Evaluate Long-Term Fate of Metal Contamination after Mine Spill; Assessing Contaminant Changes in Soil

The Guadiamar Case Study; Southern Spain

MSc Thesis
Felix Zingg

Wageningen University
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List of Acronyms

AZ	Aznalcázar
CA	Correlation Analysis
CaCl	Calciumchloride
Cd	Cadmium
CEC	Cation Exchange Capacity
CSIC	The Spanish National Research Council
Cu	Copper
DESIRE	Desertification Mitigation and Remediation of Land
DTPA	Diethylene Triamine Pentaacetic Acid
EDTA	Ethylene Diaminete Traacetic Acid
EEA	European Environment Agency
ERA	Ecological Risk Assessment
ESDAC	European Soil Data Centre
EU-HYDI	European Hydropedological Data Inventory
GGC	Guadiamar Green Corridor
GIS	Geographic Information System
GPS	Global Positioning System
HCL	Hydrochloric Acid
ICP-OES	Inductively Coupled Plasma Optical Emission Spectrometry
IRNAS	The Institute of Natural Resources and Agrobiology of Seville
JRC	Joint Research Centre
KCL	Potassiumchloride
Pb	Lead
RECARE	Preventing and Remediating Degradation of Soils in Europe through Landcare
SLM	Sustainable Land Management
SOC	Soil Organic Carbon
SOM	Soil Organic Matter
STD	Standard Deviation
Zn	Zinc

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Abstract

The mine spill accident (1998), inundating 4500ha of fertile agricultural land along the Guadiamar river with toxic sludge and releasing metals into the environment, is considered as one of the biggest environmental catastrophes in the recent Spanish history. Immediate actions have been taken directly after the mine spill, including mechanical removal of the toxic sludge from the soil surface, application of soil amendments and re-vegetation, giving priority to immobilize the metals. RECARE, a European wide project started in 2013 focusing on different soil threats is stimulating further soil research by involving local stakeholders.

In this study, the Guadiamar Green Corridor (South Spain) is assessed, aiming to obtain new knowledge and soil data on soil metal contamination. Since no harmonized soil database was available for the Guadiamar case study, a compilation of physiochemical soil data of Guadiamar is the first objective of this study and base for the RECARE project.

A subsequent spatial analysis using ArcGIS is carried out dividing the study site into land units based on geomorphology, lithology and the land use before the mine spill facilitates. Based on this the sampling area for the present study were determined.

The current situation (2014) of a selected area within the Guadiamar Green Corridor is assessed by analysing the most important soil properties, pH, soil organic carbon and soil texture, related to total and available Cd, Pb, Cu and Zn. Soil sampling, laboratory and statistical analysis have been applied in this study to assess the current situation, while data from the past 15 years is derived from literature.

Huge data variability of pseudo-total and bioavailable (EDTA extracted) metal concentrations is evident, due to natural variability and irregular distribution and inaccurate cleaning of the toxic sludge along the Guadiamar river. Since the sludge has been removed mechanically, 15 years ago, the variability of soil metal concentrations (pseudo- total and EDTA extracted) did not change. Threshold values for pseudo-total metal concentrations do still exceed the values proposed by the European Directive, and this is not expected to change fast since metals are not biodegradable.

With a neutral soil pH, soil organic carbon contents around 3g 100 g^{-1} and clayey soils the current situation of a selected area is supporting metal absorption and immobilization. Due to these soil conditions and the natural protection of the Green Corridor, which is ensuring permanent vegetation cover, environmental risks are minimized. Nevertheless, the huge amount of currently immobilized metals present in the soils of Guadiamar, form a huge stock and potential risk to the environment. Probably, the highest risk is a potential decrease of soil pH with a subsequent increase of bioavailable metals. Therefore, environmental monitoring or even repeated applications of soil amendments is essential, especially in high risk areas where soil pH is naturally low.

Keywords: mine spill, metal contamination, soil, environmental risks, metal mobility

Introduction

Nearly all food, fibre and fuel are produced on soil, with soil being also essential for water and ecosystem health. Soil is globally the second biggest carbon sink with an important role in climate functioning (Jones et al., 2012). Nevertheless, soil resources in many parts of the world are over-exploited, degraded and irreversible lost due to inappropriate land management (Van-Camp et al., 2004). In the last decades, huge soil areas have been negatively influenced or altered in multiple forms. Soils and consequently underground water have been contaminated by accumulation of harmful products from agricultural, industrial and urban activities (Jones et al., 2012). Around 3 million sites across Europe are recorded where polluting activities take place, with metals and mineral oil as main contaminants (EEA, 2014). Ensuring sustainable land use across Europe and protecting the soil from various soil threats are objectives of the European Commission, and they have to be formulated in a European legislation (Liedekerke et al., 2014).

