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Risk Assessment and Source Identification of Trace Metals in Rio de Oro, Colombia

Master of Science Thesis in the Master's Programme Industrial Ecology for a Sustainable Society

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Cover:
Pipes which lead to Rio de Oro in the back side of Central Abastos, a wholesale and storage space.

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ABSTRACT

The pollution of water bodies is a major problem for the environment and clean water sources are one of the most essential resources to maintain life on Earth. The amount of contaminants is steady increasing in the environment, which affects both the human health and the biodiversity in ecosystem. The aim of this thesis work was to locate the potential pollution sources within the industrial region of Rio de Oro, Colombia. Chemical analysis of water and sediment from Rio de Oro were performed to determine the metal concentrations. The results were then compared with the guideline values provided from different Environmental Protection Agencies. Batch tests were also conducted to observe the leachability and mobility of metals from the river sediment under different simulated environmental conditions such as, pH variations, presence of iron and humic colloids, increased temperature, air injection, re-suspension and in an undisturbed environment. The risk assessment procedure followed in this project is based on the Strategy for Environmental Risk Assessment of Contaminated Sites provided by the Swedish Environmental Protection Agency. The batch tests were performed in beakers and constantly stirred for 24 hours. The samples were then filtered and acidified for analysis of metals with inductively coupled plasma – mass spectrometry. The results of the investigation showed that most of the wastes from the industries are discharged in the river. There are many pollution sources and their contribution of the pollution of the Rio de Oro is not well monitored. The metal concentrations of the river water ranged from very low to moderate concentrations, which has slight biological effects in the aquatic environment. The metal concentrations of the river sediment are very low but are steadily increasing downstream of the studied area. This is due to the high content of organic material, which acts as an important sink for metals and the strong stream of the river is believed to transport the contaminants to settle in the calm parts of the river which is further downstream and outside the area of this study. In the batch tests, addition of humic colloids caused the most substantial leaching of metals. Release of Pb from the sediment could be observed when humic colloids were added, which is caused by the exchange of sorption sites between the sediment and humic colloids. Correlations could be observed between the leaching of Fe, Ni, Cu and Zn. It is believed that the dissolution of Fe oxides which are an important sink for metals causes release of co-precipitated and adsorbed metals. After the batch tests, most of the metals were leached to concentrations which exceed the guideline values from SEPA, which has a considerable impact on the aquatic ecosystem.

Key words: Risk assessment, trace metal, source identification, batch test, pollution, river, contamination, Colombia, Environmental Protection Agency

Risk bedömning och källidentifiering av metaller i Rio de Oro, Colombia
Examensarbete inom Industrial Ecology for a Sustainable Society

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SAMMANFATTNING

Förorening av vattendrag är ett stort problem för miljön och rena vattenkällor är en av de viktigaste resurserna för att upprätthålla liv på jorden. Mängden föroreningar ökar ständigt i miljön, vilket påverkar både människors hälsa och biologisk mångfald i ekosystemen. Syftet med detta examensarbete är att identifiera potentiella föroreningskällor i den industriella regionen av floden Rio de Oro, Colombia. Resultaten av kemiska analyser på vatten och sediment jämfördes därefter med riktvärden och standarder för metaller utfärdat av Naturvårdsverket i Sverige, Kanada och USA. Laktester utfördes med avsikten att iaktta laknings- och mobilitetsegenskaper för metaller i flodsedimentet i flera olika simulerade miljöförhållanden med variationer i pH, hög temperatur, hög syrehalt, hög turbulens och i förekomst av humus och järnkolloider. Miljöriskbedömningen i detta projekt är utförd med en metodik baserad på en strategi för miljöriskbedömning av förorenade sediment utfärdat av Naturvårdsverket. Lakningstesterna utfördes i stora bägare där sediment och flodvatten rördes om under 24 timmar för att uppnå jämvikt. Efter lakningen filtrerades och surgjordes proverna för analys av metaller med induktivt kopplad plasma – masspektrometri. Resultaten visade att industrier i det studerade området inte använde någon reningsteknik för sitt avloppsvatten utan att det släpptes rakt ut i floden. I det studerade området finns det många olika föroreningskällor som till exempel dagvatten från vägar och urbana ytor, lakvatten från ett avfallsupplag, avloppsvatten från hushåll och övervakningen av dessa källor är obefintlig. Metallhalterna i flodvattnet är från mycket låga till måttliga koncentrationer, vilket har märkbara effekter för vattenekosystemet enligt Naturvårdsverket. Metallhalterna i flodsedimentet är mycket låga men ökar ständigt nedströms på grund av den höga halten av organiskt material i flodvattnet. Metaller som är bundna till små partiklar har också svårt att sedimentera på grund av flodens höga strömningshastighet, istället sedimenterar metallpartiklarna vid de lugnare delarna av floden utanför området som ingick i denna studie och där strömningshastigheten är lägre. Lakningstesterna visade att bland de olika parametrarna var det humuskolloider som gav högst lakning av metaller. Speciellt kunde lakning av Pb från sedimentet påvisas, vilket är orsakat av utbyte av adsorptionsytor mellan sedimentet och humuskolloiderna. Korrelationer mellan lakning av Fe, Ni, Cu och Zn kunde också påvisas. Nickel, Cu och Zn har en tendens att adsorberas på Fe-oxider, vilket gör att halten upplösta metaller sänks i Fe-oxidernas närvaro och upplösning av dessa Fe-oxider gör att bundna metaller frigörs. Metallhalterna från lakningstesterna överskred riktvärdena som gäller för metallhalter i sjöar och vattendrag från Naturvårdsverket. Dessa metallhalter har en stor påverkan på det akvatiska ekosystemet enligt Naturvårdsverket.

Nyckelord: Riskbedömning, metaller, källidentifiering, lakningstest, förorening, flod, Colombia, Naturvårdsverket

Contents

Preface

In this project, a risk assessment and a source identification of trace metals are performed in a river named, Rio de Oro, which is situated in Bucaramanga, Colombia.

All the tests were conducted from February to mid May 2011 in Bucaramanga, Colombia. The water and sediment sampling have been carried out in the industrial area of Rio de Oro and the preparation for the samples before the chemical analysis was performed at Universidad Pontificia Bolivariana – Seccional Bucaramanga. All the prepared water and sediment were then transported to the department of Water Environment Technology at Chalmers University of Technology, Sweden for chemical analysis.

First of all, I want to thank my classmate and great friend, Ivan Herrera for helping me with every aspect of my thesis and making my visit in Colombia an experience I will never forget. Your effort and assistance have been priceless. I also want to thank my supervisors at Chalmers University of Technology, Associate Professor Ann-Margaret Strömvall and Assistant Professor Yuliya Kalmykova for helping me to form the thesis work and for the support through the whole thesis and Yvonne Young for providing the information on the Minor Field Study scholarship. My appreciation also goes to my supervisor in Colombia, Yolanda Gamarra Hernandes for the support of the thesis. I would like to show my gratitude to all the people at Universidad Pontificia Bolivariana for their kindness and assistance during my visit, especially Naydu Amparo Villamizar, whom assisted me with all the laboratory analysis.

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Chungfat Hoang

IV

1   Introduction

1.1   Background

Colombia, a developing country located in the north top of South America with the Andes scarring through the land. In the midst of the northern part of the Andes, there is a city named Bucaramanga with a dense population of just over a million people (DANE, 2005). In the outskirts of the city, there is a river called Rio de Oro, i.e. River of Gold. The environment along the river consists of high mountain forests, industries, dense traffic and municipalities, which are possible contributors for the pollution of the river. The pollution of water basins has been a large concern for the environment and clean water basins are one of the most important resources in the world to sustain all life forms (Mahmoud and Zeid, 1998). The increased level of contaminants such as metals in the environment has affected both the human health and the biodiversity in the aquatic ecosystem and the pollution is often generated by industries, traffic and non-point sources (Sponza and Karaoglu, 2002). The non-point sources are difficult to identify since it is diffuse and almost impossible to connect to the effluent of the source (Wang and Cao, 2005). Consequently, it is important to identify and locate the sources of pollution to be able to prevent further emissions.

Metals are often bound to sediment particles in rivers due to chemical and physical properties of the environment (Dijkstra et al, 2004). However, this equilibrium sustains only if the environmental conditions are maintained. If the river suffers variations and changes in the environmental condition, the consequences can be possible release of the metals from the sediment into the river, which will increase the concentration and the mobility of metals in the river. The elevated concentrations of metals may pose potential risks to human health, aquatic life and ecosystem function, as well as economical expenses for possible remediation of the adverse effects. Therefore, it is necessary to locate the source of pollution but also to study the mobility of the pollution of concern. It is important to learn about the behaviour of metals in the environment to avoid potential risks in the future (Centioli et al., 2008).

1.2   Aim and objective

The aim of this project is to identify potential sources of pollutions in the industrial and urban area along the river, Rio de Oro and strategically sample water and sediment in different spots in the river for chemical analysis to determine the metal concentrations. In order to assess the environmental quality of the river, the results are compared with metal concentration standards for water and sediment set by different Environmental Protection Agencies (EPA) such as United States EPA, Canadian EPA and Swedish EPA.

The aim with the thesis is also to perform a risk assessment in the form of batch tests to observe and analyze the leachability and mobility of selected trace metals in the river sediment in different simulated environmental conditions, such as

- changes in pH
- presence of iron and humic colloids
- high temperature
- air injection
- strong turbulence
- undisturbed environment.

The aim of the batch test is to determine and assess if there is any potential risks of leaching of the trace metals from the sediment into the river water.

1.3 Delimitation

The project focuses mainly on the industrial district of the river, where most of the industries in the region are located. The identification of the source of pollutions and the sampling of water and sediment are all executed within this area. The temporal aspects of the sampling are not considered in this project. The results from the laboratory analysis and the source identification will assist in the assessment of potential risks of the leaching of the trace metals into the river and future solutions will not be provided or discussed in this report.

The analysis of the water and sediment is primarily focusing on the trace metals, Ag, Cd, Co, Cr, Cu, Ga, Ni, Pb, Sr, Zn and the main elements Al, Fe and Mn and their chemical and physical properties. The influence of biological processes in the water and sediment is not discussed in this project.

1.4 Site characterization/description

Rio de Oro is a river located in the state Santander in Colombia. The field work was conducted in a specific area around Girón, a small district in the outskirts of the metropolitan Bucaramanga, where the river bypasses. The area of interest is located in the industrial area of Girón, whereas many of the local and regional industries are situated on one side along the river. The environment of the industrial area consists of high mountain forests, which stretches along the one side of the river, extremely trafficked highway outside the industries, municipalities and several construction sites. The area along the river also consists mostly of permeable surfaces.

There is currently a new construction of a bridge in the area and construction of new industries along the river. The industries along the river contribute to the traffic in the highway because of the import and export of products and merchandises. There are also many poor communities situated along the river, where the population is dense and the standard of living is low. The people live in poorly constructed houses with limited access of electricity and drinking water.

The river is situated in a valley between high mountain forests and industries which can be observed in Figure 1. This makes the river highly available for surface runoffs from both sides. The depth and the width of the river vary greatly along the river. However, it depends greatly on the weather conditions.
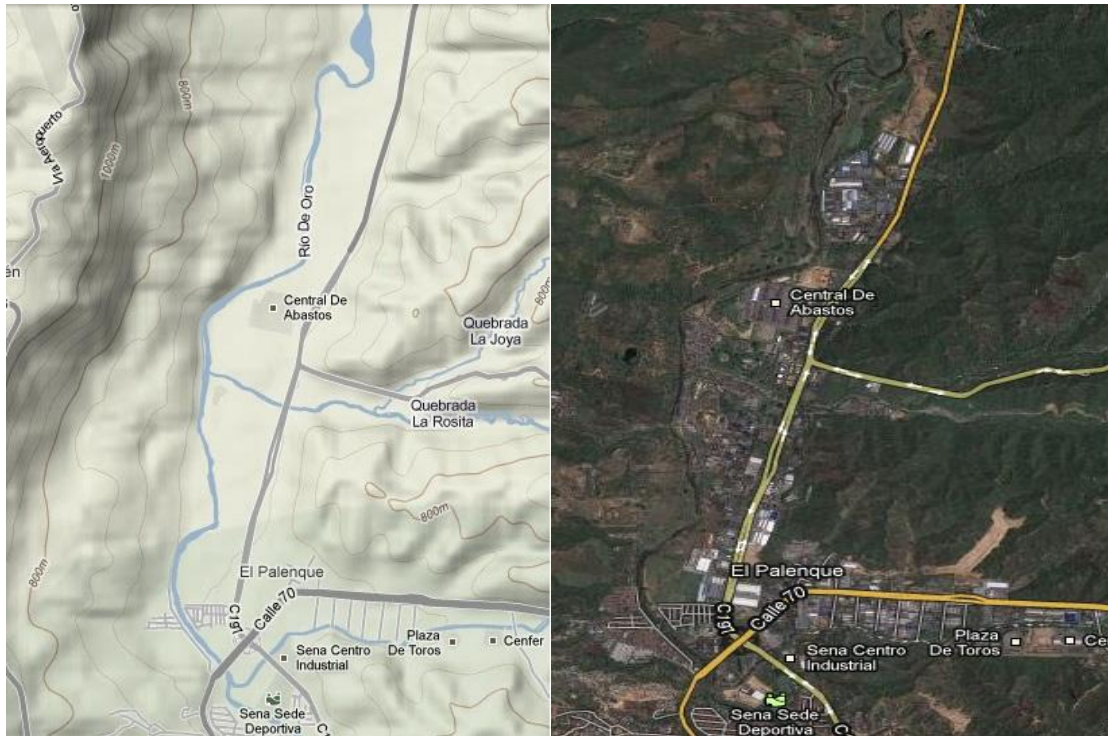
Figure 1. Left: Topographic map of Rio de Oro. Right: A satellite picture of Rio de Oro

Climate

The climate in Bucaramanga is considered tropical, as part of Colombia is situated on the Equator. Bucaramanga is located approximately 1000 m over sea level and the average annual temperature is roughly 22.8 C^o. The seasonal variations are minimal but there are short rain periods during the spring and autumn. The average humidity in Bucaramanga is 83 % and considered normal in the tropical regions. In Table 1, it can be noticed that the variations in average temperature, precipitation and humidity during the whole year are almost insignificant.

Table 1. The annually average temperature, precipitation and humidity in Bucaramanga.

Parameters	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
Average temperature (C^0)	24.5	24.5	23.2	22.3	21.5	20	21	24.5	22.7	22.8	23.1	23.8
Precipitation (mm)	81	90	121	133	110	112	106	103	98	133	119	73
Humidity (%)	80	80	82	83	88	89	82	82	83	84	85	83

2 Theoretical review

2.1 Risk assessment

There are several frameworks for conducting risk assessments from different Environmental protection agencies. In the United States, numerous frameworks of risk assessments have been published, such as *Ecological Risk Assessment* (USEPA, 1997), *Framework for Metals Risk Assessment* (USEPA, 2007) and *A Guidance Manual to Support the Assessment of Contaminated Sediments in Freshwater Ecosystems* (USEPA, 2002). The risk assessment guidances from USEPA have similar frameworks, thus published in the same organisation. The outline of the guidances is roughly structured as follow:

- problem formulation
- exposure and effect/toxicity assessment
- risk characterization
- risk management

The guidances are both educational and very instructive and the process steps are explained into details. *A guidance Manual to Support the Assessment Contaminated Sediments in Freshwater Ecosystems* (USEPA, 2002) includes the guidance for sampling strategies, chemical analysis plans and instructions how to interpret the results from the investigation of the contaminated sediments. In some parts of the guidances, it can be too confusing due to the numerous titles, subtitles and the information boxes, which makes it sometimes difficult to adapt.

