCA to illustrate the relationships between all the samples (Figure 4.15). The results obtained from the statistical analysis highlighted the most polluted sample points for each step of the BCR and the pseudo-total content. The spatial and temporal trends extracted from this study are summarised below.

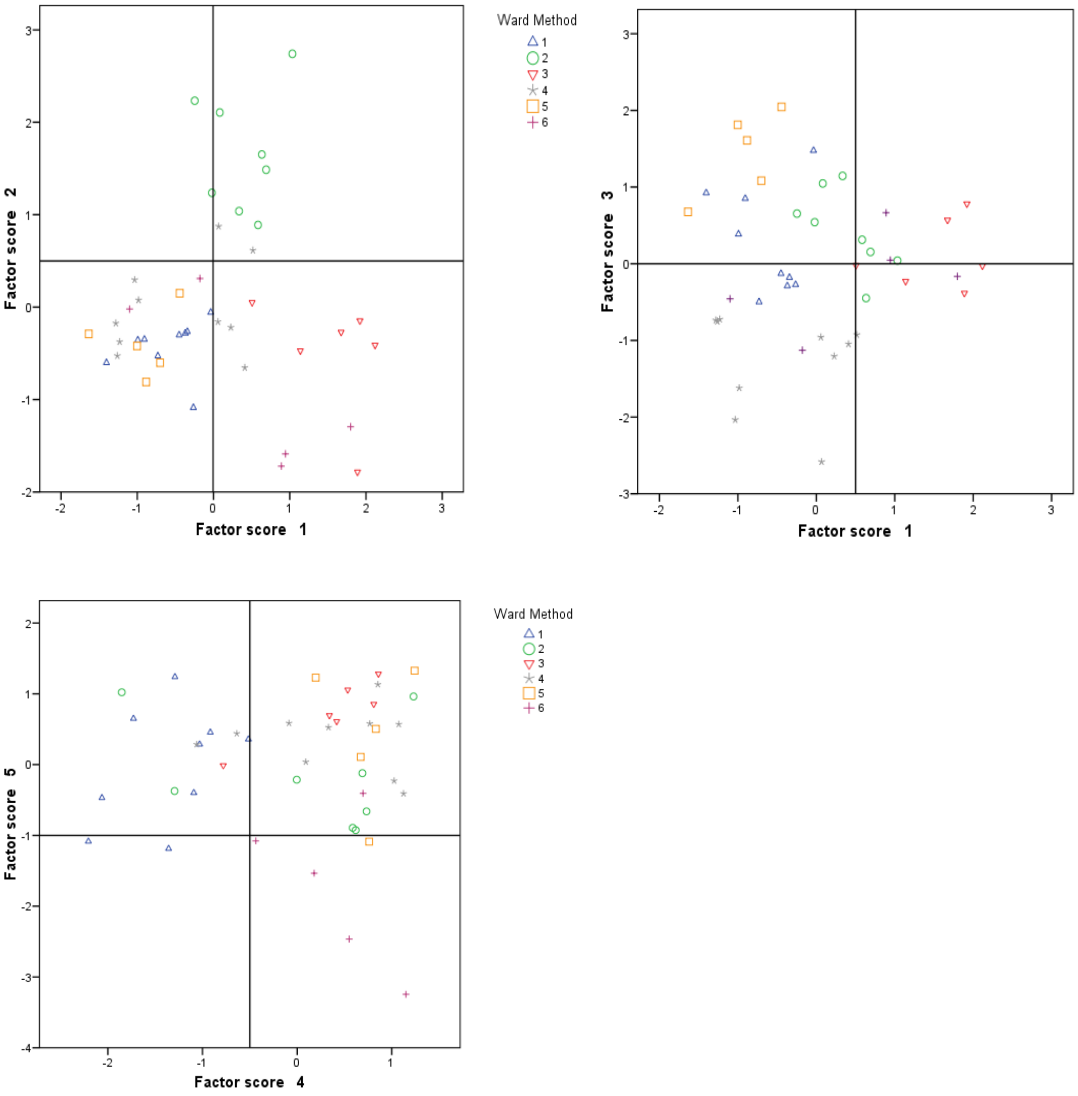
(a) Exchangeable phase



(b) Reducible phase



(c) Oxidable phase



(d) Pseudo-total concentrations

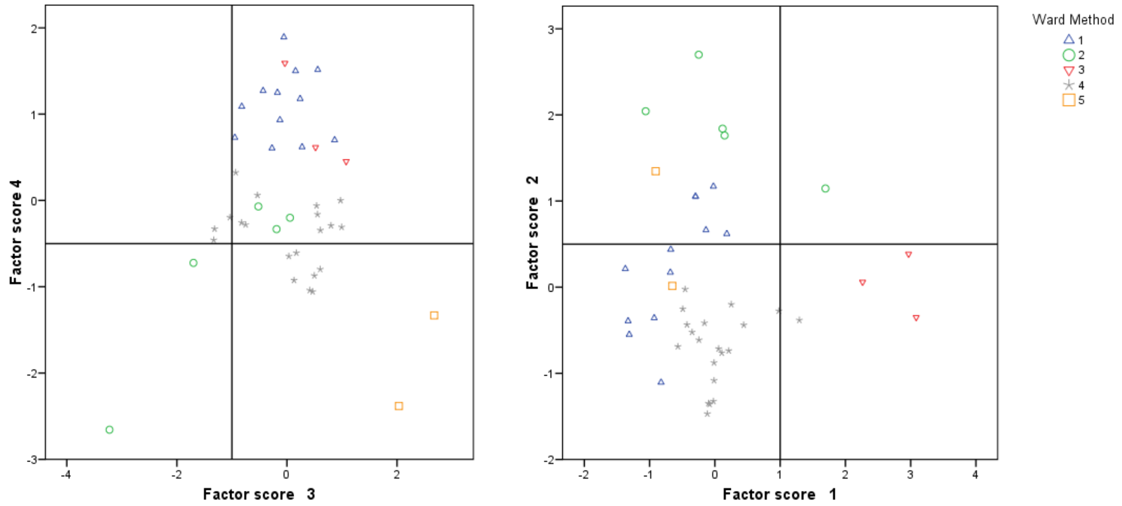


Figure 4.15: Score plots of the clusters obtained by the Hierarchical Cluster Analysis (using Ward Method and mean of Euclidean distance) for each factor score obtained by the Principal Component Analysis for the BCR three-step procedure (exchangeable, reducible and oxidable phases) and the pseudo-total concentrations.

Spatial distribution

The polluted points in the Jequetepeque basin were summarised in Figure 4.16 by taking into account the values obtained from the statistical analysis, and the sample partitioning and distribution along the basin. The same trend was observed for Cd and Zn for all the monitored points for the BCR three-steps and the pseudo total concentration. The trend suggested that there was the one source of these elements, as indicated by the EF, especially for the R1 sample. Thus, Cd and Zn were the most mobile elements, and consequently, the risk associated with them was considered very high, as the RAC suggested. Therefore, the presence and mobility of Cd and Zn due to mining activities is considered a significant concern from an environmental point of view.

All the peaks observed for As and Pb was mainly near mine sites. Their concentrations were mainly in the residual phase and secondarily bounded to the reducible phase. These peaks were only found in the Yanacocha S.R.L. Mine for Pb, whereas As was also found in the Llapa S.L. Mine. These results were in agreement those of the RAC and EF, where the same trends were observed. Then, As and Pb were not considered to be a high risk to the environment because of their slight mobility. However, the peaks of concentration due to mine sites are an issue of concern.

Major Ni and Cu peaks were found in the Ll4 and R1 monitoring sites. This is in agreement with the EF and RAC results for Cu, which indicated moderate enrichment and a very high risk at these points, respectively. Despite the high concentrations in the residual fraction, considerable mobility was found in Ll5 and Ll3,mostly in the reducible and oxidable phases for Cu and Ni, respectively. These trace elements reported high mobility and can be considered to be a very high risk to the environment according to the RAC, but their low concentration at these points indicated them as a non-significant threat to the environment.