In the framework of the RECARE project, local partners across Europe are focusing on a wide range of soil threats, including soil contamination, aiming to develop effective prevention, remediation and restoration measures by designing and applying targeted land management strategies (van Lynden et al., 2013). Alterra and Wageningen University are coordinating the FP7 funded RECARE project. Evenor-Tech and the Institute for Natural Resources and Agrobiology of Seville (IRNAS) are local partners for the specific case study site of Guadiamar, and are supporting this research with working facilities and supervision.

Taking this into account, the present research analyses the behaviour of metal contamination in Mediterranean soil along more than 10 years of recovering and monitoring activities. For this purpose the Guadiamar Green Corridor (South Spain) will be considered as case study. In 1998 occurred the mine spill accident, affecting the Agrio, Guadiamar and lower Guadalquivir river basin. It was one of the biggest environmental catastrophes in the recent Spanish history (Cabrera et al., 2008). A huge area of 4500 ha, stretching from the Sierra Morena Mountains down to the costal Doñana National Park, has been inundated with a toxic sludge containing metals such as Cd, Cu, Pb and Zn (Cabrera et al., 1999). Immediate actions were taken to remove the toxic sludge from the soil surface mechanically, and mining activities were stopped instantly. Furthermore, one of the biggest soil remediation operations in Europe was carried out, including the addition of soil amendments and using the technique of phytoremediation, trying to immobilize the contaminants (Madejón et al., 2009). Nevertheless, soil analyses indicate that pseudo-total metal concentrations on affected soils remain high, exceeding threshold values (Gawlik and Bidoglio, 2006). To minimize health risks food production was prohibited, the affected land was purchased by the regional government and converted into a natural area known as the Guadiamar Green Corridor (Hernández et al., 2004).

The Guadiamar Green Corridor is located in Southern Spain. It has a typical Mediterranean climate with mild wet winters and hot dry summers, and a mean annual precipitation of 700 mm (Olías et al., 2006). The Guadiamar drainage basin extends over two geologic features, the Palaeozoic massif and the lower Guadalquivir basin. The Guadiamar river flows over a continuous alluvial deposit with more gravels and sands upstream, grading further downstream into silt and clay (Salvany, 2004).

After the mine spill accident in 1998, the Agrio, Guadiamar and lower Guadalquivir river basins have been severely contaminated with metals and metalloids, which act toxic for humans and environment already in low concentrations, and therefore high attention needs to be given to avoid their dispersion. Metals are not biodegradable hence the affected soils remain contaminated exceeding threshold values, acting as a potential source for environmental contamination. To minimize potential environmental risks, the contaminated soils of the Guadiamar Green Corridor and the effects of soil remediation measures need to be studied thoroughly, supplemented by long term monitoring.

The following objectives have been defined to study the long term behaviour and fate of metals in the soils of the Guadiamar Green Corridor in the context of the RECARE project:

1. Compilation of a harmonized database including physiochemical soil data, based on spatial sampling in the whole case study between 1999 and 2002, as a base for the RECARE project
2. Division of the case study into land units based on geomorphology, lithology and the land use before the mine spill accident and explore land use changes
3. Assessment of the current situation (2014) of metal contamination (Cd, Cu, Pb and Zn) and soil properties (pH, SOC and soil texture) in a selected area of the case study, and compare the current situation with the past 15 years
4. Comparison of two different analytical methods, metal extraction by EDTA and DTPA, for assessing metal bioavailability
5. Assessment of potential environmental risks for a selected area within the case study

To fulfil these objectives, literature research, geo-database compilation, spatial analysis and soil sampling have been used as research methodologies.

The outline of this study is divided into three chapters. In chapter 1, the research background is provided, explaining the biophysical baseline, presenting an approach for soil contamination assessment and giving an introduction to the Guadiamar Green Corridor. In chapter 2, the framework of the Guadiamar Green Corridor is presented, explaining used material and methods and discussing the results. Chapter 3, provides conclusions and further perspectives.