The *Strategy for Environmental Assessment of Contaminated Sites* (SEPA, 2008) published by the Swedish EPA has the same outline as the risk assessment publications from USEPA, except for the risk management, which is not included. The risk assessment guidance divides the chapters into two sections, the introduction of environmental risk assessment and how to conduct an environmental risk assessment. This makes it easier to adapt and understand the many processes in strategy, as *the Strategy for Environmental Assessment of Contaminated Sites* is not written as extensive as the guidances from USEPA.

2.2 Parameters affecting the leachability of trace metals in sediment

pH

In soil and sediments, pH is known as the most important parameter affecting leachability, mobility and solubility of trace metals (Sahuquillo et al., 2003). The solubility and mobility of most trace elements increase with decreasing pH (Yang et al., 2005), except for two elements, arsenic and chromium. The most common arsenic species in water is As(V) and appears under favorable conditions of oxic environments and alkaline pH and As(III) is formed under opposite conditions (Bradl et al., 2005). There are chromium species that act as both oxidizing and reducing agents, depending on their oxidation state. Species with oxidation states below II is reducing and oxidation states above III are oxidizing. Therefore, the adsorption of Cr(VI) is increasing with decreasing pH because of the protonation of the hydroxyl

groups and organic matters, which are common components in sediments (Bradl et al., 2005).

The pH parameter is a simulation of acid rain and other anthropogenic sources such as, discharge of detergents and many other household cleaning products. Most of the trace metals tend to precipitate as oxides, carbonates and hydroxides and many other compounds under alkaline conditions. Another essential factor that affects leachability of trace metals is the adsorption of metals to organic matter. The sorption of metals in soils is highly dependent on the pH level. Trace metals are known for having a high affinity for organic matter (Dijkstra et al., 2004), whereas the organic material acts as a sink for metals in sediments. Organic carbon is recognized for binding trace metals and dissolved organic carbon (DOC) is known for mobilizing the metals. DOC is a common term for organic materials such as organic acids, fulvic acids, lignin, humic acids and many other materials. In general, the solubility of DOC is pH-dependent, whereas increasing pH also increases the solubility of DOC (Cappuyns and Swennen, 2008). At higher pH levels, elevated DOC concentrations tend to affect the metal complexation with the dissolved organic matter, which is important for the leachability of metals.

Humic colloids

Humic colloids are a major component in aquatic environment and occur from microbial decaying of plants, animal residues and other organic matter. The structure of humic colloids is complex and consists of carbohydrates, proteins, fatty acids and lignin (Malcolm and Nicholas, 1998). Humic colloids are difficult to characterize due to its heterogeneity in aquatic media. The interactions between humic substances, clay minerals and many other naturally constituents in soils and sediments have been widely studied through many perspectives through the last decades (Cornejo and Hermosin, 1996). Therefore, it is of great interest to observe how humic colloids affect the interactions of different metals in aquatic sediments. The main components in soil and sediments consist of humic substances, which origins from degraded plants and animal residues and can be found almost anywhere in the ecosystem (Garcia et al., 1994). Humic substances are greatly involved in the geochemical processes and serves as an important factor in the mobilization and accumulations of cations and heavy metals by complexation (Jones and Bryan, 1998). Although, there are several significant processes, for instance ion exchange, diffusion and precipitation in the soil and sediments, adsorption is recognized to be the main controlling mechanism, managing the formation aggregation of different micro components and transports of contaminants and nutrients. It is well known that the complexation of organo-metal acts as a sink for metal processes in soils and sediments (Cornejo and Hermosin, 1996; Jones and Bryan, 1998). However, this is due to the surface reactivity of the colloids in the organic materials. The major aspect affecting the surface chemistry of colloids is its molecular structure consisting of numerous active functional groups, where it acts as a negative ion exchanger in the complexation of heavy metals.

Iron colloids

Iron oxides are naturally occurring element in the environment. It occurs in numerous organic and inorganic forms in sedimentary media. The reduction of Fe(III) oxides plays an important role in the biogeochemical of many elements in the natural

environment (Roden, 2006). Studies in freshwater and marine environments indicate that dissimilatory Fe(III) reduction has the potential to affect the oxidation of organic materials. The dissimilatory iron reduction is affected by numerous factors such as, microbial activities, biomass quality, quantity of organic matter and the speciation and concentration of Fe(III) minerals (Hyacinthe et al., 2006). Since Fe(III) has low solubility, it prefers to accumulate in different solid ferric forms. However, the reduction of Fe(III) to Fe(II) increases its solubility and tends to release trace metals which are bound to Fe(III) into the aquatic environment (Scala et al., 2006). Natural organic matter is also known for affecting the solubility of Fe(III). Interactions between Fe(III) and natural organic matter are well known, where functional groups of humic and fulvic acids and Fe(III) often form complexes. The interactions also have a large impact on the solubilization and precipitation of metal ions (Rose et al., 1998).

High temperature

This parameter simulates thermal pollution, whereas industries and power plants discharge heated or cooled water into water bodies, which causes temperature changes that leads to both negative and positive effects on the aquatic ecosystem (Horvath and Brent, 1972; Kennedy, 2004; Vallero, 2011). Thermal pollution has grown into a global issue, since more power plants and industries are constructed to meet the needs of the society (Horvath and Brent, 1972). Temperature is an essential factor for organisms in the aquatic ecosystems. Small changes in water temperature affect many biological factors of the organism such as disorder in the reproduction and the metabolism, growth depression (Vallero, 2011). In the end, the consequences of these changes can be fatal for the population of the living organisms. Another important factor is that cold water retains more oxygen than warm water, which affects the metabolism of aerobic aquatic organisms. Warmer water increases the metabolism but in contrary there is less oxygen available in the aquatic system (Kennedy, 2004). Oxygen sufficiency in the aquatic system causes higher stress for the organisms and can be fatal.

Air injection

In water basins, the redox potential in the sediment surface is an important factor for the solubility of heavy metals and the biodegradation of organic materials. The solubility and the speciation of metals are strongly influenced by the redox potential and pH (Guo et al., 1998). The redox potentials in sediments are commonly divided into anoxic and oxic redox potentials, where the unit is presented in mV (milli Volt). Important factors that affects the redox potential in the sediment is the inorganic carbon rain rate and the oxygen concentration in the water, which determines the amount of oxygen that actually penetrates into the pore waters in the sediment and water interface (Morford and Emerson, 1999). Anoxic sediments, also referred as reduced sediments are usually occurring in the pore waters below the water and sediment interface, where the anoxic condition is dependent on the consumption and supply rate of oxygen. In sediment, where the consumption rate of oxygen is higher than the supply rate, there is a high probability of causing depletion of oxygen (Calvert and Pedersen, 1993).

The injection of air into the water simulates heavy rains and precipitation, creating an oxic environment in the water and sediment. The oxic condition leads to increased oxidation of dissolved organic matter and inorganic materials, which in turn affects the solubility and the speciation of heavy metals (Calvert and Pedersen, 1993).

Additional parameters

Loss of ignition

Loss of ignition (LOI) is a common method to determine the organic and inorganic content in sediments. The method is simple and based on sequential heating of sediment samples, which makes it easy to implement in the laboratory and extensively used (Heiri et al., 2001). Before the organic matter in the sediment is combusted in the oven, the sediment samples are dried in a convection oven at 105^0C for 12-24 hours and cooled until room temperature is reached in a desiccator. In the first sequence, the organic matter in the sediment is combusted into ash and carbon dioxide in the oven at a temperature approximately 500^0C (Veres, 2002). Since the ignition of organic matter starts about 200^0C, it should be totally depleted about 500^0C (Santisteban et al., 2004). The sediments are weighted and before and after every heating sequence to determine the weight loss. The following equation (Matthiessen et al., 2005) is utilized to calculate the loss of ignition,

$$Loss\ of\ ignition\ (\%) = \frac{Initial\ weight - Final\ weight}{Final\ weight} \cdot 100 \qquad \text{Eq. 1}$$

The ash content of the sediment is also possible to calculate with the subsequent equation (Matthiessen et al., 2005),

$$Ash\ content\ (\%) = 100 - (LOI, \%) \qquad \text{Eq. 2}$$

2.3 Trace metals

Cadmium

Application and environmental exposure

The production of Cd comes mainly as a by-product from the smelting and refining of Zn, because the metals often appear together. Therefore, the contamination of Cd often occurs in the environment of zinc, lead and copper smelters. Cadmium is mainly used in products such as electrodes in batteries, pigments, alloys and also as protection for iron and steel against oxidization (Bradl et al., 2005). There is many ways to introduce Cd into the environment and one of the main sources is the incineration of waste materials that contain Cd. Since the heavy metal is moderately volatile, it is easily introduced to the atmosphere when incinerated. Other sources of Cd are the application of phosphate fertilizers and sewage sludge in agriculture and mining and smelting operations.

Chemical and physical properties

Cadmium has several stable isotopes, ^{106}Cd, ^{108}Cd, ^{120}Cd, ^{111}Cd, ^{112}Cd, ^{113}Cd, ^{114}Cd and ^{116}Cd. The abundance of the isotopes has a great variety and the isotope with the

highest abundance is ^{112}Cd. Cadmium is transition metal in group-II B in the periodic table. The formation of precipitates often occurs in the mix with carbonates, arsenates, oxalates and ferrocyanides. Cadmium appears mostly in free Cd^{2+} and $CdHCO_3^+$ in the soil. The adsorption of Cd is a very fast process and the main influential parameters are pH, ionic strength and exchangeable cations. However, pH is a great factor for controlling the solubility of Cd. In low pH level, Cd tends to be more available in free Cd^{2+} ions, while the formation of different carbonate species ($CdCO_3$ and $CdHCO_3$) is favoured in high pH level. The adsorption of Cd is very dependent on the surrounded exchangeable cations such as Ca^{2+} and Zn^{2+}. The cations tend to compete over the sorption sites in the soil (Bradl et al., 2005).

Toxicity

Cadmium has a high level of toxicity. Concentration of Cd in plants affects the metabolic processes that lead to slower root growth, imbalance of nutrients, interference of chlorophyll production and the photosynthesis etc. Differences have discovered in a comparison of uncontaminated and contaminated woodlands, where the population of woodlice, millipedes and earthworms were noticeably reduced in the contaminated site (Ross, 1994). Cadmium has also serious effects on humans and causes bone degenerations and interferences with the metabolism of Ca, vitamin D and collagen. Continuous exposure of Cd can also have a great impact on kidneys and lungs, causing protein urea and emphysema (Nordberg, 2004)

Copper

Application and environmental exposure

Copper is well-known for the use of wire as an electrical conductor in numerous electrical products but also as cook-ware, piping systems, bactericides, fungicides, fertilizers and feed additives. The use of fertilizers, bactericides and fungicides is the most common ways to introduce copper into the environment (Calviño et al., 2008). The excess copper tends to accumulate in soils at high toxic levels for plants and even for animals such as sheep. Copper is also emitted into the environment from metal processing industries such as copper, iron and steel production (Bradl et al., 1005).

Chemical and physical properties

Copper is usually known for its heat and electricity conductivity. In the periodic table, copper is listed in the group I-B and has several isotopes but ^{63}Cu and ^{65}Cu are the most abundance with 60,9% and 30,1% correspondingly. The oxidation states for copper are I and II. In the oxidation state II, copper has the same properties as Zn^{2+}, Mg^{2+} and Fe^{2+}. Copper can be found in a great range of formations such as, sulphates, sulphides, carbonates and free ions and can be found in solution phases and in solid forms in soils. The allocation of Cu in soil components is mainly dependent on the existence of soil organic matter and Mn and Fe oxides. Copper has a strong attraction for organic matter, Fe and Mn oxides, carbonates and sulfides in the soil, which are also the most essential sinks for Cu in soil. It is proofed that copper is mostly bounded by humic materials compared to other metals and the mechanism is an efficient way to maintain Cu in the soils (Bradl et al., 2005).

Toxicity

Copper is included in the important micronutrients for plant nourishment (Xu et al., 2006). However, the amount of Cu required in the plants is very small, approximately

5 -20 ppm. Copper is included in numerous plant enzymes, which influence different essential physiological processes such as photosynthesis, seed production, respiration and many others. In the aquatic environment, free Cu^{2+} ions are shown to be the most toxic compared to other complex bounded forms. Copper is an essential micronutrient for aquatic animals but only in small concentrations. The effects of high concentrations of Cu in aquatic environment can cause disturbances in the hematological processes and enzyme activities in fishes (Adams and Keen, 2005). Copper toxicity in humans is incredibly unusual but still toxic in high concentrations. Nonetheless, there have been a few cases of acute Cu poisoning through ingestion of beverages containing high concentrations of Cu.

Lead

Application and environmental exposure

Historically, Pb has been used worldwide for several thousands of years. This is due to its enrichment in ores and chemical and physical properties which makes it easy to extract together with other metals. Lead is extensively used in many applications and products such as gasoline additives, automobile batteries, pigments, ammunitions, pesticides and different alloys. Due to the toxicity of Pb, the use of it in some applications and products has been banned in many countries. For example, Pb as a gasoline additives, ammunitions and pesticides are banned in the U.S. and most of the countries in Europe but still widely used in other countries such as China, Russia and India. Lead is introduced and accumulated in the environment in various ways, mostly by Pb dust from pigments, mining of ores, combustion of leaded gasoline and use of ammunitions in hunting (Bradl et al., 2005). There is several ways to be exposed of lead, usually by inhalation, digestion of food and water and skin contact.

Chemical and physical properties

Lead is a weak electrical conductor but it is more known for its attribute against oxidization. Lead can be found in group IV-A in the periodic table and exists in two oxidation state, II and IV. There are four isotopes of lead, ^{204}Pb, ^{206}Pb, ^{207}Pb and ^{208}Pb and the last mentioned is the most abundant with 52.3% of the total Pb isotopes. Lead can be found in many forms; however it only becomes toxic in ionic forms. Therefore, Pb is sensitive against environment with low pH level due to its solubility (Bradl et al., 2005). The most common factors that affect the chemistry of Pb in soil are the adsorption, precipitation and complexation with organic matter. The adsorption is mostly depending on the pH level in the soil, the cation exchange and the affinity of lead towards soil minerals (Segura et al., 2006). The pH level controls the surface charge of the absorbents and the level of ionization of Pb which is an important factor for adsorption. Soil with high pH level usually causes formation of hydroxides and carbonates.

Toxicity

Out of all metals, Pb is considered having the highest affinity to organic matter (Sipos et al., 2005), which reduces its mobility in the soil, hence a less of an environmental problem. In soils, the precipitation of Pb usually occurs in neutral or higher pH levels. However it becomes a serious issue when it is dissolved to ionic species in more acidic conditions. Plants show a greater resistance to Pb than microorganisms and animals. Lead poisoning tends to restrain important enzymatic functions in animals and influences the hematological and nervous system functions and

reproduction activities. As aforementioned, there is many ways for exposure to Pb, it is mainly governed by the chemical and physical forms of Pb, which makes it a severe problem of exposure to environment and humans, especially children and infants. Ingested lead can be found in the blood and the surplus often accumulates in the bones and soft tissues (liver, kidney, brain). Excessive exposure of Pb can cause disorder in the cell and protein metabolisms, badly affect the hematological and neurological systems and interference in the development of children and infants (Hsu and Guo, 2002).

Zinc

Application and environmental exposure

Zinc is used in a wide range of products in the modern society and the consumption of Zn is one of the highest in the world. The metal is included in the production of rubber, glass, vehicle tires, ointments, paints, batteries, electrical appliances and many other products. Zinc is also extensively used as micronutrients in agriculture and as coatings for steel and iron against erosion and oxidation. The environmental exposure of Zn is commonly introduced by agriculture fertilization, mining and smelting productions. However, elevated concentrations of Zn are also found in sewage sludge and stormwater runoff from urban and agricultural areas (Bradl et al., 2005).