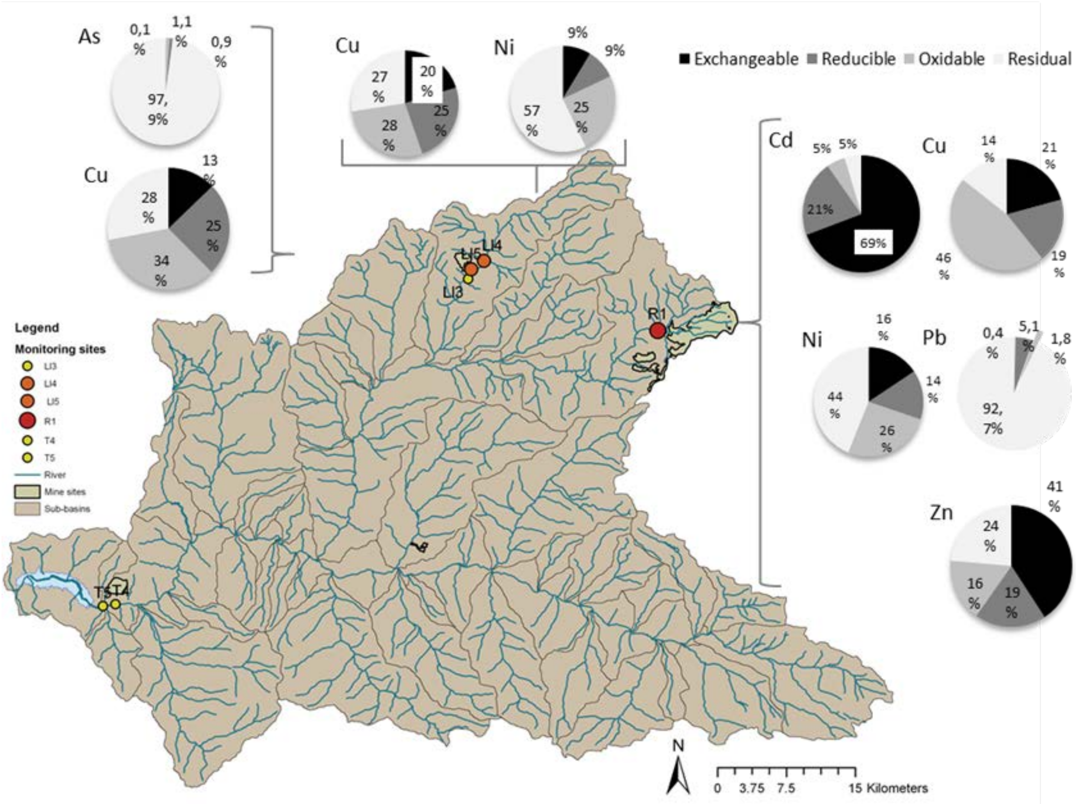


Figure 4.16: Jequetepeque basin with the points with the great, significant and moderate concentrations of trace elements (points in red, orange and yellow respectively), and the element speciation for the most contaminated points (R1, Ll4 and Ll5).

Remarkably peaks were also reported in the T4 and T5 samples for the Cu concentrations in the oxidable phase. These results were in agreement with those previous obtained in a preliminary research at the same monitoring sites (Section 4.3.1). This previous research corresponds to the first sediment monitoring, which was carried out in November 2008 and the analysis applied was the four steps of BCR protocol (Sahuquillo et al., 1999; Thomas et al., 1993; Ure et al., 1993). Despite the differences in the analytical methods, the trends of the spatial distribution of the elements and its concentration range were similar for the three campaigns developed in this Second sediment monitoring, confirming the spatial distribution of the trace elements in the Jequetepeque basin.

Al and Fe were mainly resulted in the residual fraction, emphasizing the higher concentrations for Llapa samples. Similar concentrations were obtained for the reducible and oxidable phase for Al and Fe near mine sites. At these sites the total concentration of Al and Fe slightly increased. Then, the presence of these elements is not considered a significant threat to the environment.

Temporal distribution

The temporal changes in the element distribution were evaluated by the differences between the three campaigns. The same associations were found for all the elements in June 2009, November 2009 and July 2010. Cd – Zn, and As - Pb were similar for all the campaigns, maintaining the same trends. These elements reported the highest concentrations, and according to the EF, the higher enrichments, were due to mining activities as mentioned before.

Furthermore, the Cu and Hg concentrations and their mobility increased during the wet season for almost all the samples. The Hg concentrations were higher for the samples located just downstream of the mine sites (Ll5, R0 and R1), whereas their mobility was lower than for the other samples. Higher Cr mobile concentrations were obtained during the dry season, specifically for the R1 and T samples, which was the opposite of the Cu and Hg concentrations. The increases of Cu during the wet season (winter) and of Pb and Cr during the dry season (summer) were also reported in rivers affected by the metal working industries and handicraft factories in Italy (Medici et al., 2011).

4.3.2.7. Conclusions

The grade of pollution of the different substances, the sources of contamination, and the potential effect on the 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 in order to evaluate and regulate pollution emissions.

The first three extracted sediment phases defined as the bioavailable fraction that may be released to the water column depending on the environmental conditions. This approximation was a conservative approach in order to assess the environmental implications of the element partitioning in the Jequetepeque sediment samples. Taking it into consideration, 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 for all the monitored points for the BCR three-steps and the pseudo total concentration was observed for Cd and Zn, suggesting a single source, as the enrichment factor highlights, especially for the R1 sample. Cd and Zn were the most mobile elements, and consequently, the risk associated with them was considered very high, as the RAC suggested. The presence and mobility of Cd and Zn due to mining activities was considered a great concern to the environment.

All the peaks observed for As and Pb were mainly near mine sites. Its concentration was primarily in the residual phase and secondarily bound to the reducible phase. It should be noted that peaks were only found in the Yanacocha S.R.L. Mine for Pb whereas As was also found in the Llapa S.L. Mine. This was in agreement with the RAC and EF results, where the same highlights were observed. The As and Pb were not considered to be a high risk to the environment because of their small mobility, but the peaks of the concentration were of concern due to the mine sites. Cd - Zn, and As - Pb were similar for all the campaigns, maintaining the same temporal trends.

Major Ni and Cu peaks were obtained in the Ll4 and R1 monitored sites. This was in agreement with the EF and RAC results for Cu, which showed moderate enrichment and a very high risk, respectively, at these points. The Cu and Hg concentrations and their mobility increased during the wet season for all the samples. Higher Cr mobile concentrations were obtained during the dry season, specifically for R1 and T samples, which was the opposite of the Cu and Hg mobile concentrations.

Al and Fe were principally observed in the residual fraction, emphasizing the higher concentrations observed in the Llapa samples. Similar concentrations were obtained for the reducible and oxidable phase for Al and Fe near mine sites, which increased near the mine sites. Nevertheless, the presence of these elements was not considered a significant threat to the environment.

The effect of trace elements near mine sites in the Jequetepeque basin reflected a significant threat to the environment for Cd, Zn, Pb and As, independent of the season. This work considers an effort to enhance the knowledge of the environmental quality status that may support water quality management at the basin and a necessary step towards future prevention and remedial actions.

4.3.3 Kinetic and modelling

In this section, the mobility of trace elements from river sediments by single-extraction treatments, nitric acid (under different pH), and EDTA was evaluated. Additionally, the labile with non-labile amount obtained by each extractant was compared.

Kinetic experiments were performed using time-based extraction experiments with EDTA as the added extractant. A diffusion kinetic model adapted to the sediment system, the Elovich equations and the two first-order reactions model were used to describe the experimental data.

The samples chosen in this work were obtained from the second sediment campaign. The samples were the following: Ll4 and Ll5 samples located near the Sipán S.L. Mine taken in June 2009, samples R0 and R1 placed close to the Yanacocha S.R.L. Mine obtained in November 2009 and July 2010 respectively (Figure 3.9). Results of pseudo-total concentrations obtained by the MW digestion procedure for the four points analysed were shown in Table 4.25.