Chapter 1: Research Background

1.1 Biophysical Baseline: Soil Contamination by Metals

The biophysical baseline gives basic explanations and knowledge on the behaviour of metals in the soil, on the state of metal contamination at European level and on soil remediation measures.

1.1.1 Metals in the Soil

The pollution of the environment by metals is a serious problem because most of them have toxic effects on living organisms when exceeding threshold levels and they do not decay with time, unlike many organics (Mmolawa et al., 2011; Lee et al., 2006). According to Desaules (2012) and Facchinelli et al. (2000) metal contamination can have natural or anthropogenic origin. Natural metal contents in the soil have geo-genic origin, are products of weathering and their concentration depends primarily on the chemistry of the parental material. Anthropogenic contamination originating from human activities such as industrial, agricultural or transport may lead to concentrations exceeding those from natural sources. Anthropogenic contamination originates mainly from deposition on the soil surface and therefore mainly located in the topsoil, and can be site-specific, regional or global (Mirsal, 2004).

There are essential metals such as Cu and Zn also known as “trace elements” or “micro elements” which are required in low concentrations for plant nutrition, and non-essential “trace elements” such as Cd and Pb which are phytotoxic and toxic to animals (Prasad, 2001). Different fractions can be measured in the soil and in order to understand how the metals influence the environment, it is important to distinguish between the total quantities in the soil and the amounts that can be transferred into more soluble forms, becoming bio-available. The bioavailable fraction is most crucial for assessing the environmental quality and possible health risk (Madejón et al., 2009). Metals occur in the soil solution (liquid phase) referred to as the bioavailable fraction and absorbed to solid soil particles often called the solid phase (Bolan et al., 2014). Metals interact with soil minerals and organic matter through sorption processes, which is called the ion exchange (Alloway, 1995). Both soil properties and soil solution composition determine the equilibrium between metals in the solid phase and metals in the liquid phase, which is a dynamic equilibrium (Alloway, 1995; Prasad, 2001). When concentrations of metal ions are sufficiently high, many metals can even form insoluble, precipitated forms. An important point to consider is that the toxic effect of a metal is determined more by its fraction than by its total concentration (Alloway, 1995).

Different processes influence the distribution of metals in the soil: 1) precipitation and dissolution, 2) complexion and de-complexion, and 3) adsorption and desorption. Metals are distributed over distinct fractions, distinguishing four ‘pools’: 1) soil solution, 2) exchangeable ions bound to soil particles by electrical charges, 3) as chelates[1] attached by organic ligands[2], and 4) absorbed by minerals and insoluble metallic oxides (Alloway, 1995).

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[1] A **Chelate** is a chemical compound composed of a metal ion and a chelating agent. A chelating agent (ligand) can form several bonds to a single metal ion.

[2] A **Ligand** is an ion or molecule that binds to a central metal atom to form a compound (chelate). The bonding between the metal and ligand generally involves the donation of one or more electrons of the ligand.

For all metals soil properties, management and environmental factors are of significant importance, influencing the retention and mobility of a metal in the soil, and the equilibrium between the solid phase and the liquid phase. The most important soil components absorbing metals are clay minerals and organic matter, while soil pH is influencing strongest metal solubility (Alloway, 1995). In general, elements dissolved in the soil solution are availability for plant uptake. It is important to be able to identify the different forms of metals in the soil, especially in the soil solution, in order to more fully understand the dynamics of the metal in the natural ecosystem (Alloway, 1995).

The soil is a dynamic system where changes in soil properties, management and environmental factors affect the availability of metals in a soil (Alloway, 1995). The key soil properties are pH, Soil Organic Matter (SOM) and clay minerals, which are following briefly explained based on the findings of Alloway (1995).

1) The pH of a soil applies to the H^+ concentration of the soil solution, which is in a dynamic equilibrium with the predominantly negatively charged surfaces of soil particles. Hydrogen ions (H^+) are strongly attracted to the negative charge of organic matter and clay minerals having the power to replace most other cations. In general, metal cations are most mobile in acidic conditions and reduce their bioavailability with increasing pH.

2) All soils contain organic matter, however with considerably differences in amount and type. SOM has a major influence on the chemical properties of a soil. SOM has in general a very high Cation Exchange Capacity (CEC). The CEC is a measure of the soil's ability to hold positively charges ions, resulting in a strong absorption of metal cations.