Chemical and physical properties

In the periodic table, zinc can be found in the group II-B. The oxidation state of Zn is commonly +2 and occurs in the same state naturally in the environment. There exist several isotopes of zinc, ^{64}Zn, ^{66}Zn, ^{67}Zn, ^{68}Zn and ^{70}Zn. The most abundant isotope is ^{64}Zn with 48.89%. In the nature, the amphoterism of Zn makes it able to act as both acid and base. Zinc is capable of forming water soluble chlorates, sulfates and nitrates. However, in basic environment Zn tends to precipitate as hydroxides but also form oxides, carbonates and phosphates, which are insoluble in water (Bradl et al., 2005). There are several factors governing the allocation of Zn in soils. The main factors are the pH level in the soil, soil characteristics, cation exchange capacity, organic matter and clay mineral content (Stephan et al., 2008). The availability of Zn is generally lower in alkaline soils, as Zn usually precipitates with carbonates and hydroxides.

Toxicity

Zinc acts as a micronutrient in plants and regulate several metabolic cell and enzymatic functions. As for the most trace metals, too much of it is toxic. In this case, concentrations of Zn more than 100 ppm in plants may show indication of chlorosis. In animals, zinc as many other metals serves as an essential micronutrient. Zinc has a vital purpose in the human body, since approximately 200 Zn enzymes and proteins are included in the metabolism. Cases of Zn toxicity is rather unusual, considering that it is almost impossible to reach a toxic level of Zn in a normal intake of diet (Bradl et al., 2005). Although, it is known that Zn toxicity affects the Cu metabolism in the body. The deficiency of Zn is a more common problem and it has become a widespread issue in the world. Lack of intake of Zn can cause disorder in the immune system, reproduction processes, pregnancy, growth and many other functions (Salguiero et al. 2000).

Nickel

Application and environmental exposure

Today, the application of Ni can be found in various products in the society. The element is included in the production of coins, electric components, rechargeable batteries, jewellery, a variety of alloys, kitchen wares and many other products. However, the use of Ni as an alloy in stainless steel is one of its main applications (Bradl et al., 2005). Nickel is also extensively used as catalysts for hydrogenation and methanation in chemical reactions. Elevated concentrations of Ni in the environment can be discovered around mining and smelting industries and sewage sludge (Barcan, 2002). The environmental exposure of Ni in the air mainly comes from fuel and coal combustion.

Chemical and physical properties

Nickel is included in the group VIII in the periodic system and exists in five stable isotopes, ^{58}Ni, ^{60}Ni, ^{61}Ni, ^{62}Ni and ^{64}Ni, whereas the former is the most abundant with 68.27 % of total Ni isotopes. The most common oxidation states of Ni are 0 and II. Nickel appears also in the oxidation state I and III but only under specific circumstances. In soil and water, Ni occurs as Ni^{2+} and organic and inorganic complexes. However, Ni is less likely to form inorganic complexes in water. In soil, the sorption of Ni is highly determined by the pH level (Bradl et al., 2005).

Toxicity

Nickel acts as a vital micronutrient in plants and animals. For many other trace metals, excessive uptake of Ni in plants causes phytotoxicity and leads to chlorisis, growth retardation and necrosis (Poulik, 1999). In animals, extreme levels of Ni affect the inner organs negatively and cause disorder in the nervous system. Many researches have also found carcinogenic activities in insoluble compounds of Ni in both animals and human. The main exposure of Ni to humans is via inhalation and ingestion. Chronic exposure of Ni can cause Ni allergy in the form of dermatitis. It can also results in heart and kidney diseases (Denkhaus and Salnikow, 2002).

Cobalt

Application and environmental exposure

Cobalt is a widely used metal in our society due to its corrosion resistance ability, the magnetic properties and the increase of durability in many alloys. The properties of Co make it suitable for use in various products such as ceramics, glasses, catalysts, magnets and as an alloy in different steels. Cobalt is also utilized in paints, varnishes, inks, foam stabilizers in malt beverages, agrochemicals and many other applications (Hamilton, 1994). There are both natural and anthropogenic sources of Co, where natural sources include erosion and weathering of rocks and anthropogenic sources consist mostly of mining and processing of Co in industries. Therefore, elevated concentrations of Co are most likely to be found around cobalt mining and processing industries (WHO, 2006).

Chemical and physical properties

Cobalt is located in the first transition series of group 9 of the periodic table. The oxidation states of Co are +2 and +3 and there is only one stable isotope, ^{59}Co. Co^{3+} is considered as a powerful oxidizer, which can oxidize water and release oxygen (Bradl

et al., 2005). Factors that affect the availability and mobility of Co in water and sediment are pH, organic matter content, redox potential and the presence of Fe and Mn oxides. An increase of pH tends to increase the mobility of Co in water and sediment and a decrease of pH leads to formation of insoluble hydroxides and carbonates, which reduces its mobility. Cobalt has a high affinity towards organic matter and Fe and Mn oxides, which act as an important sink for Co in water and sediment (WHO, 2006).

Toxicity

There are no records of Co as an essential micronutrient for plants, but small addition of Co is known to increase the growth (Hamilton, 1994). Cobalt is included as a component in vitamin B_{12}, which is essential for all animals, including humans (Bradl et al., 2005). Small concentrations of Co can be found in numerous vegetables, fruits, rice, oats etc. Cobalt deficiency can affect the gastric secretions, blood sugar levels and enzyme activities. In human, excessive intake of Co can cause disorder in the hematologic, neurologic, cardiac and thyroid activities (Hamilton, 1994).

Chromium

Application and environmental exposure

Chromium occurs naturally in the environment by natural sources such as, weathering of rock components, wet precipitation and runoff from terrestrial environments (Kotas and Stasickas, 2000). In the society, Cr is widely used for production of stainless steel and refractory but also as a component in pigments, leather tanning, catalysts and many other products. The processing of Cr in the industries contributes to elevated concentrations of Cr in the environment due to discharge of Cr residues. However, air depositions of Cr from steel production, coal-fired power plants and electric furnaces are currently the largest anthropogenic sources (Bradl et al., 2005).

Chemical and physical properties

Chromium is a member of group VI-B of the periodic table and it exists in four stable isotopes, ^{50}Cr, ^{52}Cr, ^{53}Cr and ^{54}Cr with ^{52}Cr being the most abundant. Chromium occurs mainly in the oxidation state +3 but it is also found in the oxidation states, 0 and +6 (Bradl et al., 2005). The solubility of Cr is highly dependent on their oxidation state and the speciation of Cr is also affected by the redox conditions, pH, competing ions, complexing components and adsorbents (Kotas and Stasickas, 2000). The high affinity of Cr(III) towards soil components reduces its mobility in aquatic environments. On the contrary, the Cr(VI) is fairly mobile since it is weakly absorbed onto soils. Chromium(III) is a Lewis acid and tends to form insoluble chromium compounds such as chromium hydroxides ($Cr(OH)_3$). In contrast, Cr(VI) is a Lewis base which occurs as an anion in aqueous media (Weng et al., 1994).

Toxicity

Chromium is a vital element in the diet of human and animals. In plants, there is no evidence of stimulatory effects on plant growth. The toxicity of Cr depends on its oxidation state. The hexavalent form is more toxic than the trivalent form, due to its high solubility and diffusivity in tissues and its ability to cross cell membranes (Bradl et al. 2005). Chromium(VI) has toxicological effects on biological systems. Inhalation and retention of Cr compounds can cause asthma, bronchitis and liver disorder. Skin exposure of Cr can cause skin allergies, dermatitis, dermal necrosis and dermal

corrosion. However, both of the Cr forms are carcinogenic to humans (Kotas and Stasickas, 2000).

Silver

Application and environmental exposure

Silver is a rare metal, which is mostly extracted from argentite (Ag_2S), hornsilver (AgCl), refining and smelting of Cu and Ni ores. Silver is known for having the highest electric conductivity of all metals. It is mainly used for photographic manufacturing, jewellery, catalysts, batteries and electrical and electronic components. It is also used in antibacterial products to prevent undesired bacterial growth. Environmental exposures of Ag are generally from disposal of photographic and electric components, mining, processing and smelting activities (WHO, 2002).

Chemical and physical properties

Silver can be found in group 9 in the periodic table. The most common oxidation states of Ag are 0 and +1, +2 and +3 are less common. Silver has two stable isotopes, ^{107}Ag and ^{109}Ag (WHO, 2002). Formation of stable complexes occurs generally from reactions between Ag+ and negative charged compounds in sediments and soils, which makes it moderately harmless in terrestrial environments. Soluble Ag is one of the most toxic metals to microorganisms and aquatic species. Small traces of Ag in aquatic environments are therefore a very serious problem. The bioavailability and mobility of Ag mainly depend on its chemical speciation, pH, alkalinity and dissolved organic matter content in the water and sediment (Bradl et al., 2005).

Toxicity

Ionic form of Ag is known for its extreme toxicity to bacteria and aquatic organisms. As Ag is rare in the Earth crust, the background levels are fairly low, environmental risks should still be accounted (Ndungu, 2011). Dissolved Ag is also toxic to plants such as phytoplankton and invertebrates. However, Ag is not particularly toxic to humans or mammals. Although, there are a few cases of argyria, derive from continual inhalation and digestion of Ag compounds (Luoma, 2008).

Gallium

Application and environmental exposure

Gallium ores are unusual in the Earth's crust and the production of these ores is extremely limited. Therefore the Ga elements are produced as a by-product of Al extraction from bauxite ores. Gallium compounds are used in the manufacture of various products including, LEDs (Light Emitting Diodes), laser diodes, solar cells and integrated circuits. Recently, Ga can also be found in medicine products to detect different diseases (Hogdkin disease and lung disease) and used as anticancer drug against and lymphoma, and as a catalyst in chemical reactions (Orthmer and Orthmer, 2004).

Chemical and physical properties

There are two stable isotopes ^{69}Ga and ^{71}Ga, where the former is the most abundant. The oxidation states of Ga are 3+, 2+ and 1+. The properties of Ga are very similar to Al in terms of atom coordination, atomic radius and amphotericity. Gallium is also

corrosive to most metals and tends to diffuse into most of the metals in liquid form. Gallium elements and inorganic Ga salts are insoluble in water.

Toxicity

In plants, the biological role of Ga in the development and functioning is unknown and there is no information about the toxicity of Ga in plants (Poledniok, 2008). Due to the insolubility of Ga compounds in water, the absorption of Ga in human and animals is poor. There is very little information about the effects of Ga to human, although internal overexposure of Ga can lead to possible kidney failure and renal damages.

Strontium

Application and environmental exposure

Strontium minerals (celestite and strontianite) are commonly converted to Sr carbonates for commercial reasons. Strontium is mostly used in the fabrication of glass and ceramic products but also in products such as pyrotechnics, pigments in paint, alloys and medicines.

Concentrations of Sr can be found in the environment due to human activities such as milling and processing of strontium, burning of coal, residues from pyrotechnic devices and the use of Sr containing fertilizers (WHO, 2010).

Chemical and physical properties

Strontium can be found in group II-A in the periodic table and exists in four stable isotopes, ^{84}Sr, ^{86}Sr, ^{87}Sr and ^{88}Sr, whereas the latter being the most abundant. In nature, the most common oxidation state of Sr is Sr^{2+}, due to its high reactivity towards oxygen and water. Strontium occurs in the Earth crust mostly as celestite (Sr sulfate) and strontianite (Sr carbonate).

In sediment and water, Sr is moderately adsorbed onto different metal oxides, clay minerals and other minerals. Strontium ions have high affinity towards organic matter and the complex formation often results in precipitation. In alkaline conditions, complex formation is increased due to the existence of Ca ions, which generally form complexes with Sr. This activity also results in precipitation, hence reducing the mobility of the Sr ions.

Toxicity

Strontium is generally not required in plants but is absorb from the soil via the natural Ca uptake of plants. In animals and human, Sr has a tendency to act as a surrogate for Ca. The absorbed Sr imitates the behavior of Ca and usually replaces the Ca in the bone. The excess and un-absorbed Sr are excreted as human feces and urine. There are currently no reports on the toxic effects of stable Sr compounds.

3 Research methodology

3.1 Risk assessment of contaminated sites

The methodology used in this study is based on Strategy for Environmental Risk Assessment of Contaminated Sites provided by the Swedish Environmental Protection Agency (Naturvårdsverket) (SEPA, 2008). The risk assessment is divided in four steps, *Problem description*, *Exposure* and *Effect analysis* and *Risk characterization*, which is described in this chapter.

Problem description

When conducting a risk assessment of contaminated sites, it is essential to define all aspects and factors of the problem of interest. This stage of a risk assessment is the most important part, as an elaborate definition of the problem, objectives and a well designed strategic plan facilitates the execution of the risk characterization. Therefore, it is necessary to define the objects clearly, obtain valuable information concerning the contaminated site and plan every task in detail.

The risk assessment analyses a specific potential contaminated area according to the potential polluters in the region, potential existing contaminants and the exposure pathways of contaminants (Sternbeck et al., 2008). Nonetheless, a site characterization is necessary, which includes a visually description of the contaminated area (Sprenger et al., 1997). The sources of potential polluters are important to be identified, which makes it possible to connect the contaminants in the polluted area with the potential source. Consequently, the types of chemical components and parameters for the analysis should be defined and the possible exposure pathways identified. Hence, conducting a conceptual map, where the relations between the sources of pollution, exposure pathways of the contaminants and the recipients are described visually, would be of great assistance in the assessment.

Previous reports and historical information of the contaminated site are of great assistance when formulating the problem (Marrella, 2007). For instance, information regarding the hydrology, geotechnical and mechanical conditions, chemical and physical conditions affecting the leaching of contaminants of the site is valuable since the characteristics of the contaminated site determines the fate and transport of the contaminants (Hansen et al., 2005). Thus, the system boundaries must be defined both temporal and spatial due to season variations, rain periods, location, different environmental conditions and many other factors. The method of the exposure and the effect analysis should already be decided in this stage to avoid unnecessary costs of experiments and research further in the assessment. The problem definition serves as a fundamental foundation when conducting a risk assessment. Therefore, it is essential that the definition of the problem is well conducted.

Exposure analysis

The second stage of the risk assessment is the exposure analysis. The main purpose of this analysis is to quantify the major sources of pollution and the quantity of the contaminants but also to identify the transport of the contaminants to the recipients. The quantification of contaminants in the surface sediment plays an important part in

the transport of the contamination since the contaminants on the surface of the sediment is most likely to spread to other recipients. It is therefore, easier to put boundaries on the system investigated and recognizes the different recipients and the pollution types within the system.

The quantity of the amount of contaminants, which is exposed to the receptors such as animals, fishes and organisms are also of great interests and should be compared to guidelines for water and sediment quality criteria or maximum effect concentrations. Measurements have to be taken to quantify the concentration of the contaminants. Considerations about the variation of contaminant concentrations in the surface water and the hydrology of the watercourse should also be taken when sampling the objects (river water or sediment) of interest.

In water and sediment, the fate and transport of contaminants consist of numerous dynamic processes, such as chemical, physical and many other processes. It is therefore of great value for instance to obtain information about solubility of different compounds in water and the binding relations between contaminants and sediment to increase the understanding of the contaminant´s behaviour in environment.