Table 4.25: Pseudo-total concentrations for the four elements analysed from second sediment monitoring by MW digestion. Units in mg·kg^{-1}

	Al	Fe	Zn	Cu	Ni	Pb	Cd	As	Organic matter %
Ll5	37,138	70,753	135	563	16.3	46.1	1.3	234	6.19
Ll4	57,534	40,881	198	861	16.8	16.8	0.3	45.4	6.30
R1	10,743	34,660	156	681	3.4	1026	1.6	582	4.85
R0	76,688	40,026	377	394	14.1	104	8.2	84.5	8.72

4.3.3.1. Single extraction by HNO_3 and EDTA

The risk assessment of mining areas requires an accurate characterization of the wastes because of the higher trace element solubility at low pH (Conesa et al., 2008). Based on this consideration, the single extraction by HNO_3 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 around 1, the maximum amount of these six trace elements was extracted (data not shown); an increase of pH led to a rapid decrease in trace concentrations, and in fact, concentrations after pH = 4 were lower than 5 $mg \cdot kg^{-1}$ for most of the trace elements. The results indicate that higher amounts of trace elements are leached with pH values ≤1, which indicate extreme conditions.

In order to evaluate the leachability of trace elements, the results of HNO_3 extraction at pH = 4, was compared with the EDTA extraction (Table 4.26). Thus, the EDTA extraction resulted in higher concentrations of leached trace elements than the acid extraction. Furthermore, extraction by EDTA showed higher values of Cu and Zn in all samples and in most cases values were four-fold that of the concentration leached by acid treatment.

Table 4.26: Trace elements extracted by HNO_3 (pH=4) and by EDTA treatment on the four sediments. Units in $mg \cdot kg^{-1}$

	Ll5		Ll4		R1		R0	
	HNO_3	EDTA	HNO_3	EDTA	HNO_3	EDTA	HNO_3	EDTA
Zn	19.96	43.73	27.95	42.20	40.61	39.00	91.97	200.52
Cu	39.14	152.00	82.38	328.25	215.91	258.58	8.65	273.56
Cd	0.61	0.71	0.16	0.22	0.69	0.65	2.64	7.84
Pb	0.15	5.56	0.14	4.75	2.78	90.18	0.32	18.73
As	0.04	0.50	0.10	3.17	0.77	3.86	0.12	5.39
Ni	0.88	1.88	0.67	1.70	0.97	0.46	0.82	2.62

The trace elements showed different ratios of extraction with respect to the total amount of elements in the sediments (Figure 4.17). For HNO_3 extraction, Cd extraction was around 40% in all sediments, while extractions of Zn and Cu were lower than 20%. In general, sediment sample R1 resulted in higher ratios. Such difference in leachability may 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 trace elements are capable to forming complexes with organic matter at pH values above 3.

The EDTA extraction reported higher leachability than acid treatment for all trace elements. This can be explained by the fact that EDTA extracts organically-bound, oxide-bound, and carbonate-bound fractions of trace elements from the sediments (Nguyen et al., 2010). In general, sediment sample R0 resulted in higher values by EDTA extraction than other sediments samples. This may be due to the higher amount of organic matter (Table 4.25) in this sediment, which makes the bioavailability of the traces elements higher than with other sediments.

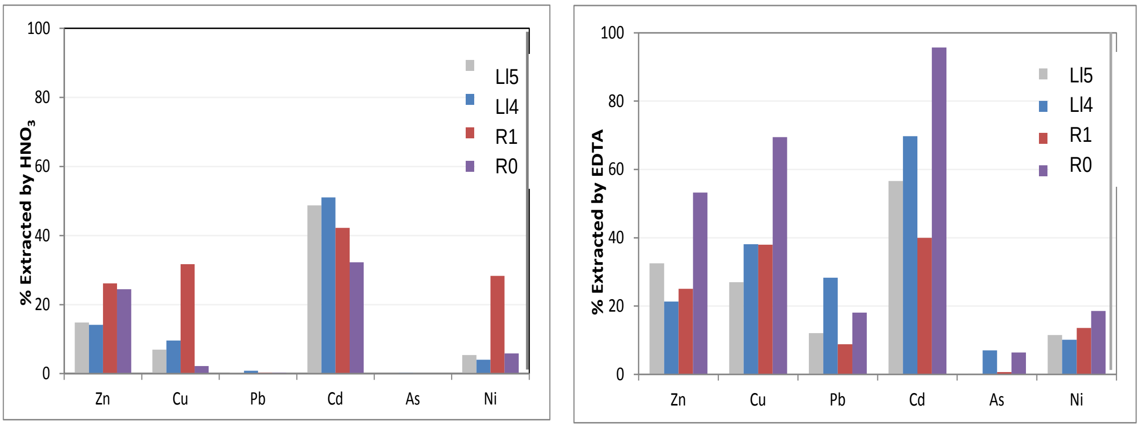


Figure 4.17: Ratio of trace elements leachability from four sediment samples after EDTA and HNO_3 extraction

With the purpose of risk assessment, EDTA extraction procedure would be more protective because of its higher leaching capacity than acid treatment at $pH = 4$. It should be noted that, if acid treatment is performed at lower pHs, the leachability will increase significantly for elements with an intermediate mobility (e.g. Cu and Ni) and especially for fixed elements (e.g. Pb), as an increase in acidity causes a considerable increase in extractability (Sahuquillo et al., 2003). For instance, Cu and Pb increased their leachability on average in four sediments to 80% and 40%, respectively, after acid extraction at $pH \leq 1$. As pHs near 2 were reported from some researchers from the Universidad Nacional de Cajamarca (personal communication) is possible than trace elements release from the sediment to the water column; thus, a more conservative scenario should be considered.

4.3.3.2. Kinetic extraction by EDTA

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 Elovich equations were used only for As, Ni and Cd, since experimental data of these trace elements did not show two stages behaviour. The two first-order reactions model was used for Cu, Pb and Zn. It was fitted to the experimental kinetic data using the non-linear regression analysis from the program GraphPadPrism5$^{®}$ (Trial version; http://www.graphpad. com; last access April, 2012) (Santos et al, 2010).

The values of the coefficient of correlation, r^2, and the relative error, SEE, for the three models are presented in Table 4.27 for the Diffusion model, the Elovich equation and the two first-reaction model. A relatively high value, close to 1 of the coefficient of correlation and low value of S.E. were used as criteria for the best fit. Additionally, the parameters D_t from the Diffusion model and Q_1 and Q_2, from the two first-order reactions model were given in Table 4.27.

Table 4.27: Coefficient of correlation (r^2) and relative error (SEE) associated with diffusion model fitting for extraction by EDTA

Trace Element	Sample	Diffusion model			Elovich equation		Two first-order reaction equations					
		SEE	r^2	D_t ($cm^2 \cdot s^{-1}$)	SEE	r^2	Q_1	k_1	Q_2	k_2	SSE	r^2
As	Ll5	0.04	0.9	3.74×10^{-11}	0.06	0.93	-	-	-	-	-	-
	Ll4	0.08	0.9	3.57×10^{-9}	0.35	0.83	-	-	-	-	-	-
	R1	0.02	0.9	1.53×10^{-9}	0.24	0.81	-	-	-	-	-	-
	R0	0.06	0.9	9.86×10^{-9}	0.05	0.90	-	-	-	-	-	-
Cd	Ll5	0.02	0.9	1.21×10^{-11}	0.02	0.91	-	-	-	-	-	-
	Ll4	0.02	0.8	5.18×10^{-13}	0.04	0.61	-	-	-	-	-	-
	R1	0.02	0.9	1.58×10^{-11}	0.02	0.83	-	-	-	-	-	-
	R0	0.01	0.9	1.00×10^{-9}	0.04	0.80	-	-	-	-	-	-
Ni	Ll5	0.19	0.9	1.27×10^{-9}	0.48	0.60	-	-	-	-	-	-
	Ll4	0.08	0.9	8.61×10^{-10}	0.28	0.80	-	-	-	-	-	-
	R1	0.06	0.9	7.28×10^{-11}	0.09	0.84	-	-	-	-	-	-
	R0	0.03	0.9	1.15×10^{-9}	0.27	0.82	-	-	-	-	-	-
Cu	Ll5	0.02	0.9	2.52×10^{-6}	-	-	9.6	0.022	66.8	0.001	0.02	0.98
	Ll4	0.02	0.9	1.07×10^{-5}	-	-	29.6	0.020	118.4	0.002	0.03	0.99
	R1	0.02	0.9	5.93×10^{-6}	-	-	20	0.011	91.7	0.002	0.02	0.99
	R0	0.03	0.9	3.99×10^{-6}	-	-	21	0.021	70.2	0.002	0.01	0.98
Pb	Ll5	0.02	0.9	3.59×10^{-9}	-	-	0.4	0.008	2.3	0.001	0.03	0.97
	Ll4	0.03	0.9	2.29×10^{-9}	-	-	0.3	0.035	2.2	0.001	0.03	0.96
	R1	0.04	0.9	1.10×10^{-6}	-	-	9.2	0.006	36.4	0.002	0.03	0.98
	R0	0.06	0.9	6.51×10^{-8}	-	-	1.0	0.002	9.9	0.002	0.04	0.98
Zn	Ll5	0.12	0.9	8.54×10^{-7}	-	-	7.7	0.001	35.3	0.001	0.10	0.97
	Ll4	0.08	0.9	2.79×10^{-7}	-	-	4.8	0.074	22.0	0.002	0.07	0.96
	R1	0.05	0.9	2.34×10^{-7}	-	-	7.6	0.007	13.4	0.002	0.03	0.98
	R0	0.03	0.9	4.04×10^{-6}	-	-	21.8	0.014	65.3	0.002	0.02	0.99