3) Clay minerals are very important for the absorption of metals having a comparatively large surface area and a permanent negative charge, along with a high CEC. Clay minerals rarely exist in a pure form; they usually have organic colloids and hydrous oxides linked to them. The combined organic-mineral complexes play an important role in controlling ion concentrations in soil solutions.

Studied Metals

Cadmium (Cd)

"Cadmium has no essential biological function and is highly toxic to plants and animals. However, the concentrations of Cd normally encountered in the environment do not cause acute toxicity. The major hazard to human health from Cd is its chronic accumulation in the kidneys. With the estimated half-life for Cd in soils varying between 15 and 1100 years, this is obviously a long term problem and pollution needs to be prevented or minimised wherever possible" (Alloway, 1995).

Normally, Cd occurs in soils as Cd^{2+}. The dynamic equilibrium between Cd on the solid phase and the Cd in the liquid phase depends strongly on the pH (Alloway, 1995). At pH level below 6.5 (Figure 1), Cd^{+2} occurs primarily dissolved, while with increasing pH, cadmium precipitates to other forms which are less soluble (Smith et al., 1995). As well Alloway (1995) discusses that Cd absorption increases with increasing pH, up to a pH of 8 where Cd is entirely absorbed. However, Cd concentrations in the soil solution depend as well on the concentration of ligands in the soil solution and the stability of such metal-ligand (chelate) complexes (Alloway, 1995). Cd tends to be more mobile and therefore more available for plants than many other metals such as Pb and Cu.

Copper (Cu)

"Copper is one of the most important, essential elements for plants and animals. The level and distribution of total and extractable Cu in the soil profile varies with soil type and parent material.

Copper is specifically absorbed in soils, making it one of the trace elements which moves the least" (Alloway, 1995).

Cu is efficiently retained from plant uptake due to the formation of stable complexes with organic compounds (Landner and Reuther, 2005), having high affinity for sorption by organic and inorganic soil colloids[3] (Alloway, 1995). The Cu^{+2} ion is dominant in the liquid phase of acid soils and occurs dissolved if soil pH is lower than 4.5 (Figure 1), while the metallic Cu^0 is chemically rather inert and dissolves very slowly even in acidic conditions (Landner and Reuther, 2005).

Lead (Pb)

"Lead is neither an essential nor a beneficial element for plants or animals. When Pb is released into the environment it has a long residence time compared with most other pollutants. Lead and its compounds tend to accumulate in soils and sediments where, due to their low solubility and relative freedom from microbiological degradation, they will remain far into the future" (Alloway, 1995).

Soil profile studies show that there is little evidence that Pb is lost through leaching processes, in which the organic fraction is largely responsible for the absorption of Pb to the soil. Furthermore, pH and CEC are major soil properties involved in the immobilization of Pb. In soils with high organic matter contents and a pH between 6 and 8 Pb forms insoluble complexes. At a pH below 3.5 (Figure 1) Pb becomes more soluble and may leach out (Alloway, 1995; Smith et al., 1995).

Zinc (Zn)

"Zinc is an essential trace element for humans, animals and higher plants. Higher plants predominately absorb Zn as a divalent cation (Zn^{2+}), which acts either as a metal component of enzymes or as a functional, structural, or regulatory cofactor of a large number of enzymes" (Alloway, 1995).

Zinc tends to have the strongest sorption at a pH above 7, changing its species depending on soil pH (Smith et al., 1995). Below pH 7.7 Zn^{2+} is the predominant species, while $ZnOH^+$ is more prevalent above this pH (Alloway, 1995). At a pH of 5 (Figure 1) Zn is completely dissolved and at a pH around 8 Zn is strongly absorbed by clays and organic matter (Alloway, 1995).

Relation Between Soil pH and Bioavailability of Metals

Organic matter and clay particles form strong complexes with metals, and with increasing organic matter and clay content the solubility of most metals decreases due to increased absorption (Takáč et al., 2009). However, it is well known that metal solubility and therefore their bioavailability is greatly determined by the soil pH (Violante et al., 2010; Marques et al., 2009), and higher proportions of mobile fractions occur in acidic soils (Takáč et al., 2009). The pH influences metals adsorption, retention and movement in the soil (Violante et al., 2010). Cationic metals are more soluble at lower pH levels, while for anionic elements rising the pH has the opposite effect (Violante et al., 2010). However, most metals occur in cationic forms in the soil (USDA, 2000). In Figure 1 the absorption of Pb, Cu, Zn and Cd in relation to the soil pH is presented. For example, Pb and Cu are already mostly absorbed at a pH around 5 while Zn and Cd are still in soluble form at the same pH.