Effect analysis

In the effect analysis, it is essential to observe if the present concentrations of contaminants have any toxic effects on the animals (benthic and pelagic) and the natural environment within the system boundaries defined in the previous section Problem Description. Environmental guidelines for water and sediment quality criteria have been set by many international organisations to identify the potential risks the contaminants can pose. The guidelines for water and sediment qualities are often divided in two or more categories, where a high toxic and a less toxic threshold are set. The measurements on the contaminants of the objects of interests should be compared with their specific guidelines to assess the current state of the river. The study of the short term and long term adverse effects of the contaminants is also of major interests for the risk characterization.

Risk characterization

A risk characterization is based on the results from the exposure and the effect analysis. The results from the exposure and effect analysis are used to assess if the current situation pose possible risks for the environment and characterize the type and size of the risks within the system boundaries defined earlier in the risk assessment.

There exist different approaches in risk characterizations such as chemical and biological analysis and one or several approaches can be selected to increase the understanding of the potential risks. The evaluation of the approach and its sensitivity and uncertainty should also be included in the risk characterization. After the approach has been selected, the results are weighted and evaluated separately, depending on the amount of approaches utilized.

Similar to the selection of approach, a weighting method should also be selected to assess the different results gained from exposure and effect analysis. A final discussion on the strengths and weaknesses of risk assessment should be conducted to develop and improve the risk characterization.

4 Experimental methodology

4.1 Preparation of equipment

For the laboratory and field work, a range of equipments are required to be able to perform the intended tasks. The analysis of interest in this project is trace metal contamination, therefore plastic equipment was chosen for the sampling and storage of the samples because plastic materials are less probable to contaminate the samples with metal ions than glass bottles (Reeve, 2006). The equipment utilized for the field work are:

- a shovel for sediment sampling
- 250 ml plastic jars for the sediment samples
- 500 ml plastic jars for the water samples
- rubber buckets for the beaker tests
- water containers with the volume of 3.79 liter for beaker tests

The equipments used for the laboratory experiments are:

- filtration device
- pump
- 0.45µm cellulose acetate filters
- one multiple spindle stirrer with six slots
- one liter glass beakers
- an aquarium air pump
- magnetic stirrer
- magnetic stirrer with a hotplate
- glass pipettes

Figure 2. Ongoing process of a batch test. Left: There is a multispindle stirrer mixing sediment and river water. Right: Hotplate with a magnetic stirrer and a beaker with air injection.

The equipment are washed and rinsed with distillated water prior to the laboratory experiments to avoid contamination of the samples. The plastic containers and the glass wares are washed with acid (HCl 10 %) and rinsed with distillated water to guarantee the elimination of possible contamination of trace metals (Reeve, 2006). Cleanliness of the equipments is essential in laboratory experiments, in order to obtain accurate and useful results.

4.2 Preparation of colloids

Humic acid solution

The humic acid is used in the beaker test to simulate availability of organic matter in the river and how it affects the physical and chemical properties of the metals in the sediment. Humic acid (0.2g) was suspended in 100 ml of 2.5 x 10^{-4} M sodium carbonate. The humic acid and sodium carbonate solution were mixed with a magnetic stirrer for 60 minutes and then filtered through a 0.2 µm membrane filter (Florence, 1982) and the filtrate was stored in a refrigerator at 8°C.

Iron(III) solution

Due to the lack of iron(III) nitrate hexahydrate, a substitute of chemical was made. Instead, the iron(III) chloride hydrate was used and 10 g of iron chloride was dissolved in 50 ml of distilled water and then 5 g of sodium hydrogen carbonate was added slowly over 30 minutes. After the mixing the solution was filtrated through a 0.2 µm membrane filter. One ml of the solution was then diluted to 500 ml distilled water (Florence, 1982).

4.3 Sampling locations

There was a total of seven sampling points, five for the screening of trace metals in the river water and sediment (1-5) and two for the batch tests (A-B). Both river water and sediment were sampled in each point.
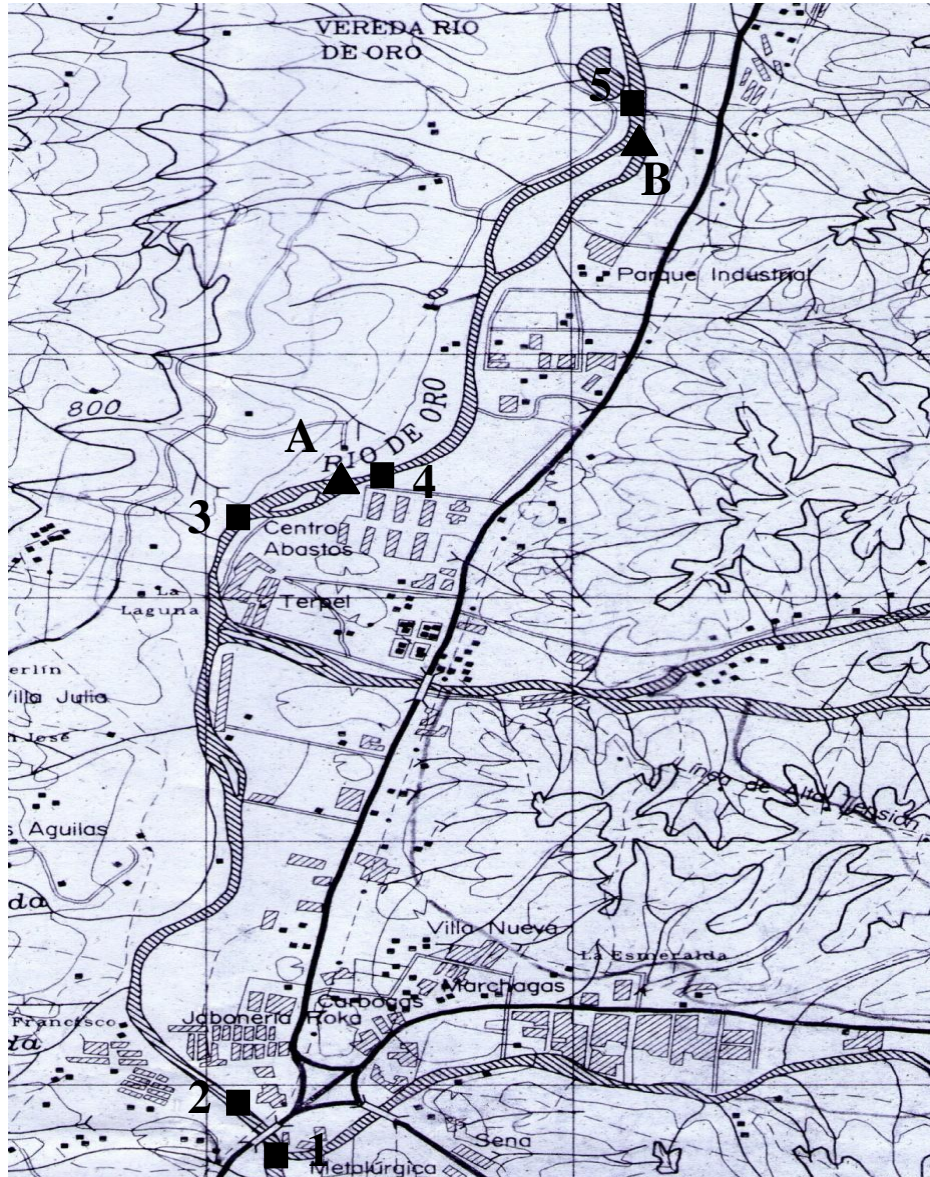

Figure 3. A map over Rio de Oro and the sampling locations, 1-5 are for the screening of trace metals and A-B are for the batch tests

4.4 Sampling procedure

Water

After the site characterization, five spots were carefully chosen to sample the water and sediment from the Rio de Oro in the industrial district. Due to variation of depth and strength of the stream in the river, the sampling in the middle of the river was impossible to perform. Therefore, the water sampling was performed manually with the plastic jars in the shallow parts of the river. During the sampling, the plastic jars were turned downstream, which caused less turbulence in the water in order for the prevention of stirring up the sediment. The plastic jars were always rinsed thoroughly with river water before sampling and performed before the sediment sampling to avoid sediment particles in the water samples.

Sediment

Due to the same reason as the water sampling, the sediment samples were also taken in the shallow parts of the river. A shovel was used to facilitate the collection of the sediment. The depth of the sediment samples was approximately 0-20 cm. For the trace metals, a smaller quantity of sediment was collected in one spot and a greater quantity of sediment collected for the beaker tests in several adjacent spots.

4.5 Trace metals

Water preparation

The preparation of the water samples from Rio de Oro was necessary in order to preserve the metal contents. The preparation process was divided into two sub-processes, filtration and acidification. The water samples are both analyzed for total and dissolved metal concentrations. The samples were vacuum filtered with cellulose acetate filters with the pore size 0.45 µm into a plastic tube with a volume of 50 ml. To create a vacuum during the filtration, an electric pump was used. Throughout the filtration process, the filtration devices were carefully rinsed with distilled water and sample water after each filtration to avoid contamination from previous filtration. The content of the sample was also shaken before each filtration to obtain a good mixture. All the plastic tubes were filled up to 45 ml.

After the filtration was finished, the filtered water samples were acidified to prevent the metals in the samples to precipitate. The acid used for the acidification was concentrated nitric acid. The volume of the acid added to each sample was 0.45 ml, i.e. 1% of the sample size. Then, the samples were stored in a refrigerator at a temperature below 8^0C until further analysis.

For the total metal concentration analysis, the filtration process was left out.

Sediment preparation

Loss of ignition

Crucibles were cleaned with water and soup, dried in a convection oven for 0.5 hour at 105^0C and weighed. Afterwards, wet sediment samples were added to the crucibles

and re-weighed before the samples were placed in the oven at 117^0C for two hours. Then, the samples were cooled in a desiccator to room temperature for one hour before they were weighted again. The purpose of placing the samples in a desiccator is to avoid absorbance of moisture from the atmosphere into the dried sediment samples.

Subsequently, the dried samples were put in a pre-heated oven at 600^0C for three hours. The crucibles with the sediment ash samples were cooled down in a desiccator for two hours. After the samples have reached room temperature, they were weighed with the crucibles to note the final weight. The loss of ignition and the ash content were then calculated by Eq. 1 and 2.

Finally, the samples were placed in small plastic bottles with the volume 30 ml for further analysis.

Sample digestion

Sediment

The sediment samples were ignited / combusted at 550^0C and the rest were sent to an external laboratory, ALS Scandinavia AB for metal analysis. The analysis was performed according to the method SS 02 81 13-1.

Water

Before the water samples were analysed for concentrations of trace metals, they were digested to recover all the metals from the water. The digestion is performed in a microwave, Mars 5 apparatus. First, 9 ml of water sample was placed in Teflon containers with 1 ml nitric acid (HNO_3). Thereafter, the Teflon containers were put in the microwave for digestion.

After the digestion, the solutions were diluted 10 times with distillated water (8.9 ml) and internal standard (0.1 ml) were added before further analysis in the ICP-MS (Inductively Coupled Plasma – Mass Spectrometer).

4.6 Batch tests

The batch tests were performed twice separately with river sediments from two different sampling points in the river. The river sediments in the beaker test are first dried in a convection oven at 105^0C for 24 hours. In order to obtain a liquid/solid (L/S) ratio of 5, 250 ml of river water and 50 g of dried sediment was mixed in each beaker. The stirring speed in the multiple spindle stirrer was 140 rpm and all the samples were covered with plastic foil during the test to avoid evaporation and contamination of the solutions. The parameters in the beakers are further modified to simulate different environmental conditions.

High pH – A high pH value in this test was considered to be approximately under 10. The desired pH value was obtained with careful addition of 2 M of NaOH in constant mixing to get the water, sediment and NaOH evenly distributed.

Low pH – The desired pH value was approximately 4. In order to obtain the values, careful addition of HNO_3 (1%) was performed. A pH meter was used to measure the pH level under titration to reach the pH level of interest. The content of the beaker was constantly mixed to avoid sedimentation of particles.

Strongly mixed – The sediment particles and the river water were strongly mixed with a magnetic stirrer in the beaker in 200 rpm.

High temperature – The beaker was heated up to 50^0C with a hot plate. The water and sediment sample was gently mixed with a magnetic stirrer to distribute the heat evenly over the whole beaker.

Colloids – Humic acid, iron(III) solution and a mixture of the both of the colloids were divided in three separate beakers.

- Humic acid – The humic acid concentration of interest was set to 100 mg/l. Stoichmetric calculations were used to calculate the total volume of humic acid added. The volume of humic acid was 15.7 ml
- Iron(III) solution – The iron concentration of interest was 20 mg/l which was slightly overestimated. Stoichmetric calculations were used to calculate the total volume of the iron(III) solution, which needs to be added to reach the decided concentration. The volume used was 80.65 ml.
- Mix of humic acid and iron(III) solution – After some calculations the volume of humic acid was 20.75 ml and 104 ml of the iron(III) solutions (Florence, 1982).

Air injection –During the experiment, an aquarium air pump was used to simulate the air injection. The input of air will create an oxic environment and increase the oxidation of organic and inorganic matter in both water and sediment. The air injection will increase the sediment redox potential, which in turn will increase the solubility of the metals in the sediment and water.

Undisturbed environment – The water and sediment are undisturbed without any addition of chemicals and mixing.

5 Results and discussion

5.1 Source identification

Figure 4. The potential sources and industries are marked in the map over Rio de Oro
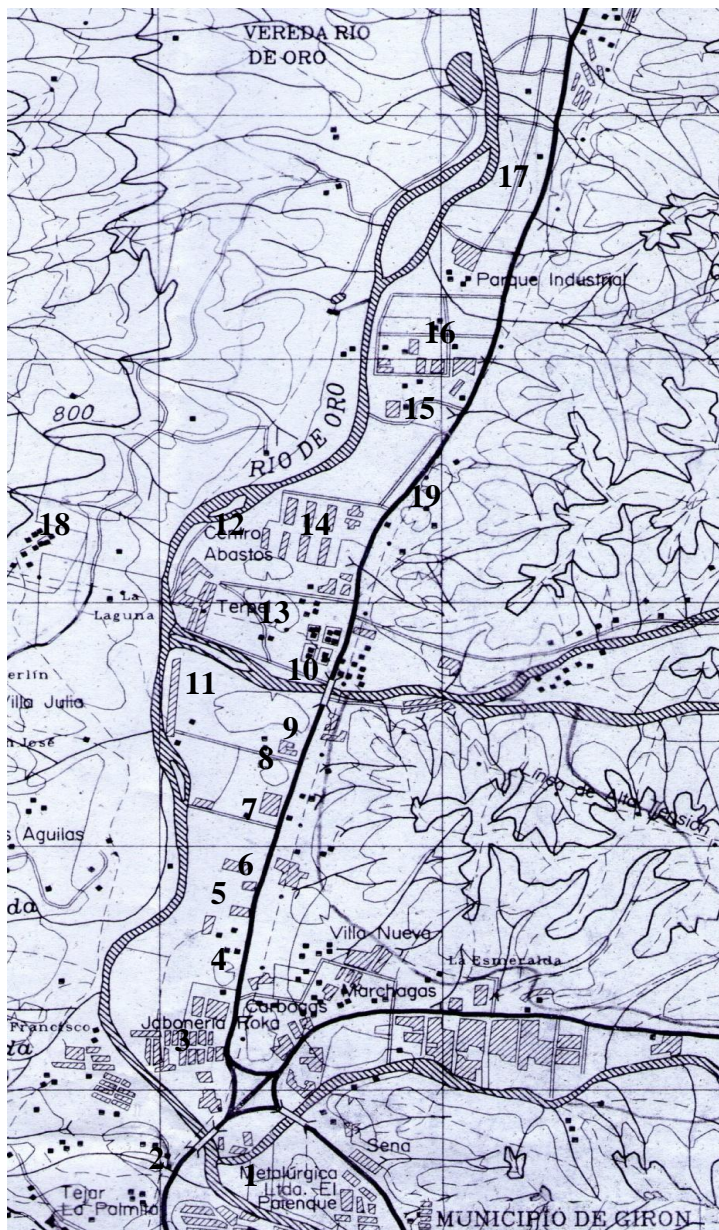
In Figure 4, the locations of different industries and potential sources of pollution along Rio de Oro are marked on the map.