The coefficients of correlation the two first-order equation were slightly higher than those of the diffusion model, however, a good correlations was also obtained by this model, which indicates that can describe the desorption process from the four sediments studied (Ll4, Ll5, R0 and R1). The Elovich equation reported poor description of the experimental data with values of SSE higher and lower correlations r^2 if compared with values obtained with Diffusion model and two first-order equations. Hence, it can be concluded that, in the studied sediments, the Elovich equation is not adequate to describe the EDTA extraction of As, Cd and Ni in the all range of extraction times (0–24 h).

For the diffusion equation, the mean values of r^2 is higher than 0.94, with most values higher than 0.98, while on the other hand the relative error follows the same trend observed for the r^2. Thus, the diffusion model can properly describe the extraction rate data for As, Cd, Ni, Cu, Pb and Zn for all the sediments analysed.

The extraction rate data of Zn, Cu, Pb, Cd, As, and Ni by EDTA for the four sediments was shown in Figure 4.18. The 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 is slower.

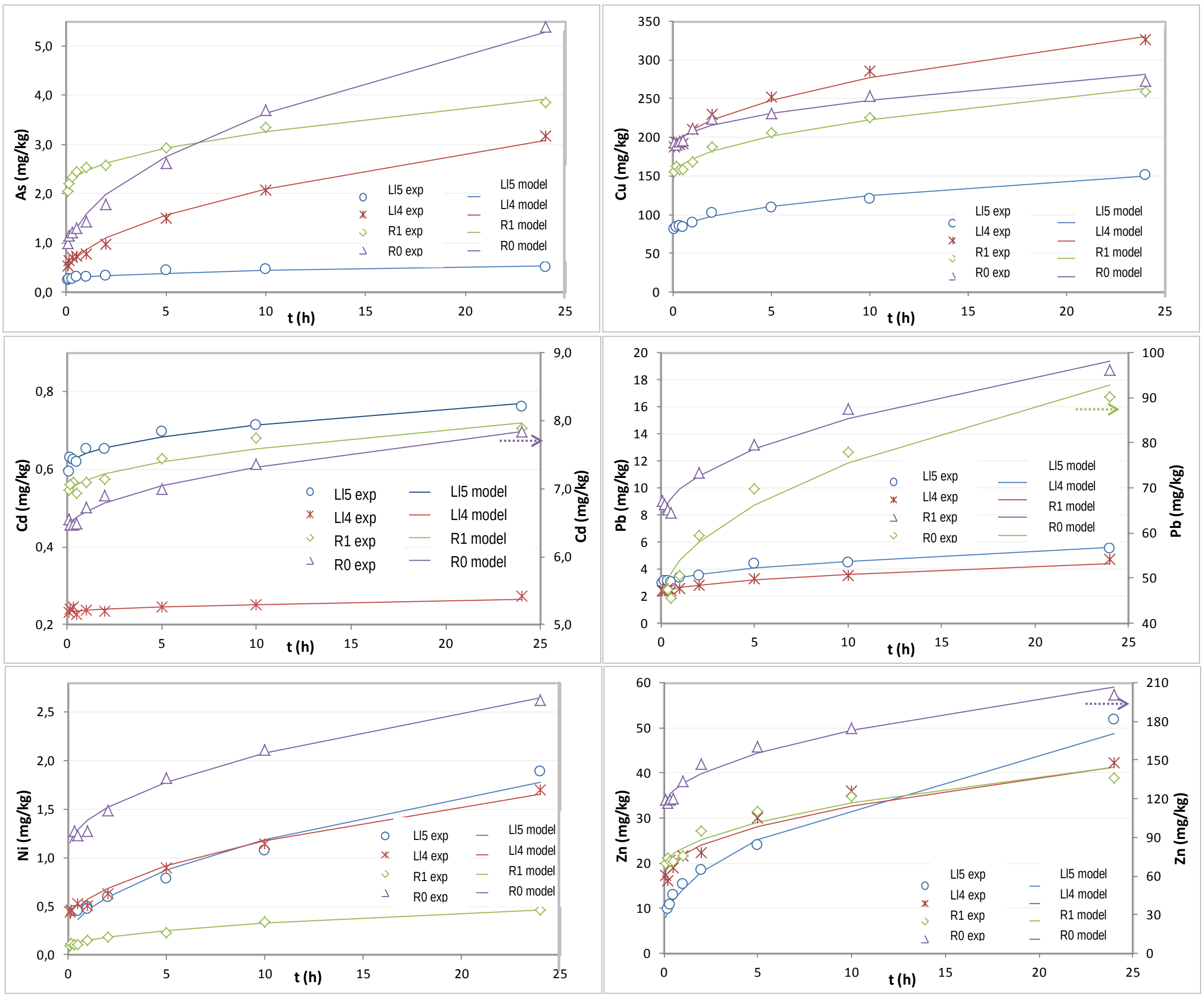


Figure 4.18: Experimental and fitted extraction rate data of As, Cd, Ni, Cu, Pb and Zn by the diffusion model

The amount of traces associated with short extraction rate is related to the fraction easily extracted, while the second fraction is related to extraction of complexes which requires more time to dissociate (Fangueiro et al 2005). On the other hand, As, Ni and Cd observed a lineal behaviour which indicates that few amount of trace elements were extracted and only the exchangeable and weakly adsorbed species were released. The same trend was observed for other sediments. The amount of trace elements released by the EDTA extraction after 1 hour is low compared to the total trace elements content determined by the MW digestion procedure (Table 4.25 and 4.26) as showed in Figure 4.18 and Table 4.27.

The extracted fraction with EDTA of most of the trace elements and for all sediments was below than 20 %, except for Zn in Ll5, Cu in Ll4, R1 and R0, and Cd for all samples. This is in agreement with the results obtained for SES (section 4.3.2 of this thesis); where higher extraction rates for the mobile phases of the BCR procedure (the three first phases) were obtained for Cd and Zn for all the samples, and for Cu in Ll4, R1 and R0.

4.3.3.3. Conclusions

The extraction experiments indicated that EDTA caused higher mobility of trace elements that acid treatment (with HNO_3). The extraction by EDTA procedure can be more protective because of its higher leaching capacity than acid treatment at pH=4, which is an important issue in view of risk assessment. The acid treatment 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 highest extractability was observed for Cd in all sediments, either by acidic or EDTA treatment, with an extraction of 90% after 1 hour. The rate of extraction by EDTA was slow as demonstrated by extraction after 1 hour.

The extracted fraction with EDTA of most of the trace elements and for all sediments was small being below than 20 %. Cd at all the samples, Zn at Ll5 and Cu at Ll4, R1 and R0, presented higher extraction rates. This is in agreement with the results obtained for SES (section 4.3.2); where higher extraction rates for the mobile phases of the BCR procedure (the three first phases) were obtained for Cd and Zn for all the samples, and for Cu in Ll4, R1 and R0.

The diffusion model was used successfully to describe the kinetic extraction of trace elements in four sediments. The two first-order model was also properly used to describe the experimental extraction of Cu, Pb and Zn. The parameters obtained by the kinetic models showed that Cd is the slowest to be extracted followed by Ni, As, Pb, Zn and Cu.