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[3] **Soil colloids** are soil particles, usually consisting of clay and humus, which are suspended in water.

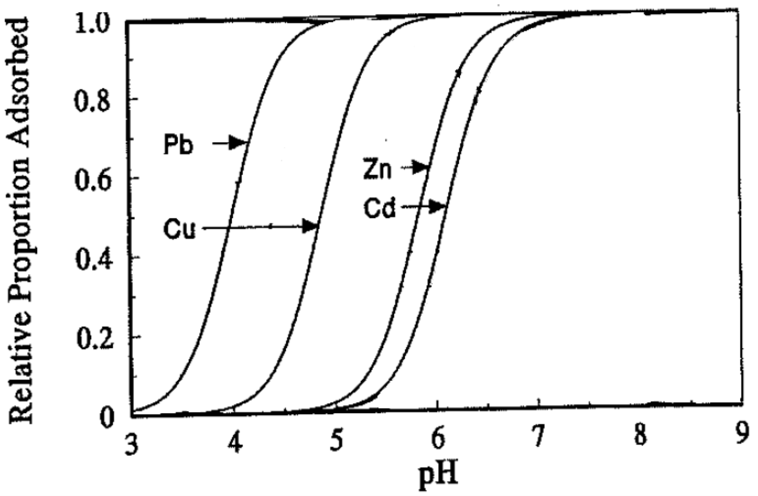

Figure 1: Absorption of Pb, Cu, Zn, Cd onto hydrous ferric oxide (Evans et al,. 1995)

1.1.2 State of Metal Contamination at European Level

Soil contamination can be distinguished in contaminated sites (local contamination) and contaminated land (diffuse contamination). Contamination is the occurrence of pollutants causing a loss of soil functions by altering the natural environment. This phenomenon is a result of industrialization and an intensive use of chemicals (Liedekerke et al., 2014). The relation between soil contamination and waste management is obvious as well (Van-Camp et al., 2004). The state of soil contamination at European level is difficult to quantify since there is a lack of legislations motivating to identify contaminated sites and many European countries lack soil inventories (Jones et al., 2012). Data on diffuse contamination is generally more limited than for local contamination. However, estimates exist showing that sites where potentially polluting activities occur are at about 3 million in Europe (EEA, 2014). Main contaminants affecting European soils are heavy metals with 37% and mineral oils with 33% (EEA, 2014). While some locations, depending on the degree and form of contamination, may only require limited measures to stabilize the situation, others require urgent and intensive remediation. Prevention depends strongly on environmental protection policies having strong links to land use policies (Van-Camp et al., 2004). In 2006 the European Commission prepared a framework Directive to establish common principles to protect soils across Europe (Rodríguez-Lado et al., 2008). Nevertheless, some European countries developed their own soil quality standards for heavy metals and finally only threshold values related to application of sewage sludge in agricultural soils have been defined at European level (Rodríguez-Lado et al., 2008). Attempts have been made by Rodríguez-Lado et al., (2008) to map heavy metals in the topsoil of 26 European countries by using the FOREGS Geochemical database, with limited success. The mapping accuracy showed for Pb considerable satisfactory, for Cu and Zn marginally satisfactory and for Cd unsatisfactory accuracy. However, these contamination maps of Europe are so fare unique and therefore presented in Figure 2.

Some positive trends are reported, for example that with improved data collection the number of recorded sites is expected to grow, and that remediation evidence exists for almost 80’000 contaminated sites in recent years (EEA, 2014). Attempts are made to generate less waste and to better prevent accidents with improved security measures. Furthermore, most European countries have new legislations controlling industrial wastes better (Jones et al., 2012). The emission trends of heavy metals are continuously decreasing since 1990 according to the EEA (2014).