1. Wastewater from municipality
2. Bridge construction
3. Soap factory
4. Plastic products manufacture
5. Fertilizer production
6. Cooking oil production
7. Animal feed factory
8. Plastic manufacture
9. Brick manufacture
10. Natural gas distribution station
11. Mechanical workshops for heavy duty vehicles
12. Invasion community
13. Distribution station of fuels
14. Storage and wholesale
15. Chicken processing facilities
16. Industry park
    a. Metal factory
    b. Dairy factory
    c. Electric cable factory
17. Mining activties
18. Chicken farms
19. Traffic

Conceptual map

Figure 5. Conceptual map of the industrial region of Rio de Oro

The conceptual map shows the potential pollution sources mentioned in Section 5.1. The exposure pathways are also illustrated. The high mountain forest provides Rio de Oro with high organic content runoff. The red houses with the red roofs symbolize the municipality and the black roof houses represent the invasion community. Their contribution of pollutions consists mostly of human waste and littering. The influents are also displayed in the conceptual map. The trucks characterize the traffic in the region, where the exhaust gases emitted are the main pollution. The numerous industries in the industrial area are portrayed as the two facilities with chimneys and the silos. Most of the industries use end of the pipe solution where the discharges end up in Rio de Oro. The construction of the bridge and the mining activities and their contribution of pollution can be seen in the conceptual map. The chicken farms which are located in the forest mountains contribute with chickens manure runoff. The pollution consists of nutrients and pathogens and not so much of metals.

Potential sources

In this chapter, the potential sources will be identified and their possible contributions to the pollution of Rio de Oro. The potential sources will be presented in written and visually.

Runoff and wastewater from invasions

Invasions are common in Colombia, where poor people build their residence in deserted areas and around water bodies. The housings are poorly built with limited access to water and electricity. All types of wastes generated from the population in the invasions are released in the nearest water body. The wastes consist of human feces, organic material, plastics, electronic components and many other waste products. The waste management in the areas is not controlled by the authorities and the current situation is solved without any treatment or end of pipe solution.

The population of the invasions areas consists of a significant percentage of the total population, which makes it a huge problem related to the amount of pollution and generation of waste.

Wastewater and municipality

Solid wastes and wastewater from the municipality of Giron can be found as an influent of Rio de Oro (SIGAM, 2002). The wastewater is not treated and discharged straight into the river. Only 2% of the domestic sewage is treated in Latin America (Inglezakis and Poulopoulos, 2006). In the wastewater, large amounts of solid wastes are included such as plastic products, organic materials, food and many other products. Animals such as vultures, birds, iguanas and dogs can be seen around the areas of the influent.

Emission from traffic

Outside the industries along the Rio de Oro, there is a highway. Due to all of the industries in the area, the traffic is very dense. In Colombia, railway can rarely be found mostly because of the mountainous landscapes, which makes it unsuitable for railway tracks. Therefore, all merchandises, products and raw materials are transported by trucks that mostly use a fuel called ACPM, Aceite Combustible Para Motores, it is a version of diesel fuel (FEDEPALMA, 2004). The emissions from combustion of diesel fuels consist of soot and fine particles, where various metals are included and attached to these particles. A wide range metals have been found in the diesel emissions such as Al, Fe, Mn, Cd, Pb, Zn, Ni and many other metals (Wang et al., 2003).

Figure 6. Wastewater and solid waste from an influent to Rio de Oro

Leaching from construction and mining

Within the system boundaries, there is a construction site, where a new bridge is built over Rio de Oro, since the last bridge fell and broke down a few years ago during a hard rainy season. The new bridge is not only constructed for connections for the both sides but also to support the demanding traffic in the area. Wastes such as metal residues, soil particles and organic material from the construction of the bridge are a possible contributor of pollution.

Activities of mining can also be found along the river, where the mining materials are sand and rocks for other construction sites (SIGAM, 2002). The effects from the mining and the construction of the bridge are possible contributors of increased metal and organic material in Rio de Oro, since there is no control or management of their environmental activities.

Landfill leachates

In the outskirts of Bucaramanga, there is a landfill, which receives wastes from the whole region. The landfill leachates are poorly treated with limited processing before being discharged into Quebrada la Iglesia, which is a creek nearby the landfill. The landfill treatment consists of physical and chemical treatments (EMAB, 2010). The leachates are initially filled in sedimentation pools to allow the larger particles and elements to settle. Subsequently, the leachates are treated with aluminum sulfite, hydrochloride acids (30%) and flocculating agents for reducing the bacterial activities and for further sedimentation before it is released into the creek. The creek is an influent of Rio de Oro with many other creeks, which makes it a possible source of pollution

Figure 7. The construction of the new bridge over Rio de Oro

Figure 8. Chemical treatment of the leachates in the landfill.

Industrial effluents

Along the river in the industrial area, two influents can be observed. The first influent comes from a stream situated between Bucaramanga and a small municipality. According to SIGAM, 2002, the domestic and industrial wastes from Bucaramanga and the leachates from the landfill treatment are discharged in this stream. The leachates can be seen in Figure 9, whereas the color of the leachate is black. There is no clear evidence how the leachate affects the environment, although it appears to be heavily polluted.

The second influent can be found further up in the river. The influent consists of two rivers, Quebrada Joya and la Rosita combines into one stream. After some observation of the influent, the stream appears to be very foamy, which indicates heavy pollution of household cleaning products such as detergents. In Figure 10, foams can be observed but also a typical building constructed in the invasion communities to the right of the picture.

Figure 9. Treated leachates discharged in Quebrada la Iglesia

Figure 10. There is a second influent further up the river. The stream is currently foamy.

Most of the sources are point sources but in this case, the sources are not monitored or controlled by the government and pollutions is released without any treatment or end of pipe solutions by the industries. Invasions/favelas are considered a large contributor to polluting the river but in contrary, it is difficult to handle and monitor all the pollution from the invasions/favelas since the population is too large. It would also be too expensive for the government to relocate the populations in the invasions. Only short term solutions are used to handle this kind of issues although long term visions of preserving the environment should be prioritized.

There are numerous industries along Rio de Oro after careful surveillance such as, fiber glass manufacture, animal feed production, brick production, metal industry and dairy production. The industries are not cooperative to provide information about their discharges and other information regarding the pollution of the river. Due to these circumstances, vague estimations of their waste discharges and pollution have been performed.

Potential sources, contaminants and estimated risks

In Figure 11, it is an illustration of the risk of the amount of pollutants generated by the potential sources. Leachates from the landfill are mostly released in one of the influents of Rio de Oro, which displays similar risks.

Sources	Metals	Nutrients	Organic pollutants	Pathogens
Invasions		Medium risk	Medium risk	Medium risk
Wastewater & municipality	Low risk	High risk	High risk	High risk
Construction & mining	High risk			
Traffic	Medium risk	Low risk	Low risk	
Landfill leachates	Medium risk	High risk	High risk	High risk
Influents	Medium risk	High risk	High risk	High risk
Industries	High risk	Low risk	High risk	Low risk

Low risk	
Medium risk	
High risk	

Figure 11. The potential pollutants discharged by the potential sources and the estimation of the risks

5.2 Trace metals

Water

The metal concentrations in the water from the different sample points along Rio de Oro, are shown in Table 3. The concentrations are compared with water quality standards from the Swedish, Canadian and the U.S. Environmental Protection Agency.

Table 3. The metal concentrations of the sediment in the five sample points in Rio de Oro and the guideline values from SEPA, USEPA and CEPA

	Samples (µg/l)					Guidelines (µg/l)		
Elements	1	2	3	4	5	SEPA*	USEPA**	CEPA***
Ag	0.8	0.9	1.1	0.9	0.8		3,2	
Al	144	166	180	183	172			
Cd	0	0.1	0.1	0	0	0.01	0.25	0.01
Co	0.5	0.3	0.5	0.5	0.4			
Cr	1.9	1.5	2.2	2.4	2	0.3	11	20
Cu	2.9	4.3	4.4	3.7	3.9	0.5	1.45	4
Fe	196	171	226	258	181			
Ga	0.5	0.4	0.6	0.6	0.5			
Mn	127	39	142	145	71			
Ni	4.2	3	4.3	4.5	4	0.7	52	150
Pb	0.7	0.5	0.6	0.5	0.5	0.2	2.5	1
Sr	65	58	70	70	70			
Zn	13.7	13.3	14.4	13.7	13.2	5	120	30

* (SEPA, 2000). Swedish EPA

** CCC - The Criterion Chronic Concentration - CCC) is an estimate of the highest concentration of a material in surface water to which an aquatic community can be exposed indefinitely without resulting in an acceptable effect (USEPA, 2009). USA EPA

*** (CEPA, 1999). Canadian EPA

The Cd, Cu, Cr, Ni, Pb and Zn concentrations in the different sample points are considered low and moderate, which is in the range of causing effects on the biological reproduction and the ecosystem (SEPA, 2000). The elevated metal concentrations can be originated from different point sources causing short term effects on the biological life in the aquatic system. Although Cd concentrations were only observed in the second and third sample point, the condition should be considered as serious since Cd is a very toxic metal (Ross, 1994). Chromium, Pb and Ni are also toxic metals and should be regarded as severe, even in small concentrations.

In the water samples, concentrations of Ag, Co, Ga and Sr can be observed. These metals are considered rare. Silver is very toxic to aquatic organisms in low concentrations (Bradl, 2005). The Ag levels from all the sample points are in the range of 0.8 - 1.1 µg/l, which is below the CCC of 2.6 µg/l from USEPA. According to (WHO, 2006), the guidance value for Ag is 20 µg/l. The Co concentrations from the sample points range from 0.3 - 0.5 µg/l. Cobalt is considered to have less toxic effect to aquatic organisms in freshwater containing elevated concentrations of Ca^{2+}, since Co ions tend to compete with Ca ions in fish gill binding sites (WHO, 2006). Although the concentrations of Ag and Co are below the guideline values from WHO (World Health Organization), the metals should still be taken in to consideration in risk assessments

The concentrations of strontium are in the range 57.8-70.1 μg/l. The average concentration measured derived from surface water and groundwater in the US was 1.1 mg/l (WHO, 2010), which is far more than the concentrations from Rio de Oro. Currently, there is little information regarding the toxicity of Sr to humans and Sr has low acute toxicity to freshwater organisms.

There is no available data on the guideline value for Ga from the EPAs respectively. Gallium occurs naturally in nature and there are no reports on toxicity towards aquatic organisms.

Aluminium, Fe and Mn are main elements naturally occurring in varying concentrations in the environment. These metals are of interest to the study because they could form colloids, i.e. small particles in nanoscale. These colloids could be carrier of trace metals (Tipping et al, 2002).

The low concentrations of the metals can depend on the neutral pH level in the river (SEPA, 2000), which leads to possible precipitation of the metals, whereas the metals tend to form complexes with organic materials, carbonates, hydroxides and other chemical compounds (Bradl, 2005). Another factor that causes the low concentration of toxic metals is the strong stream and the large flow of the river, which dilutes concentrations of the contaminants.

The organic material may be important in this scenario because organic materials have high absorption capacity for many trace elements in rivers and act as a sink for trace metals (Cornejo and Hermosin, 1996). Since the climate is tropical, it provides large amounts of organic material for the river. The seasonal variations in Bucaramanga are almost insignificant, due to its geographical location (SIGAM, 2005).

Moreover, the guideline values provided from SEPA, USEPA and CEPA are based on level conditions in respective countries. Therefore, it should be noted that the environmental conditions and the ecosystem functions in Colombia differs widely and the elevated metal concentrations in the river can be caused by the diverse geological and environmental systems. The tolerance levels for effects on the aquatic environment and organisms are higher in both USEPA and CEPA. The effect levels from USEPA and CEPA are considered high and very high concentrations in SEPA.

Nitrogen, organic matter and turbidity

According to the results presented in Figure 12, the total nitrogen concentrations are 20–50 times higher than the SEPA guideline value for lakes and water courses of 0.3 mg/l and classified as extremely high. There is a small deviation in sample number 2, where the nitrogen concentration drops substantially to 5.8 mg N/l for the total nitrogen and 3.9 mg N/l for the dissolved nitrogen. The nitrogen concentrations are still considered extremely high. Factors that could have affected the nitrogen concentration in sample point 2 can be the manual sampling of the water, which can cause inconsistency in the chemical content. Generally, the total nitrogen levels are constant through the five sample points for both total and dissolved nitrogen. The slightly higher total nitrogen concentration in the first sample point could have been affected by the influent wastewater of Rio de Oro. The influent which is heavily polluted by the landfill leachate and the wastewater from the surrounding municipality is a possible contributor to the high levels of nitrogen in Rio de Oro. Chemical analysis performed by Herrera, 2011 showed nitrogen concentrations up to 2000
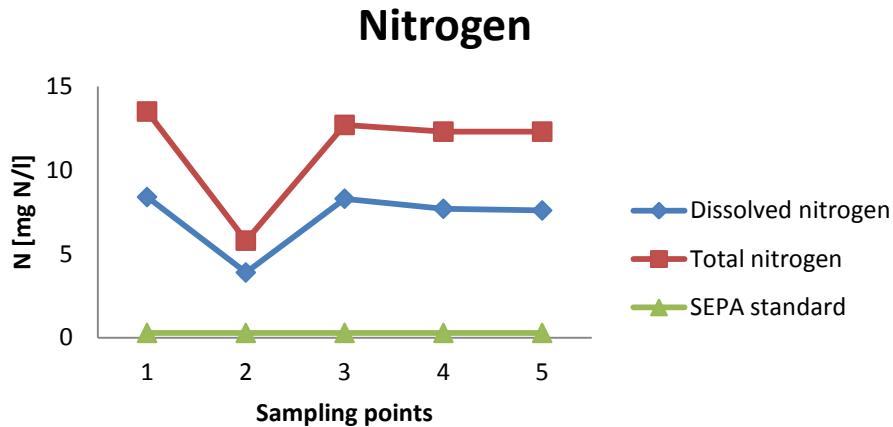
Nitrogen

Figure 12. The nitrogen concentrations in the five water samples from Rio de Oro

mgN/l in the landfill leachate, which is tremendously high. The landfill leachate is obviously diluted by the stream but should be considered as an important factor in polluting the environment.

In Figure 13, it can be observed that the TOC and DOC concentrations are high in the first sampling point but it is declined in the second point. According to SEPA, 2000, the concentration is considered very high when >16 mg TOC/l. The enhanced concentration in the first point can be due to the influent in Rio de Oro, where incomplete mixing might have caused the high concentration.

The TOC concentration of the second point is classified as moderately high, 8 - 12 mg TOC/l (SEPA, 2000).

A consistency in the concentration can be noticed in the last three points, which is in the range of very high concentration. The high TOC levels in the water samples are maybe derived from the dense forest mountains and the discharges from the industries. In the dense forest mountains, the biodegradation of trees and plants occurs very fast due to the tropical climate all seasons in the area. In tropical regions, the biodiversity is considered to be higher than in non-tropical areas, which also increases the degradation of biological materials and the intermittent rain tends to flush down all the material into the river.