In view of the results obtained in this study, it can be concluded that the mobility of traces elements can be significant only under extremely acidic conditions ($pH \leq 1$); this should be taken into account in the potential scenario of acid mine drainage.

4.4 Ecological Monitoring

The ecological quality of the upper part of the basin was assessed in this section. An ecological monitoring was carried out to gain knowledge about the existence of macro-invertebrates at the upper part of the basin. The sample collection was applied in July 2010. Then, the ECOSTRIAND protocol for Andean rivers up to 2,000 m.a.s.l. was developed applying the IHF, QBR-And and ABI indexes (Acosta et al., 2009). This protocol is a qualitative index that evaluates if the monitoring points are considered “good” or “bad” following the WFD recommendations.

Additionally, a quantitative analysis of the macro-invertebrates was applied. Then, a baseline of the macro-invertebrates at the upper-part of the Jequetepeque basin was obtained with data from 18 monitoring sites. A comparative evaluation between the baseline and four additional points was developed. These points were located near mine sites with a double purpose: (i) evaluate if there are some similarities between the macro-invertebrates and the sediment analyses and (ii) validate the analysis developed with the ECOSTRIAND.

4.4.1 Qualitative Analysis

A total of 22 monitoring sites were analysed, 18 points were defined as reference sites. The reference sites were validated by the ECOSTRIAND protocol (Figure 4.19). Four additional points were included in order to evaluate its ecological status, R1, R2, Ll3 and Ll5. These points were located at the same sites than the water and sediment monitoring.

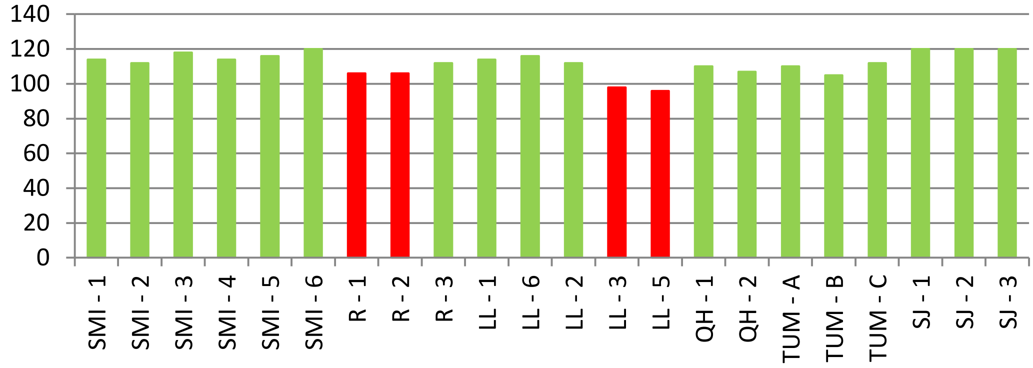


Figure 4.19: Results for the reference sites validated by the ECOSTRIAND protocol. Green bars are the reference sites and Red bars are other monitoring sites.

The results obtained for the three developed indexes and the physic-chemical parameters measured at field were given in Table 4.28. IHF value indicated if there are some constraints to limit the habitat of the benthic communities. It is considered that below 40 there is a limitation, while above 75 is considered an optimum habitat (Acosta et al., 2009; Pardo et al., 2002). QH-1 sample reported a punctuation of 39 and may expose some restraints to the habitat for the development of the benthic community (red colour, Table 3.6).

QBR-And gave very good values (blue colour) and good values (green colour) following the ECOSTRIAND protocol (Table 3.9) for 68.2% of the monitoring sites (Table 4.28). Bad quality of the river bank was obtained for Ll5 (orange colour), which present a strong alteration of the bank river.

The Andean Biotic Index, ABI, is determined by a qualification of the macro-invertebrate taxonomic identification. The characterization is made following the ABI index where each family has a value depending on the pollutant sensitivity of each family (Acosta et al., 2009). The final punctuation is obtained adding the assigned value of each family presented in the sample. Very good values (blue colour, Table 4.28) were obtained for 77% of the samples; good values are obtained for the 13.6% of the sampling sites (Green colour, Table 4.28). One sample, located downstream the Yanacocha S.R.L. Mine site, reported moderate ranges of quality (yellow colour) while the other sample located near the other mine (Sipán S.L. Mine site), was considered as bad quality status (orange colour).

Table 4.28: Results obtained of IHF, QBR-And and ABI indexes for the 22 monitoring sites.

Sampling point	pH	EC (µS/cm)	Streamflow (m3/s)	IHF	QBR – And	ABI
SMI - 1	7.62	69	0.0005	53	80	83
SMI - 2	8.15	53	0.128	58	75	94
SMI - 3	8.18	59	0.019	59	85	106
SMI - 4	8.01	85	0.050	57	70	134
SMI - 5	7.97	36	0.202	70	95	115
SMI - 6	7.56	44	0.028	52	100	118
R - 1	7.73	417	0.492	67	80	44
R - 2	7.68	380	0.826	68	85	63
R - 3	8.22	60	0.129	64	85	72
LL - 1	8.1	35	0.315	66	100	100
LL - 6	8.84	148	0.119	65	85	130
LL - 2	8.35	99	0.335	65	75	134
LL - 3	8.07	173	0.907	77	65	97
LL - 5	7.24	1225	0.038	51	50	17
QH - 1	8.27	124	0.0005	39	100	79
QH - 2	8.18	76	1.014	47	73	86
QH - 3	8.2	219	0.244	58	70	95
QH - 4	7.81	144	0.113	48	100	111
TUM - 1	7.9	78	0.029	58	85	110
SJ - 1	8.73	313	0.033	70	95	100
SJ - 2	8.78	349	0.093	71	80	93
SJ - 3	8.62	319	0.016	61	100	65

After the development of the three indexes, the ECOSTRIAND was obtained (Figure 4.20). All the reference sites presented very good or good quality status (blue and green colours respectively). Then, the different macro-invertebrates families obtained at the 18 reference sites guarantee the biodiversity in the Jequetepeque basin.

On the other hand, only the points located near mine sites showed some alterations. R1, near the Yanacocha S.R.L. Mine reported a regular ecological quality status of its river. Ll5, near the Sipán S.L. Mine, obtained terrible ecological status, being the worst point monitored at the basin. The sampling points located downstream of the affected points with regular or bad ecological status, R2 and Ll3 (located downstream R1 and Ll5 respectively), can be considered good. It should be mentioned that in both cases the streamflow increased considerably (Table 4.28). Then, the dilution effect may help in order to give better ecological status. This is in agreement with the ABI and QBR-And obtained values and also the EC values obtained for those points, being decreased for the R2 and Ll3 with respect to R1 and Ll5.