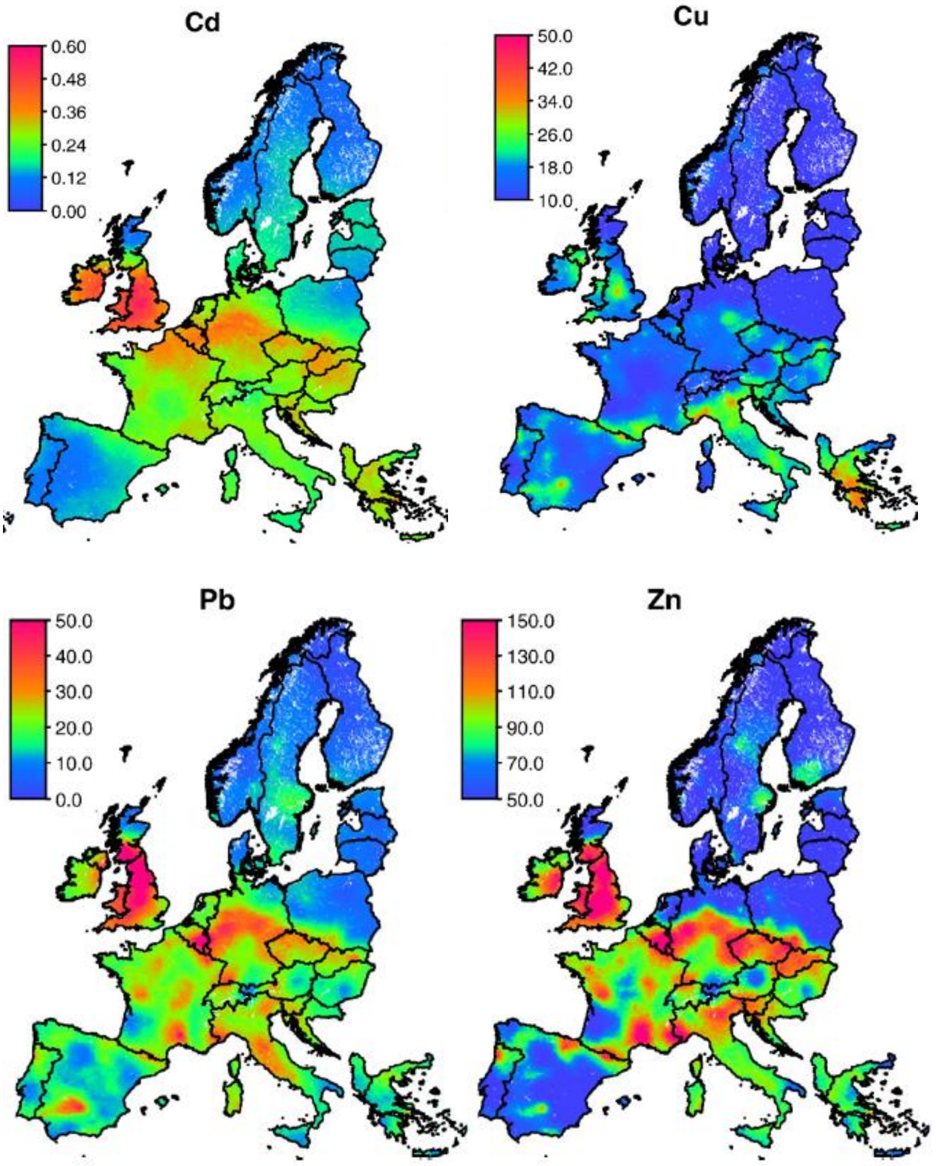

Figure 2: Maps of Cd, Cu, Pb and Zn concentrations [mg kg^{-1}] in European topsoil (Rodríguez- Lado et al., 2008)

1.1.3 Soil Remediation Measures

The ultimate goal of soil remediation is not only to remove the contaminants, but also to restore the capacity of the polluted soil to perform according to its potential, thus to restore soil health. Metals cannot be destroyed biologically but only transformed from one oxidation state or complex to another (Epelde et al., 2006; Marques et al., 2009). The traditional technique of soil excavation and off-site disposal still accounts for one third of the remediation practices in Europe. A number of technologies have been developed to achieve decontamination and soil remediation, which can be categorized into three groups of techniques, physical (e.g. air stripping, dual phase vacuum extraction, thermal treatment), chemical (e.g. soil washing, chemical oxidation), and biological (or bioremediation) (Liedekerke et al., 2014). Bioremediation offers several advantages over physical and chemical treatments used in soil decontamination of certain compounds such as metals. Purification costs of bioremediation are between two and four times cheaper than conventional technologies (Ali et al., 2013). However in any case, before selecting a specific technique it is necessary to know the concentration of the metal, the chemical form, the soil type and the size, location and history of the contaminated site (Prasad, 2001). Due to the enormous costs, intensive labour, alteration of soil properties and disturbance of soil micro-flora, all associated with physical removal (soil excavation) of the contaminated soil, the development of chemical and biological in-situ techniques has been stimulated to economically remediate contaminated soils (Ali et al., 2013; Epelde et al., 2006), and therefore the techniques of phytoremediation and soil amendments are explained further.