Another factor for the contribution of the high concentration of TOC is the discharges of wastewater from municipalities, industries and landfills. The discharges usually contain fertilizers, pesticides, surfactants and solvents from direct use (Visco et al., 2005).
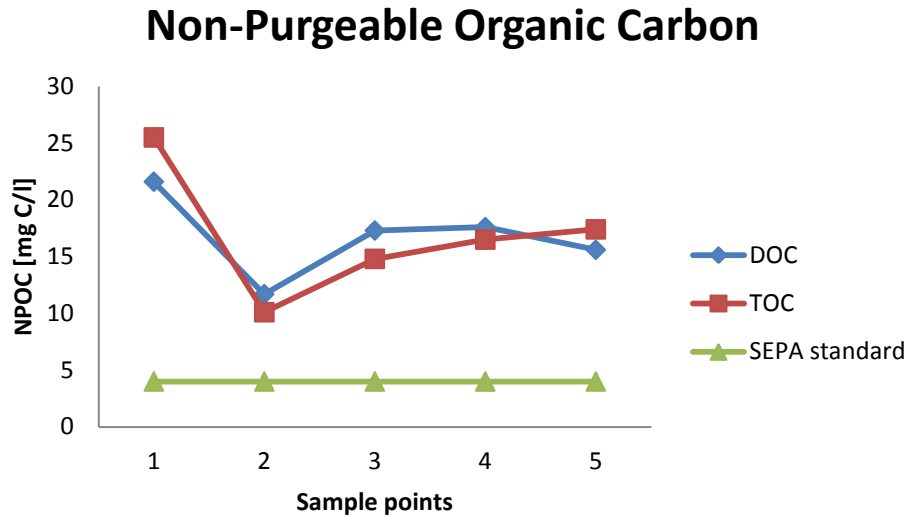
Non-Purgeable Organic Carbon

Figure 13. The DOC and TOC concentrations in the water samples from Rio de Oro

The turbidity of the river water in all sample points is significantly higher than the recommended turbidity standard from the SEPA for lakes and watercourses (SEPA, 2000), which can be observed in Figure 14. The high turbid level of a lake or watercourse is < 0.5 NTU units.

In the first sampling point, the turbidity is over 200, which can be interpreted as highly elevated levels of total suspended solids in the river water. The dense mountain forests along the river may be a contributor of organic material such as twigs, soil, silt, sand, branches, plants and leafs, which affects the turbidity of the river especially in cases of rain. The tropical climate leads to fast growth of trees and plants, which generates organic materials to the river in all four seasons. In the beginning of the sampling boundaries, there is an influent, whereas wastewater from the municipality of Giron is discharged into this influent, which could have affected the turbidity of the river, due to incomplete mixing of the influent and the river.
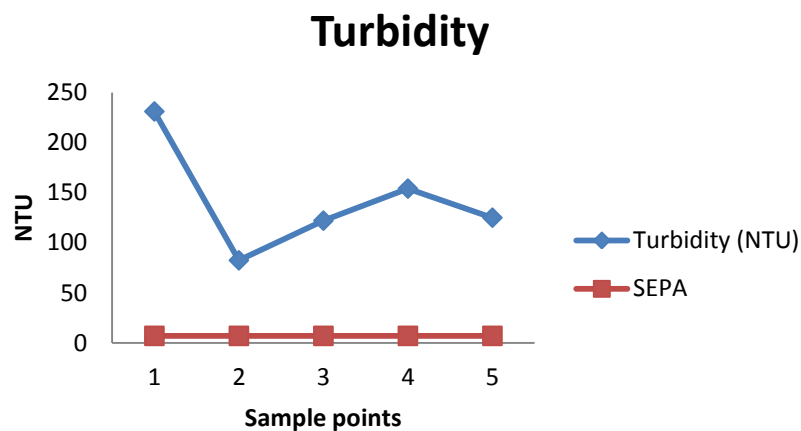
Turbidity

Figure 14. The turbidity of the river water from the five sampling points in Rio de Oro.

Sediment

Table 4 shows the metal concentrations of Cd, Co, Cr, Sr, Cu, Ni, Pb, Zn, Fe and Mn in the river sediments and the guideline values from the SEPA, CEPA and Wisconsin Department of Natural Resources, US.

The metal concentrations of Cd, Cr, Cu, Ni, Pb and Zn in the sediment are not considered toxic according to the standards for soil quality criteria in the SEPA, 1999, except for Cr and Ni in sample points 4 and 5, whereas the concentrations are classified as low concentration. Chromium has a very high level of toxicity in the aquatic environment and Ni is both toxic and carcinogenic and preventive actions should be taken to avoid escalations of the metal concentrations.

Table 4. The metal concentrations in the sediment from the five sample points in Rio de Oro and the guideline values from SEPA, CEPA and U.S.

	Samples (mg/kg DS)					Guidelines (mg/kg DS)		
Elements	**1**	**2**	**3**	**4**	**5**	**SEPA***	**CEPA****	**US*****
Cd	0.1	0.1	0.1	0.1	0.14	0.8	0.6	0.99
Co	1.46	2.38	2.02	5.26	4.17			
Cr	3.25	6.55	5.39	12.2	12.6	10	37.3	43
Cu	1.81	2.66	3.07	8.03	8.71	15	35.7	32
Fe	3770	7110	8380	13300	15100			
Mn	51.8	78.6	68.1	149	168			
Ni	2.11	3.06	3.42	7.69	7.82	5		23
Pb	1.15	2.09	1.81	4.5	4.59	50	35	36
Sr	3.95	5.75	6.5	11.2	16.4			
Zn	8.43	10.4	14.7	30.9	34.8	150	123	120

* (SEPA, 1999)

** ISQG - Interim Freshwater Sediment Quality Guidelines (CCME, 2002)

*** TEC - Threshold Effect Concentration - lower effect level at which toxicity to benthic-dwelling organisms are predicted to be unlikely (CSST, 2003)

According to CCME, 2002, the metal concentrations of Cd, Cr, Cu, Ni, Pb and Zn are all under the threshold effect level and possibly not a toxic threat to the aquatic organisms in the sediment and water interface.

This can be due to many factors, for instance the strong streams of the river, which prevents the metals to settle in the sediments until it reaches the calm part of the river and in Figure 14, it can be observed that the successive increase of metal concentrations from sample point 1 to 5, suggests that the metal compounds are transported a distance by the strong stream in the river before settling. It is almost certain that higher concentrations of metals in the sediment can be found further in the river outside the system boundaries, which might occur in toxic levels, since the metal concentrations are gradually increasing. The manual sampling method used in this project, which is explained further down in the report could have affected the results too.
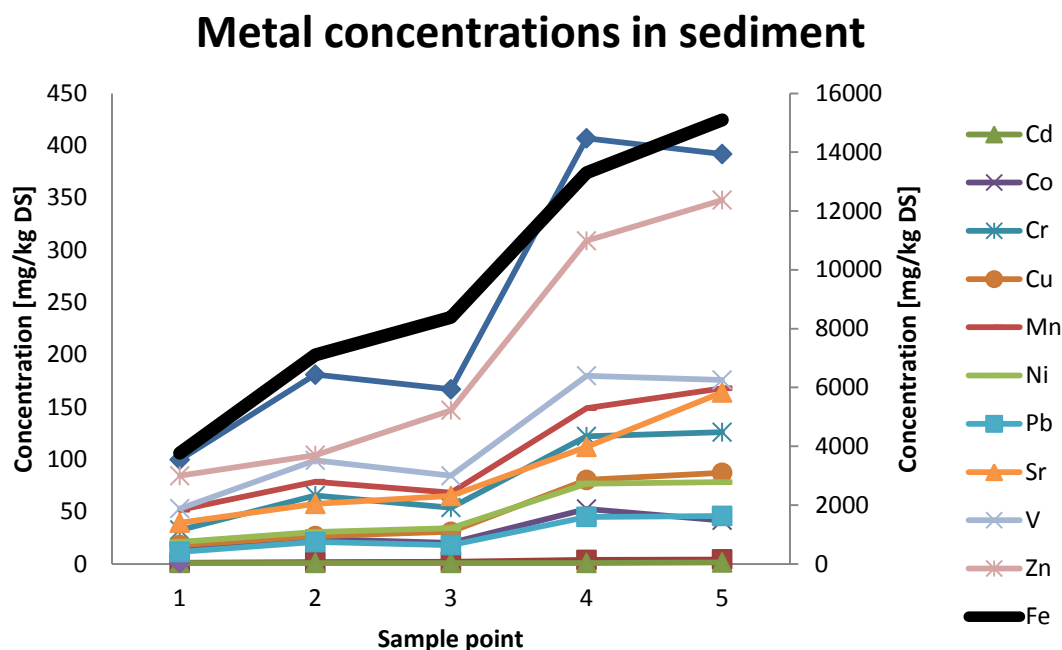
CHALMERS, *Civil and Environmental Engineering*, Master's Thesis 2012:1

Figure 15 . The metal concentrations in the sediment of Rio de Oro. Fe concentration on the right y-axis and the rest on the left y-axis.

In Figure 15, a positive trendline of the metal concentrations in the sediment can be observed along the river. A correlation between the Fe and Mn with the trace metal concentrations in the sediment can be noticed. This shows the binding relations between Fe and Mn oxides and Cd, Cu, Ni, Pb and Zn. Iron and Mn oxides are well known to have high absorption ability for metals (Bradl et al., 2005). Iron and Mn absorb the metals and form larger aggregates, which tend to attach to larger solid particles or precipitate. Therefore, the larger aggregates are believed to follow the strong streams of the river for settlement further in the river.

Organic content

The mean value of the organic content (loss of ignition) of all the samples is 4%, which is very low for river sediments in countries with tropical climates, where the tropical vegetation generates a large amount of tree and plants residues all year around. The residues and soil particles are probably washed into the nearest watercourse, affecting the total organic matter concentration.

Metals are known for having high affinity for organic matter. The metals in the river are most likely to bind to the organic matter (Bradl et al., 2005), where they are settled in a less turbulent part of the river.
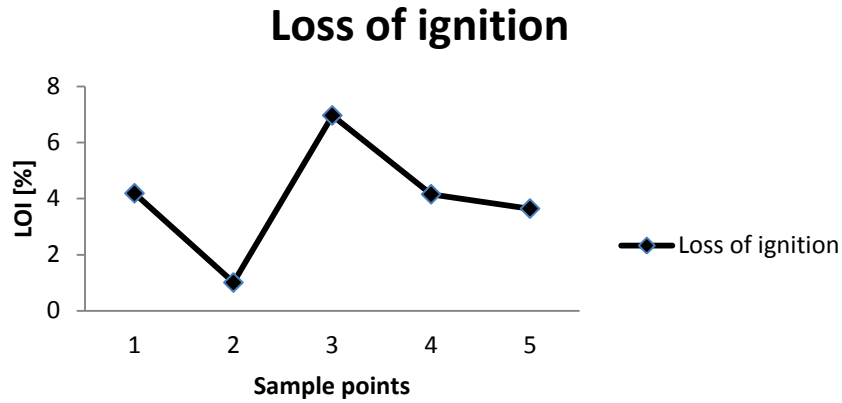
Loss of ignition

Figure   16. The organic content (LOI) of the sediment samples from Rio de Oro

5.3 Batch test

The figures in this chapter are divided in two graphs to differentiate the metals as there is a great variation of the amount of leached metals. The tests are performed separately with river sediment from two different sampling points of the river.
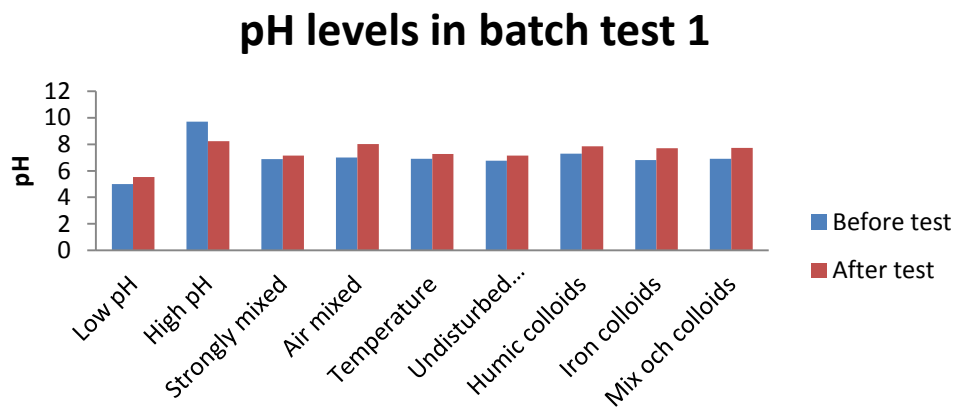
Buffer capacity

pH levels in batch test 1

Figure 17. The initial and final pH levels in the different parameters in batch test 1
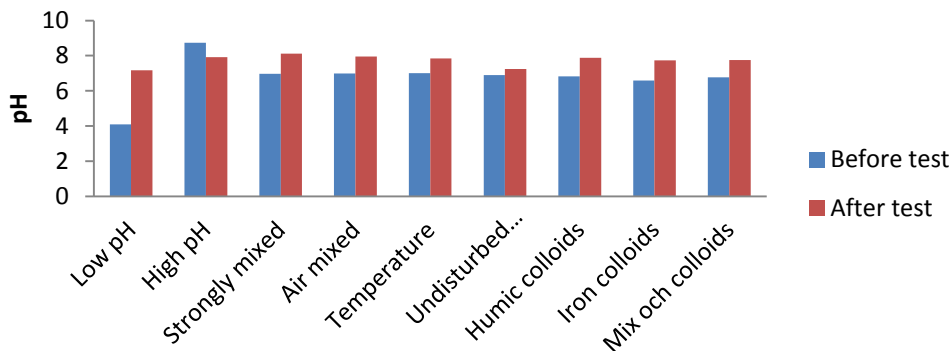
Figure 18. The initial and final pH levels in the different parameters in batch test 2

During the batch tests, pH levels were measured in each beaker with different environmental condition before and after experiment, which can be observed in Figure 17 and 18. The time of the experiments was set to 24 hours. In the first batch test, the final pH levels were higher than the initial pH levels, except if the pH was already high initial. The same tendency could be noticed in the second batch test, which showed clearly how the sediment affects the pH level. At the low pH, the acidic solution was buffered to a decrease in pH. According to the Swedish EPA, a neutral pH level in lakes and rivers should be > 6.8 (SEPA, 2000) and most of the final pH levels in both batch tests were above 6.8. The reasons for the high buffering capacity can be the high concentration of basic substances such as carbonates in the sediment particles, which are released during the experiment.

Batch test 1

In Figure 19, it is noticeable that after the batch test, the metal concentrations have increased, compared to the reference water. Aluminium and Fe are the metals that have leached the most in the experiment, especially at the high pH, addition of humic and the mix of colloids. Aluminium and Fe are abundant and occur natural in the Earth crust. It should be taken into consideration that of the parameters, iron and mix of colloids, iron(III) has been added, which affected the Fe concentrations.

Concentrations of Sr could be found leached in noticeable amounts. Strontium occurs naturally in the Earth crust as minerals and can be introduced to the environment by natural weathering of the mineral or by human activities such as milling and processing of the Sr minerals. According to WHO, 2010, the average concentration of Sr in surface and ground water in the U.S. was 1.10 mg/l. The amount of Sr leached is in the range of 73.5 – 151.4 μg/l, which make the Sr concentrations under all conditions to end up below the average concentration.