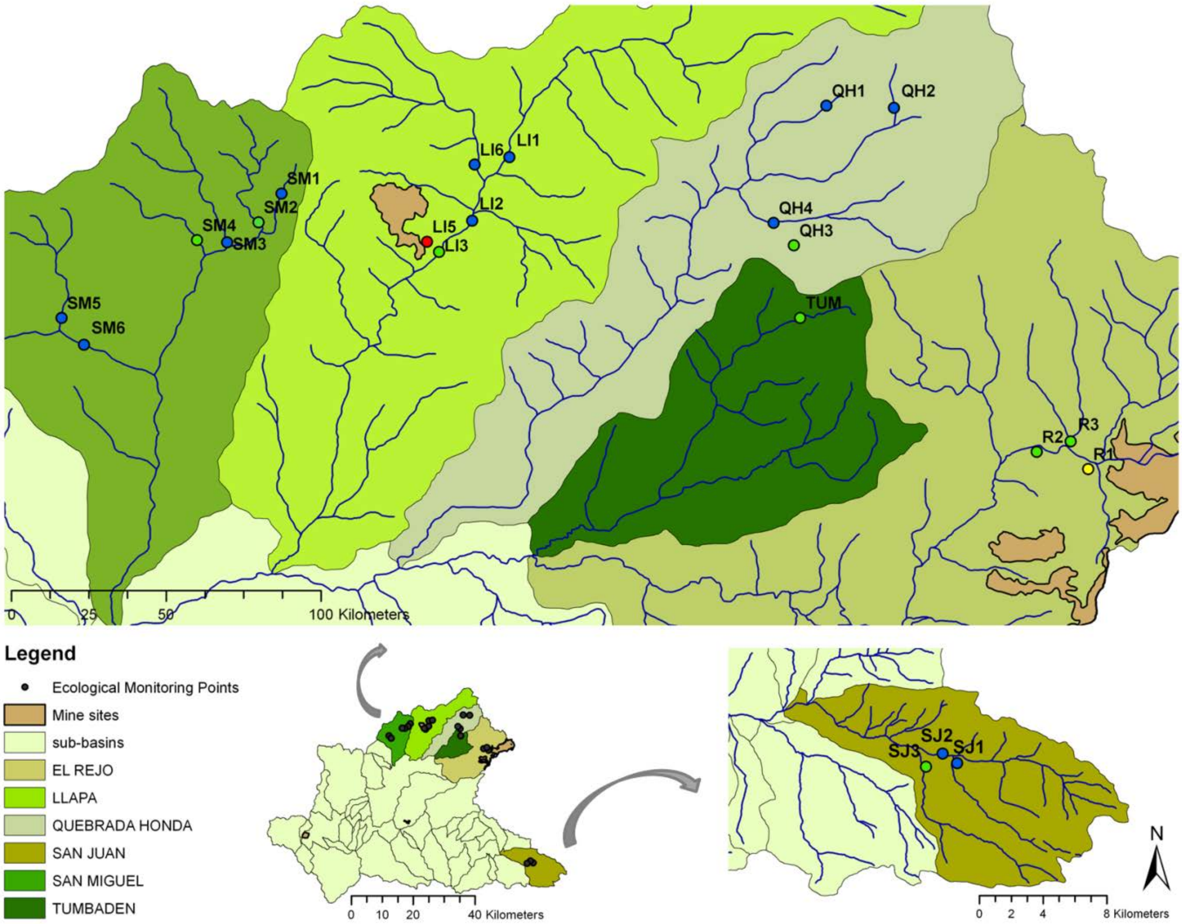


Figure 4.20: Ecological Status River Andean obtained for each sample. Blue points are considered very good ecological status, green are good, yellow are regular, and red are terrible ecological status (Table 3.9).

4.4.2. Quantitative Analysis

The 18 reference sites monitored were defined in order to obtain the baseline of the upper-part of the Jequetepeque basin (2,000 m.a.s.l.) as no effect was reported and the human perturbations was not modified the characteristics of the river. Then, the family number of the macro-invertebrates was quantified as a baseline (Chovarec et al., 2000). Each reference site had the same typology (ecotype), with the same environmental conditions (i.e. climate, vegetation and geomorphology). The families obtained at these points were adapted to these specific environmental conditions. Figure 4.21 gave the 28 families of macro-invertebrates that present the ecotype at the upper-part of the Jequetepeque basin.

The baseline was compared with other monitoring points. It allowed the determination of the ecological quality status for the monitored points (EC, 2000; ISO, 2000). The ecological quality at a given point is determined as the percentage of change between the reference conditions from the ecotype (Resh et al., 1995; Moss et al., 1987; Wright et al., 1984). Then, a comparative evaluation between the baseline and four additional points (R1, R2, Ll3 and Ll5) was developed. These points were located near mine sites: R1 downstream of the Yanacocha S.R.L Mine site, Ll5 downstream of the Sipán S.L. Mine site, and R2 and Ll3 downstream of these points respectively.

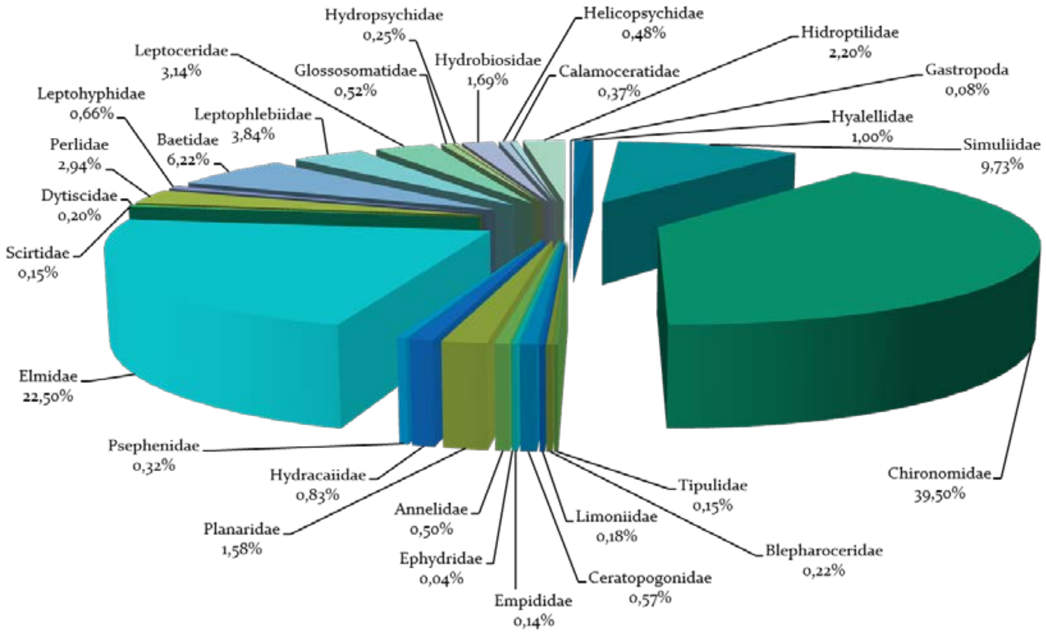


Figure 4.21: Baseline of macro-invertebrates at the upper-part of the Jequetepeque basin.

The comparative analysis of the ecological quality status was developed following the % of deviation to the ecotype (Alba-Tercedor et al., 2002) as Table 4.29 showed. It was made with a double purpose: (i) validate the analysis developed with the ECOSTRIAND and (ii) evaluate if there were some similarities between the macro-invertebrates and the sediment analyses

Table 4.29: Quality status for each % of deviation to the ecotype

Ecotype (%)	Quality status
≥ 100%	Very good
61 – 100%	Good
36 – 61%	Regular
15 – 36%	Bad
≤15%	Terrible

As mentioned before, 28 families of macro-invertebrates were reported at the upper-part of the basin, being considered the representative families of this site (ecotype). Table 4.30 showed the ecotype and the obtained values for each point. The ecological quality of the monitoring points was considered regular for Ll3 and R2 (with a deviation to the ecotype of 57 and 46% respectively), bad for R1 (32% of deviation to the ecotype) and terrible for Ll5 (with only 15% of the ecotype).

Verliidae taxon was only obtained in R2, which is considered a family with medium tolerance to organic pollution (Dominguez and Fernandez, 2009). The Ephemeropter order is very sensitive to the contamination, except for the Baetidae family which is the family more tolerant of this order (Dominguez and Fernandez, 2009). This is in agreement with the obtained samples, where only some Bateidae were found at Ll3 and R2.