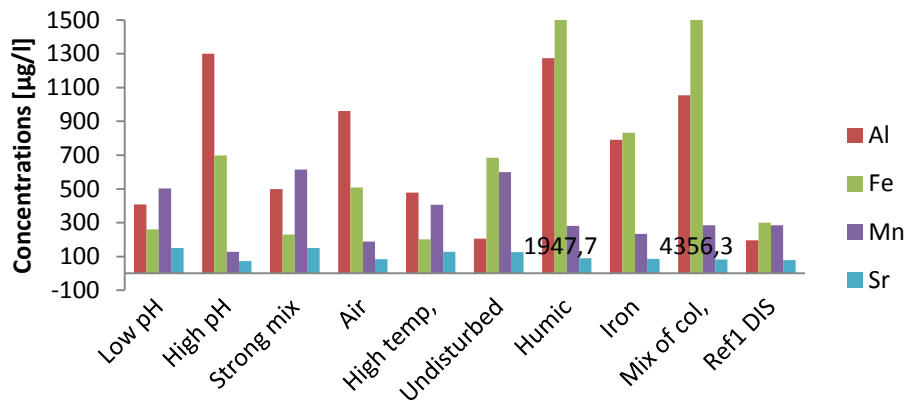# Batch test 1 - Metal concentrations in the river water [µg/l]

Figure 19. The Al, Fe, Mn and Sr concentrations leached from the sediment in the batch test 1.

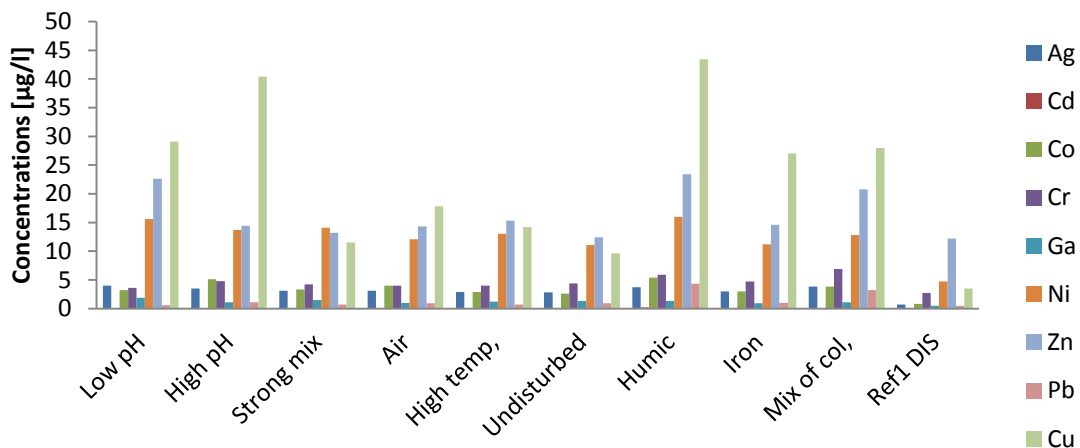# Batch test 1 - Metal concentrations in the river water [µg/l]

Figure 20. The Ag, Cd, Co, Cr, Ga, Ni, Zn, Pb and Cu concentrations leached from the river sediment in batch test 1

Figure 20 illustrate that higher amounts of Cu have been leached, especially in the changes of pH and addition humic, iron and mix of colloids. Under the other conditions, the Cu has leached in moderate amounts.

Moderate amounts of Ni and Zn have been leached and for Ni, the leaching amount is almost constant through all the parameters. There is a slight variation of the amount of leached Zn but the parameters, low pH, addition of humic and mix of colloids have contributed most to the Zn leaching. In the reference parameter, it can be observed that the concentration of Zn is higher than expected, which in this case could have contributed to less leaching.

Small traces of leached Ag, Cr and Cd could also be found. These metals are considered having high toxic effects on biological organisms in small concentrations and it is therefore important to observe their behaviour under different environmental conditions.

Copper compounds have a high affinity to both organic matter and Fe and Mn oxides (Bradl et al., 2005). In the batch test, a correlation between the leached Cu, Zn and the Fe can be observed. Because the Fe compounds tend to bind with metals, the dissolution of Fe from the sediment into the water will cause release of the attached metals. There is also a probability that the dissolved metals reabsorbs onto other materials (Palumbo et al., 2001). In Figure 19 and Figure 20, it can be observed that with leaching of Fe from the sediment follows significant amounts of leached Cu and Zn.

Concentration of leached metals Vs SEPA guideline values

The concentrations of Cu, Cr, Cd, Ni, Pb and Zn are displayed in Figure 21 and compared with the SEPA guideline values to observe the amount of metals that have dissolved into the water.

The SEPA guideline values ranges from very low to moderate, high and very high concentration in the different figures. It can be observed that all the metal concentrations are above the very low concentration in all of the figures, which is interpreted as having slight risk of biological affects according to SEPA 2000. The concentrations of Cd, Cr, Ni and Zn are fairly constant in all of the parameters and concentrations range from very low to high concentrations, except for Ni, where the levels are just below moderate concentrations.

The Pb concentrations in the beakers with addition of the humic and mix of colloids are slightly above and below the high concentration level and are considered as causing growing risks of biological effects.

For the Cu concentrations, the parameters that have the most significant leaching of Cu are high pH and addtion humic colloids. The metal concentrations reach just below the very high concentration value, which is considered to affect the survival of aquatic organisms even in short term exposure.
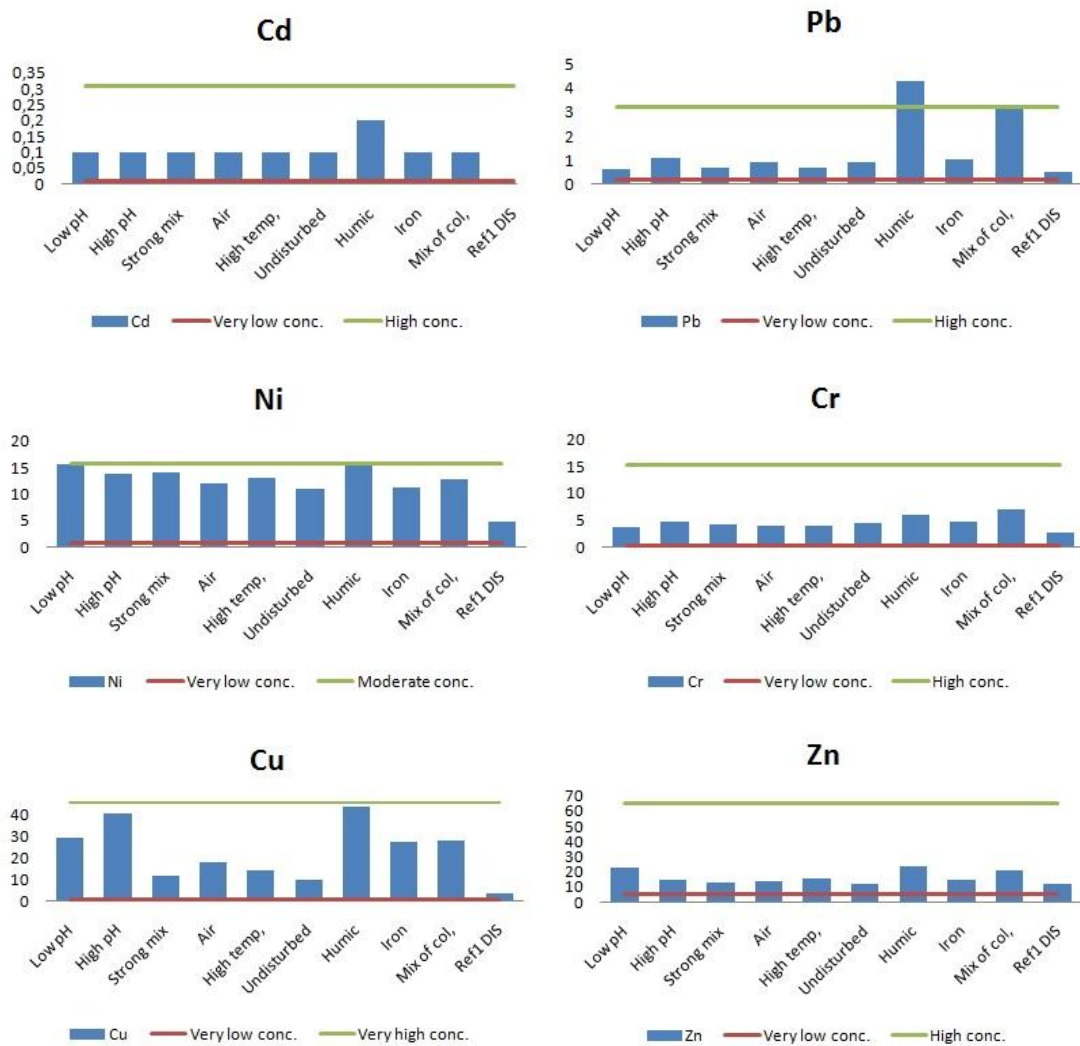
Figure 21. Comparisons of the leached amount of Cu, Cd, Cr, Ni, Pb and Zn in batch test 1 and the SEPA guideline values in unit μ/l (SEPA, 2000).

Batch test 2

Figure 22 illustrates that the second batch follows the same tendency as the first batch test, especially the amount of Fe and Al leached for the addition of humic and mix of colloids. Significant amount of leached Mn and Sr can be observed when the pH was high.

The high temperature showed very high concentrations of leached Co, Cu and Ni. High temperature in the water leads to less dissolved oxygen, which could have decreased the oxygen level in the batch. In anoxic environment, metals such as Cu, Ni and Zn have increased mobility. The metals have the ability to form insoluble sulphides as well as soluble complexes with sulfur compunds (Gerringa, 1991). Reduced metal compounds of Fe, Mn and Co are more soluble in reduced form than oxidized (Özturk, 1995), which explains the high solubility of Co in the solution. For the dissolved Fe and Mn, there is a high probability that they precipitate after forming complexes with sulphides, carbonates etc, as Fe and Mn have only leached in small amounts.
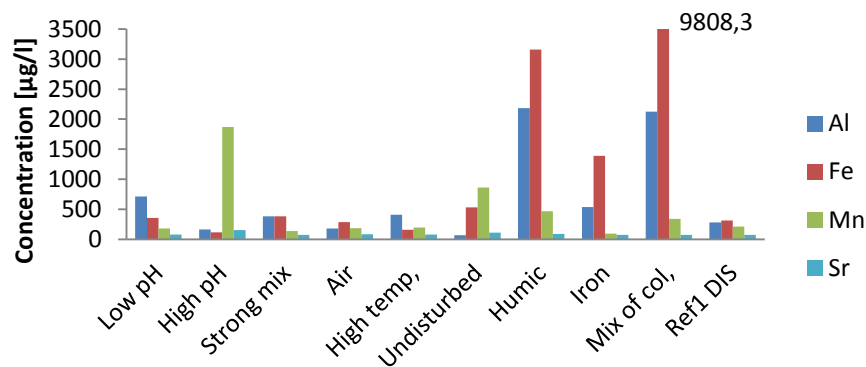
Figure 22. Al, Fe, Mn and Sr concentrations leached from the batch test 2
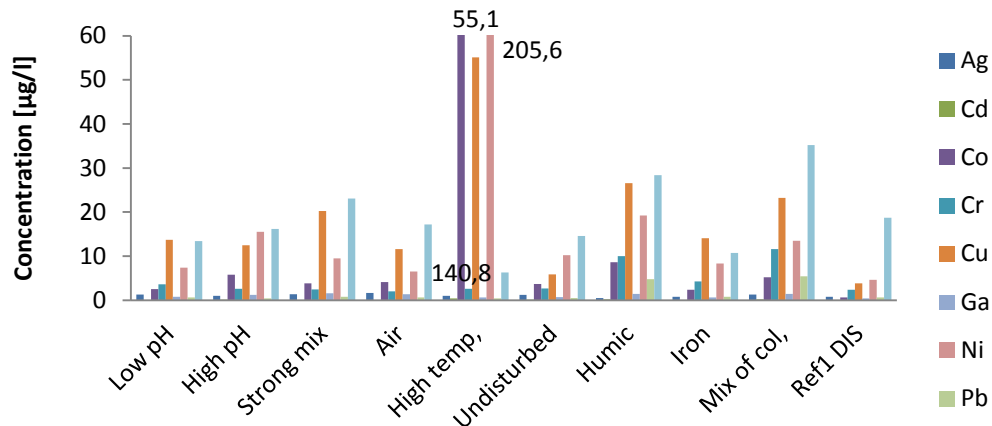

Figure 23. The Ag, Cd, Co, Cr, Ga, Ni, Zn and Pb concentrations leached from batch test 2

Zn and Cu are leached in moderate amounts in the humic and mix of colloids, which follows the same pattern as the first batch test. Chromium has leached in noticeable amount when addition of humic and mix of colloids. In Figure 22 and 23, correlation between Fe, Al, Cu and Zn can be observed. Release of Fe and Al in the sediment also leads to dissolution of other elements attached.

Concentration of leached metals Vs SEPA guideline values

The concentrations of Cd, Cr, Cu, Ni, Pb and Zn leached from the batch test are compared with the SEPA guideline values in Figure 24. The guideline values are classified from very low concentration to high and very high concentration.

Most of the dissolved metals released due to the change in parameters are below the SEPA guideline values and the levels of metals are considered to have small risks of causing biological effects in the aquatic environment.

For the Cd, Cu and Ni, the high temperature parameter causes high leaching. Levels of Cd and Ni exceed the high concentration guideline values and the Cu concentration is just above the very high concentration guideline value. Cd and Ni concentrations are causing growing risks of biological effects in the aquatic ecosystem. The Cu level is considered to affect the existence of biological organisms in the watercourse, since the concentrations are above the very high concentration >45 µg/l referred to the SEPA values.

The dissolved Pb concentrations in the batch test show the same leaching pattern of Pb as in the first batch test, where the parameters of humic and mix of colloids cause most leaching. The Pb concentrations in those parameters are just above the high concentration according to the SEPA guideline values.
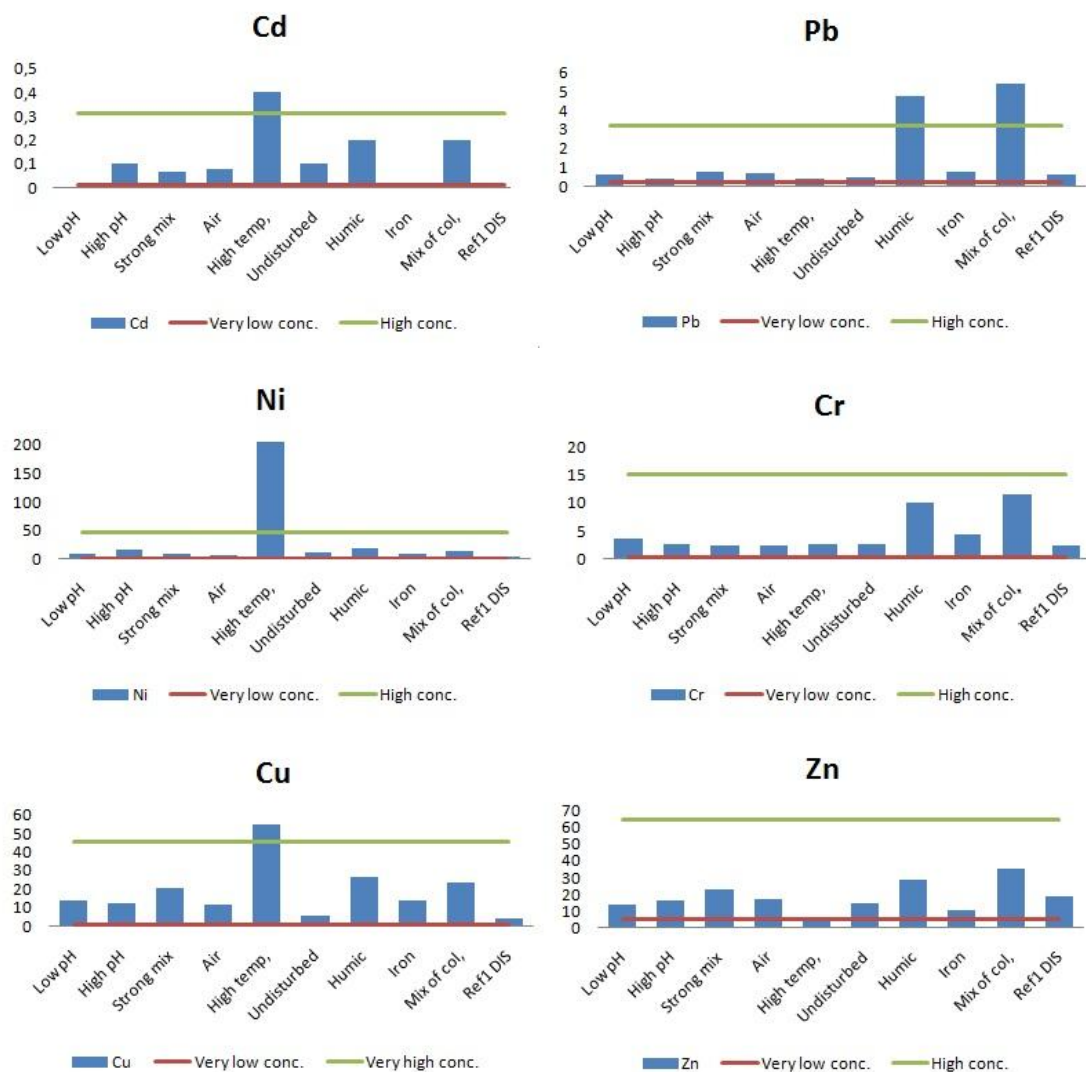

Figure 24. Comparisons of the leached amount of Cu, Cd, Cr, Ni, Pb and Zn in batch test 2 and the SEPA guideline values in µ/l.

pH

The leaching of the metals could have been higher at the low pH in both batch tests but according to the pH measurements executed before and after the experiments, the solutions were considered to have a high buffer capacity especially in the second batch, which could have affected the leaching of the trace metals. In environment with neutral and high pH levels, metals tend to form precipitation with carbonates, sulphites, hydroxides and many other compounds, which decreases the dissolved metal concentrations in the water phase.

Colloids

Free metal ions in water solutions occur as positively charged ions or complexed with ligands such as dissolved organic matter (DOM). The metal complexes are relatively stable (depending on the ligand) and remained in the same state, while the free ions tend to couple with negative charged sorption sites. Colloids are negatively charged non-settling nanoparticles and are known as metal carriers. Trace metals binded to colloids are often stable and prevent adsorption to settling particles. The theoretical efficiency order of sorption of the trace metals is Pb > Cu > Ni > Cd > Zn according to the ligand field stabilization energy (LFSE) effect (Kalmykova, 2009). All the trace metals are expected to complex with humic acid. Metals with high stability constants (Cu, Ni and Pb) are likely to remain in complexes while those metals with lower stability constants (Cd and Zn) can change the ligand to another negatively charged sorption sites (Kalmykova, 2009).

The addition of humic colloids and the mix of colloids cause significant leaching of metals in both batches, where Al, Fe, Cu, Ni and Zn are the main leaching metals in the aforementioned parameters. Copper in the oxidation state II, is isomorphous with Fe^{2+} and Mg^{2+} and has strong affinity for organic matter, carbonates, Fe and Mn oxides (Bradl et al., 2005), which explains the same behaviour in leaching with humic and mixed colloids. The same leaching pattern could be observed for Ni and Zn. Nickel ions also prefer to couple with DOM. Zinc ions prefer primarily to complex with iron colloids and usually have a low stability constant but these behaviours are not totally reflected in the results. The leaching of Zn in both batch tests is approximately the same for the humic and mix colloids and even lower for iron colloids. The complexation of metal ions and iron colloids is weaker than metal and humic acid complexation, which explains less leaching with addition of pure iron colloids.

Lead in both batches shows the same leaching patterns in the mentioned parameters but in lower concentrations. Pb has a high affinity for dissolved organic matter, according to Newcombe and Dixon, 2006, where Pb^{2+} was added to water samples in an experiment, which showed that Pb was bound to dissolved organic matter and colloidal matter extensively. The release of Pb from the sediment in the batch tests is probably caused by the addition of humic colloids, where Pb exchanged sorption sites from the sediment to the organic colloids. In such way, the presence of humic substances is increasing the solubility of the toxic metals, Cu, Pb and Zn (Jones and Adams, 1998).

As the pH level was above the normal conditions, it could have increased the anionic forms of humic acid in the batch test solutions and this aqueous complexation between the metal ions and ligands can increase the mobility of heavy metals

(Bradl et al., 2005). The results show that the humic and iron colloids are able to transport the metals through filters and the particles are likely to be smaller than the pore size of the filter used in the experiments, which is 0.45µm.

Strong mixing, high temperature, air injection and undisturbed environment

The metal concentrations from these parameters are quite constant during the batch tests. The parameters did not contribute to any elevated concentrations in the leaching processes. There is one exception in the second batch test, where the high temperature leached a significant amount of nickel, copper and cobalt in the metal analysis, although the same parameter from the first batch test did not show any surprising concentrations. According to Vallero, 2011, increased temperature in the water increases the solubility of toxic substances, which increases the exposure. The temperature change decreases the dissolved oxygen level in the water, which will lead to a reduced environment. That will explain the high leaching of Co, Cu and Ni in the second batch for the high temperature parameter.

The leaching patterns of the metals in the batch tests are very similar, especially the high pH, humic and iron colloids and the mix of colloids. The leaching concentrations of the metals should not be used as guideline values but more as an overview of the leaching potential in different environmental conditions and to assess the current situation.

5.4 Risk characterization

The risk assessments are performed in regard of

1. Source identification
2. Concentrations of selected metals in water
3. Concentrations of selected metals in the sediment
4. Assess the potential risks of the leaching of trace metals from the sediment into the river water

Source identification

The samplings were performed within the industrial area of Giron. The industries are located along the river and regarded as an important contributor in the pollution of the river along with several other sources of pollution such as, the invasion communities, wastewater from municipalities around the river, traffic, influents, landfill leachates constructions and mining. A conceptual map was conducted to get an overview of the pollution sources. The region scrutinized is therefore considered a high risk pollution area.

Concentrations of selected metals in the river water

The selections of metals were Ag, Al, Cd, Co, Cr, Cu, Fe, Ga, Mn, Ni, Pb, Sr and Zn. Some of the metals such as Ag, Cr, Cd, Cu, Ni and Pb are regarded as very toxic to the aquatic organisms and other metals which are less toxic. The levels of metals in the water are compared to the guideline values from SEPA, USEPA and CEPA for

lakes and watercourses. The guideline values from SEPA are lower compared to the guideline values from CEPA and USEPA. The metal concentrations are compared with the guideline values from SEPA and most of the metals are in the range of very low concentration to moderate high concentration according to SEPA, 2000. Very low concentration poses no risks or very slight risks and moderate concentration causes biological impacts on the reproduction of the organisms in the aquatic environment. There was only Cu that was classified as moderate high concentration in four of the five river water samples. The CEPA and USEPA guideline values are all above the metal concentrations from the river.

Measurements of the TOC, DOC and turbidity in the river water were also conducted. TOC and DOC concentrations in the all water samples were 2-6 times higher than the guideline values from SEPA. The turbidity levels in the water were 150-460 times higher than insignificant turbidity values from SEPA. High TOC, DOC and turbidity levels can be interpreted as high organic content in the water. Because organic materials have a high affinity for metals, they can act as carrier in the water and transport metal compounds along the whole river. The high organic content can also affect the oxygen levels in the watercourse and cause oxygen deficiency, which in turn affects the biological organisms.

The metal concentrations and the additional measurements of TOC and DOC in the river are posing potential risks for the survival of the biological organisms in the aquatic ecosystem.

Concentrations of selected metals in the sediment

The following metals were analyzed in the sediment, Cd, Co, Cr, Cu, Fe, Ni, Mn, Pb, Sr and Zn. The metal concentrations were compared with sediment guidelines from SEPA, CSQG (Canadian Sediment Quality Guidelines) and CBSQG (Consensus Based Sediment Quality Guidelines from the U.S.). The CBSQG are presented as TEL (Threshold Effect Levels), all concentrations below this level are regarded as not toxic to benthic organisms. CBSQG is only taking account for the effect and cause of sediment contaminants to benthic organisms and not the bioaccumulations and biomagnifications of contaminants.

All of the metal concentrations from the analysis showed that the metals were in the very low concentration range according to SEPA. There were some exceptions for the concentrations of Cr and Ni, whereas concentrations in sample points 4 and 5 were considered as low concentrations according to SEPA.

The strong stream of the river is believed to transport the contaminants further in the river and not allowing contaminants to settle in the sediment. A gradual increase of the metal concentrations in the sediment can be observed from the first sample point to the fifth. The contaminants are believed to settle further up in the river and in the calmer parts. Therefore the level of contaminants further up in the river, outside the system boundaries might be higher and more toxic to the organisms. But within the system boundaries, the settlements of the contaminants are highly dependent on the strength of the stream. Since several metals are in the range of very low concentration, the current situation should be considered as no risk within the system boundaries. The situation might worsen in the future and outside the system boundaries.

Batch tests – Leachability of metals from sediment

Two batch tests were conducted with two different sediments from Rio de Oro. According to the sediment analysis in Section 5.2.2., the metal concentrations are increasing further up in the river. Therefore, one of the sediment sample used in the batch test is believed to contain higher metal concentrations. Unfortunately, analysis was not conducted to observe the metal concentration in the sediment before the batch test.

In the first batch test, the most significant leaching of metals occurred for change in the pH and addition of humic and a mixture of humic and iron colloids. Iron, Al, Cu, Mn, Ni, Sr and Zn are the primary metals of leaching, where Cu, Ni and Zn are the most toxic. Strontium occurs natural in the Earth crust in small amounts and there are no reports of toxicity towards aquatic organisms. The leaching of Fe and Al are correlated with the leaching of Cu, Ni and Zn, as the leaching patterns are relatively similar. The release of Fe is considered to cause release of other metals as well, since Fe oxides act as co-precipitation surfaces and adsorbents for trace metals.

Six (Cu, Zn, Pb, Cd, Ni and Cr) of the metal concentrations after the batch tests were compared with the guideline values from SEPA. Among the metals, Cu and Ni were the metals that reached to high concentrations, which leads to growing risk of biological effects in the aquatic ecosystem and all of the six metals exceeded the SEPA guideline values which generate slight biological effects.

The leaching pattern in the second batch test is rather similar to the first batch test, except for some deviations in the pH and high temperature parameter. Increased temperature led to high dissolved concentrations of Co, Cu and Ni, which are classified as high and very high concentrations according to the SEPA guideline values. These metal concentrations have a very great impact on the survival of the biological organisms in the ecosystem, even in short-term exposure.

The batch tests simulate an artificial environment in extreme conditions to predict future leaching behaviour of the trace metals. The different environmental conditions are therefore accelerated to display the potential risks generated by leaching the metals from the sediment in the future.

Risk factors

Risk factor refers to a process or a factor in an ecosystem, which can generate potential consequences by the exposure and distribution of a contaminant or contaminants within a time frame in near future. The strong stream of the river is an important factor affecting the distribution of the contaminants, causing re-suspension of particle bound contaminants which in turn increases the retention time of the contaminants in the water body. This causes higher exposure time and bioavailability of the contaminants in the water for biological organisms. Increased bioavailability of metals in the water can have biological effects in the aquatic ecosystem. Different parameters which affect the leachability and bioavailability of metals are addition of humic colloids, pH variations and increased temperature in the river. A slight change in these parameters can disrupt the geochemical cycle of the metals in the river sediment. Rio de Oro leads to Rio Magdalena, which is the main water source of many cities in Colombia. The river is also an important water resource for animals, where bioaccumulation can be an issue and in turn can lead to biomagnification. The

high amount of TOC and DOC in the river could also be an issue in the future, since it causes oxygen deficiency for the aquatic organisms in the river. The nitrogen level in the river exceeds the recommended level, which could affect the drinking water and cause human health issues, since Rio de Oro leads to Rio Magdalena

5.5 Factors affecting the results

Manual point sampling

Due to the variation of the depth, width and flux of the river, it was not possible to use a boat to sample in the centre of the river. Therefore, the sampling of water and sediment were performed by the river banks. According to (Reeve, 2006), sampling away from the main flow is unadvised. The sampling should have been in the main flow where there is complete mixing but unfortunate the circumstances did not allow it. As a result, there is a risk that the results from the water and sediment samples are not representing the whole river but only different points in the river.

Another important factor that affects the results is the strong stream of the river that creates a large variation of the contents of the river, hence making point sampling not suitable for this type of situations. One solution to overcome this obstacle is to use an automatic water sampler, whereas the sampler is programmed to handle the sample operations from the water source of the operator's interests. Most of the automatic samplers measure flow volume of the river and is able to take several samples in an interval of time. Nevertheless, this type of sampling is more fitted for the conditions of this study than point sampling.

Amount of samples

All of the samples taken in Colombia will be prepared and acidified for analysis in Sweden, since the budget was not enough to get the samples analyzed in Colombia. Therefore, a maximum amount of sample was set to a total of 50 samples in which 10 samples are used for the screening of metals in both water and sediment. The system boundaries of the project are covering a large area, which makes it difficult to use five samples to represent the whole area.

6 Conclusions

Most of the sources of pollution in the industrial area are point sources but the emissions are not monitored and often not treated. The chemical analysis shows a downstream trend of increasing metal concentrations, it is therefore believed that the metal concentrations are even higher outside the system boundaries.

According to the results from the water samples in the industrial region of Rio de Oro, the concentrations of Cd, Cr, Cu, Ni, Pb and Zn exceeds the guideline values from SEPA and ranges from low to moderate concentrations, which cause minor biological effects and disorder in the ecosystem. Further pollutions can create greater impacts on the living organisms in the ecosystem. Therefore, the current situation in Rio de Oro is classified as medium risk.

In comparison with the sediment quality standards for lakes and watercourses from SEPA, CEPA and USEPA, Most of the metals showed concentrations in the less toxic range. The low metal concentrations are believed to be caused by the high organic matter in the river water and the strong stream of the river, which carries the metals to settle in less turbulent parts of the river. This is confirmed by the chemical analysis of the sediments that showed increasing metal concentrations further down the stream. Although the results show low concentrations of metals in the sediment in the industrial region of Rio de Oro, it is believed that the metal concentrations are higher further down the river, outside our system boundary.

In the batch tests, the parameters that contributed to the highest leaching of trace metals are addition of humic and a mixture of humic and iron colloids, whereas metals in the sediment are believed to complex with the negatively charged adsorption sites of the humic colloids. The leaching pattern of Pb, Cu, Ni and Zn clearly shows the leaching effects in the presence of humic colloids.

The dissolution of Fe oxides in the batch test releases other metals which are complexed with the Fe compounds. Correlations can be observed in the leaching patterns of Cu, Pb and Zn in the batch tests, where the metals exhibited increased solubility in the presence of iron colloids.

The leaching of metals under the impact of the other parameters was low due to the buffer capacity of the sediment, which leads the metals to precipitate with carbonates, sulphates, hydroxides and many other compounds. This prevents the metals to exist in the water as free ions and in combination with the strong stream of the river, the pollutants are diluted and carried further down the river for settlement.

It would also be of interest to screen for organic contaminants, pathogens and nutrients such as nitrogen and phosphorus in the area. More samples should be conducted to increase the certainty of the results. Manual sampling in this case was concluded to be inappropriate for the conditions of Rio de Oro and it created a lot of uncertainties in the results.

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