Table 4.30: Score obtained for the Ecotype, Ll3, Ll5, R1 and R2 samples at family level, and % deviation of the samples

Class	Order	Family	Ecotype	Ll3	Ll5	R1	R2
Gastropoda			1	0	0	0	0
	Amphipoda	Hyalellidae	12	0	0	0	0
Insecta		Simuliidae	121	13	0	100	123
		Chironomidae	492	98	20	280	763
		Tipulidae	2	8	0	0	0
		Blepharoceridae	3	70	0	0	8
		Limoniidae	2	0	0	0	0
		Ceratopogonidae	7	3	10	3	3
		Empididae	2	0	3	0	0
	Diptera	Ephydridae	1	0	0	0	0
Oligochaeta		Annelidae	6	0	0	0	3
Turbelaria	Tricladia	Planaridae	20	13	0	0	0
Aracnida	Acari	(Hydracaiidae)	10	0	0	8	3
		Psephenidae	4	3	0	0	0
		Elmidae	280	130	0	25	3
		Scirtidae (Heliodidae)	2	0	0	0	0
		Veliidae*	0	0	0	0	1
	Coleoptera	Dytiscidae	2	0	0	0	0
	Plecoptera	Perlidae	37	78	0	108	95
		Leptohyphidae	8	0	0	0	45
		Baetidae	77	310	0	10	0
	Ephemeroptera	Leptophlebiidae	48	50	0	0	0
		Leptoceridae	39	20	0	0	5
		Glossosomatidae	7	0	3	0	0
		Hydropsychidae	3	35	0	0	0
		Hydrobiosidae	21	23	0	10	0
		Helicopsychidae	6	3	0	0	0
		Calamoceratidae	5	0	0	0	0
	Trichoptera	Hidroptilidae	27	3	0	180	18
	% of Deviation to the ecotype			0.57	0.14	0.32	0.43

On the other hand, Perlidae had strong presence for the samples R1, R2 and Ll3 than for the ecotype, while was absent in Ll5. It may be due to a higher sensitivity to inorganic pollution than other families until some extent, explaining the increase at these samples and the total absence at Ll5 where the water pollution is higher (as section 4.2 described). The same trend was observed for Blepharoceridae, being highest for Ll3 and R2 than the ecotype and then being absent for Ll5 and R1. Then, Blepharoceridae may be more tolerant than other families (and for that reason at Ll3 and R2 its abundance increases) until some extent (and for that reason there is absent near mine sites), being in agreement with the findings of this work (section 4.2 and 4.3).

Chironomidae, which is a family with big tolerance to organic pollution (Dominguez and Fernandez, 2009) seemed to be tolerant to inorganic pollution. It is higher for R2 than the ecotype, with a high presence at R1 and Ll3 and one of the families presented at Ll5. Ceratopogonidae and Empididae had strong presence at Ll5. Its presence and abundance at points near mine sites can be due to its high tolerance to inorganic pollution. Additionally, R1 reported higher abundance of Hidroptilidae, which is the least sensitive of the Thichoptera order. Then, Chironomidae, Ceratopogonidae, Empididae and Hidroptilidae are families that can indicate inorganic pollution.

Comparing the results obtained with the ECOSTRIAND classification obtained, the same trend was observed (Ll5 is the worst point followed by R1 and then Ll3 and R2). The quantitative analysis shows a decrease of the ecological quality, from good to regular at Ll3 and R2, and from regular to bad at R1. The ECOSTRIAND protocol was developed mainly for organic pollution. Nevertheless, as (i) similarities are presented in the quantitative analysis, and (ii) the results obtained give the same trends as described for the trace element concentrations obtained in water and sediments (section 4.2 and 4.3 of this thesis), the results are considered valid for inorganic pollution. Then, the ECOSTRIAND protocol, as an easy and economical qualitative tool, is useful in order to assess the significant trends of ecological pollution at the basin.

4.4.3 Conclusions

The ECOSTRIAND protocol was developed by the evaluation of three indexes, IHF, QBR-And and ABI, at 22 points at the upper part of the Jequetepeque river. The indexes values supported the hypothesis on the sampling points, being 18 considered as reference sites while the other 4 points, located near mine sites, were defined as control points.

All the reference sites reported very good or good quality status for the ECOSTRIAND results. Then, the different macro-invertebrates families obtained at the 18 reference sites guarantee the biodiversity in the Jequetepeque basin. On the other hand, only the points located near mine sites presented some alterations. One point, near the Yanacocha S.R.L. Mine gave a regular ecological quality status of its river while other point, near the Sipán S.L. Mine, obtained terrible ecological status, being the worst point monitored at the basin. The other two control points, located downstream the affected points, can be considered good.

A quantitative analysis of the macro-invertebrates was developed to gain knowledge about the effect of inorganic pollutants in the macro-invertebrates from the upper part of the Jequetepeque basin. An ecotype was developed with the reference sites. The control points were compared with the ecotype, obtaining worst ecological results for all the points than with the ECOSTRIAND results, but maintaining the same trends.

The ecological monitoring carried out by the ECOSTRIAND protocol gave the same trends as described for the trace elements obtained in water and sediments. Then, the ECOSTRIAND protocol is considered a useful tool to assess the ecological pollution at the basin.

It should be mentioned that, more efforts are needed in order to proper validate the ECOSTRIAND protocol. In order to consider rigorous data, two different campaigns at each season should be developed. In this sense, a specific project is developing three additional monitoring campaigns that may complement the investigation started at this work. Additionally, the families considered tolerant to inorganic pollution at this study are considered a first effort for further surveys. Despite of the similar trends obtained for the water, sediment and ecological surveys, the conclusions extracted are still insufficient in order to develop an easy and adapted protocol to the region.

5. Conclusions

Surface water quality represents an international concern, particularly towards future prevention and remedial actions. For this purpose, knowing the status of the water quality related to the current pressures and impacts is essential. Environmental efforts in the Andean region must focus on water quality management and the evaluation of impacts and pressures on the aquatic ecosystem due to mining activities. Numerous social conflicts in the region are against mining activities, with the largest grievance being the contamination of water and its extent. In this context, developing tools to prevent, protect and improve the water quality of fresh water resources in a sustainable way with an ecosystem approach is an initial step towards future prevention and remedial actions. In this thesis, a continuous simulation model and an environmental monitoring program were developed that took into account the WFD requirements.

To prioritise the IWRM, the applied environmental model SWAT characterises the dynamics of the basin, recognises possible interactions with the quality status of the water and evaluates the pressures from anthropogenic activities at the basin. The Jequetepeque basin was automatically calibrated and validated successfully with the SCE-UA algorithm without large amounts of data (11 years). Five different cases of sub-basin discretisation were evaluated with and without the slope criterion. Extremely good hydrographs and statistics (NSE, RSR and PBIAS) were obtained for all cases. As a result, the influence of the slope in run-off simulations is a less influential factor than the sub-basin discretisation. The best results were obtained with the default sub-basin discretisation, the same discretisation used in the calibration. However, increasing the number of HRUs by decreasing the threshold values did not give better results with the default sub-basin discretisations. Finally, the characterisation of the basin gave information regarding its dynamic behaviour and quantified the water bodies and the interaction between the upper and middle part of the basin.

The environmental monitoring program consisted of water monitoring, sediment monitoring and ecological monitoring. The results obtained from the water, sediment and ecological data presented trace element pollution near mine sites and quantified the impact to the Jequetepeque basin. A complementary effort to collect available data at the basin was processed with the same methodology to assess the environmental status of the basin.

Concentrations of dissolved trace elements in water samples from the CAO and Stratus studies at the Rejo sub-basin were elevated. High concentrations of As, Mn, Pb, and nitrate were reported during the dry season, whereas high concentrations of Ag, Cu, Hg, Ni, Se, Tl, and Zn were obtained during the wet season. Differences in peaks between the months of sampling did not seem to follow any trend. The highest peaks were found in November and August, which could be due to mining operations, where dams and water treatment plants can alter the hydrological response of the basin. Correlation analysis demonstrated that no seasonal trends were observed in the Rejo sub-basin.

Water samples from the DESA data and the water monitoring developed in this work were analysed to investigate the distribution of trace elements and their sources along the Jequetepeque basin. Major peaks were observed primarily near the mine areas. The most polluted area of the basin was located downstream of the Sipán S.L. Mine, where the mining was the source of TDS, TSS, sulphate, Al, As, Ca, Cd, Cu, Cr, Fe, Mg, Ni, and Zn. Additionally, the Rejo sub-basin contributed significantly, with peaks of Al, As, Fe, Cu, Ni, and Pb near to the Yanacocha S.R.L. Mine. Samples obtained from the middle part, near the reservoir, presented homogeneous values, which indicates a natural source. Sulphates, Ca, Mg, chloride, TDS, TSS, nitrite and nitrate, and ammonium peaks were primarily located at the Rejo sub-basin and at the middle of the basin, which are likely connected to a mixed source of anthropogenic activities, such as fertilisers and flocculants from the mine treatment plants.

The concentrations of the DESA data were higher than the concentrations from the study developed in this work. Additionally, the concentrations were also higher than the CAO and Stratus concentrations. The temporal trends showed the highest concentrations for the samples taken before 2005, particularly the Cu and Fe concentrations. The closure of the Sipán S.L. Mine in the Llapa sub-basin and the ending of the mine extraction in the Rejo sub-basin in 2005 provide a plausible explanation for this. It is therefore not surprising that the implications on human health by water ingestion in the region decreased after 2005. Nonetheless, the levels of Cr and As indicated adverse effects and the levels of Al, Cd, Cu, Fe, and Pb have significant effects on human health, creating a significant risk for the population in these areas. Considering the lack of water facilities and trace element remedial plans in the region, special attention should be paid in regulatory policy, and further efforts in mine remedial processes must be taken.

The bioavailable fraction of trace elements was evaluated by the BCR protocol. This fraction may be released from sediment to the water column depending on environmental conditions. Sequential extraction was used to assess the environmental implications of the element partitioning in the Jequetepeque sediment samples. The order of mobility from the sediments to the water column was the following: Cd (94%) >> Cu (67%) > Hg (61%) > Zn (53%) >> Ni (37%) > Pb (32%) >> Cr (19%) > Fe (12%) > As (11%) > Al (10%). Cd and Zn exhibited the same trend for all monitored samples, suggesting the same source as the enrichment factor results highlighted, particularly near the Yanacocha S.R.L. Mine site. Cd and Zn were the most mobile elements, and consequently, their presence and mobility due to mining activities was considered a significant threat to the environment.

In general, the peaks observed for As and Pb were near mine sites, where their concentrations were primarily in the residual phase and secondly bound to the reducible phase. It should be noted that the peaks were only found in the Yanacocha S.R.L. Mine for Pb, whereas As was also found in the Llapa S.L. Mine. This result agreed with the results obtained from the risk assessment and the identification of the trace elements sources. Thus, As and Pb were not considered a high risk to the environment because of their minimal mobility; however, the concentration peaks were a concern due to mining. Summarising, the most polluted area was located downstream of the Yanacocha S.R.L. Mine site for Cd, Zn, Pb, and As and was independent of the season.

Additionally, major Ni and Cu peaks were obtained near mine sites, which agreed with the results for Cu, which showed moderate enrichment and an extremely high risk at these points. The Cu and Hg concentrations and their mobility increased during the wet season for all the samples, whereas higher Cr mobile concentrations were obtained during the dry season. Al and Fe were principally reported at the residual fraction. Similar concentrations were obtained for the reducible and oxidisable phase for Al and Fe, which increased near mine sites. Nevertheless, the presence of these elements was not considered a significant threat to the environment.

The most polluted area of the basin for sediment samples was located downstream of the Yanacocha S.R.L. (an active mine), whereas the most polluted area for water samples was located downstream of the Sipán S.L. Mine (which is closed). Mining generates large amounts of sediment that are susceptible to transporting trace elements downstream, whereas acid mine drainages are usually related to abandoned mines. Accordingly, the results obtained were in agreement with the type of mining impacts: the active mine reported the highest trace elements concentrations in the mobile fractions from sediment samples, whereas the closed mine gave the highest concentrations in water samples. Cd, Pb, As, and Cu reported several similarities for water and sediment samples, which are the trace elements that presented the highest risk to the environment at the basin.

Sediment samples give middle- and long-term information of pollution trends, whereas water samples only report the instantaneous concentration at the sampling time. Taking this into account, Hg, Ni, and Zn are a concern in the Jequetepeque basin in the middle- to long-term (as the sediment samples indicated), whereas Cr, Al, and Fe should be considered for future risk assessments (as the water monitoring highlighted). In view of the lack of water facilities and trace element remedial plans in the region, special attention should be paid in regulatory policy and further remedial efforts that must be taken. This work considers a baseline of the environmental quality status that may support water quality management at the basin and is a necessary step towards future prevention and remedial actions.

Additionally, trace elements kinetics was assessed to complement the environmental evaluation. The release of trace elements at low pH values, as found near mine sites, was considered to be a concern. The extraction experiments indicated that EDTA caused a higher mobility of the trace elements than that of the acid treatment (with HNO3). The extraction by the EDTA procedure can be more protective because of its higher leaching capacity than acid treatment at pH=4, which is an important issue in view of risk assessment analyses. The acid treatment at a lower pH increased the leachability for elements with an intermediate mobility (Cu, Ni), where the acidity caused a considerable increase in extractability, particularly for fixed elements (Pb). The highest extractability was observed for Cd in all sediments for both the acid treatment and the EDTA treatment, with an extraction of 90% after 1 hour. The rate of extraction by EDTA was slow, as demonstrated by the extraction time being 1 hour. The extracted fraction with EDTA of most of the trace elements for all sediments was small, less than 20%. The same trends of extractability were found in the analysis by EDTA, nitric acid and with the BCR protocol. Additionally, Cd, Cu and Zn reported the highest concentrations at the same points for each analysis.

The diffusion model was used successfully to describe the kinetic extraction of trace elements in four sediments. Two first-order models were also used to properly describe the experimental extraction of Cu, Pb, and Zn. The parameters obtained by the kinetic models showed that Cd was the slowest to be extracted, followed by Ni, As, Pb, Zn, and Cu. In view of the results obtained in this study, it can be concluded that the mobility of trace elements is significant only under extremely acidic conditions ($pH \leq 1$). This should be taken into account in the potential scenario of acid mine drainage. Thus, attention should be given to the areas near the Sipán S.L. Mine, where acid mine drainage may occur as the water monitoring reported.

The Ecological Status River Andean protocol (ECOSTRIAND) was developed by evaluating three indexes (IHF, QBR-And and ABI) at 22 points at the upper part of the Jequetepeque river. The indexes results supported the hypothesis made on the sampling points, i.e., 18 points were considered as reference sites, whereas the other 4 points, located near mine sites, were defined as control points. All the reference sites gave very good or good quality status for the ECOSTRIAND results. Then, the different macro-invertebrates families obtained at the 18 reference sites guaranteed the biodiversity in the Jequetepeque basin. Only the points located near mine sites achieved some alterations. One point, near Sipán Mine site, obtained terrible ecological status and was the worst point monitored at the basin. The point near the Yanacocha S.R.L. Mine reported a regular ecological quality status. The other two control points, located downstream of the affected points, can be considered good.

A quantitative analysis of macro-invertebrates was developed to gain knowledge about the effect of macro-invertebrates due to inorganic pollutants in the upper part of the Jequetepeque basin. An ecotype was developed with the samples from the reference sites. The control points were compared with the ecotype, obtaining worse ecological results than with the ECOSTRIAND results; however, the same trends were maintained for all the points.

The ecological monitoring performed by the ECOSTRIAND protocol gave the same trends as described for the trace elements obtained from the water and sediment monitorings. Thus, the developed protocol, a simple, economical qualitative tool, is useful to assess the significant trends of ecological pollution at the basin, which is considered a first effort to advance towards an ecological status quality index in the Andean region in a holistic way, emphasising mine pollution assessment.

The developed environmental monitoring and the tools of evaluating water quality were used to describe the grade of pollution at the basin, particularly due to mining activities, and their associated human and environmental risk. The different approaches in this work (evaluating water quality and quantity, sediments and biota) highlighted the pollution in water quality terms near mine sites. The outcomes of this research would support water quality management filling a gap in the environmental monitoring in the Andean region.

Future research

Despite the similar trends obtained for the water, sediment and ecological surveys, the conclusions extracted are still insufficient to develop a simple and adapted protocol to the region. More effort is required to properly validate the ECOSTRIAND protocol. At least two different campaigns during each season should be developed and properly analysed. Additionally, the families considered tolerant to inorganic pollution in this study are considered a first effort for further surveys.

In this sense, a specific project is developing with the Universidad Nacional de Cajamarca and the Universidad de Barcelona. This new study is focused on developing three additional monitoring campaigns to obtain more accurate information. Additionally, eco-toxicological tests on the sediment samples from samples near mines are included in this project. The objective is to establish the relationship between the obtained families, the sediment and water trace element contents and the eco-toxicological results. Finally, the relationship between trace elements, families of macro-invertebrates, and the eco-toxicological tests at each sampling point will be analysed. It is considered an on-going research that may complement the investigation that began in this work with hope to develop a simple economic tool to apply proper environmental monitoring that supports water quality management in Andean basins with mining activities.

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