Phytoremediation

Phytoremediation is a relatively recent technology and an area of active current research. New efficient metal hyperaccumulators[4] are being explored and molecular tools to better understand the mechanisms of metals in a plant are being tested (Ali et al., 2013). Research is even undertaking genetic engineering of plants to improve their metal uptake, translocation and sequestration (Marques et al., 2009). Ali et al. (2013), perceives phytoremediation as a cost-effective, efficient, eco-friendly and solar driven technique, while Epelde et al. (2006) characterize phytoremediation as a socially accepted and aesthetically pleasing technology to clean up contaminated sites. Phytoremediation is a technique using plants and their associated rhizospheric[5] microorganisms to remove, degrade, or immobilize various contaminants from contaminated soils, sediments and water (Marques et al., 2009). Therefore, phytoremediation can be used for restoration contaminated sites, where the original vegetation disappeared due to toxicity of the soil, by developing a healthy vegetative cover. Vegetation cover reduces contaminant migration by wind and water erosion and leaching and activates microbiological activity and their functionality (Epelde et al., 2006; Soudek et al., 2012). Phytoremediation is considered as a durable land management practice improving soil quality, and it can even be combined with the production of energy crops such as Jatropha (Ali et al., 2013). Phytoremediation is applicable at very large scale and has low installation and maintenance costs (Ali et al., 2013). In this respect, phytoremediation appears highly promising. On the other hand, it also suffers from some limitations. Its efficiency is limited due to slow growth rate of hyperaccumulators, it is mainly applicable to sites with low to moderate levels of metal contamination, there is a risk of food chain contamination and it is limited by climatic and geological conditions (Ali et al., 2013; Marques et al., 2009).

In literature phytoremediation is often divided into different techniques such as phytostabilization, phytoextraction, phytofiltration, phytovolatilization, phytodegradation and phytodesalination, while the different techniques make use of different plant properties (Ali et al., 2013). Phytostabilization is the most useful technique to immobilize metals through plants, while phytoextraction is the main technique to remove metals from polluted soils, by accumulating the pollutants in harvestable biomass (Ali et al., 2013; Krzy et al., 2013; Marques et al., 2009). Factors affecting metal absorption by plants are the bioavailable metal concentration, the metal movement to the root surface, the transport from the root surface into the root, and the translocation from the root to the recipient parts (Alloway, 1995). The absorption by the roots can be passive or active and differs between metals. Passive uptake involves diffusion processes, while active uptake takes place against the concentration gradient and requires metabolic energy. Furthermore, interactions between elements can affect absorption in a synergistic or antagonistic way (Alloway, 1995). Of high importance is the selection of plant species tolerant to the site specific metal concentrations.

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[4] An **hyperaccumulator** is a plant capable of growing in soils with very high concentrations of metals, extracting these metals through their roots, and concentrating extremely high levels of metals in their tissues

[5] The **rhizosphere** is the narrow region of soil that is directly influenced by root secretions and associated soil microorganisms

Soil Amendments

Soil amendments allow manipulating soil factors, such as pH, organic matter, redox potential, CEC, microbiological activity etc. (Epelde et al., 2006). Most common soil amendments are calcareous products, organic and inorganic fertilizers. Liming the soil is very effective in controlling metals mobility and therefore can be considered as an environmental protection practice, and this also applies for organic fertilization (Matos et al., 2001). In general, by applying calcareous amendments such as lime, pH is increased and metals become immobilized. On the other hand some chemical fertilizers, such as urea and ammonium sulphate, have an acidic effect on the soil and by lowering the pH metal concentrations in the soil solution increase (Prasad, 2001). Further, when applying organic fertilizer such as compost and manure or inorganic fertilizer such as NPK microbiological activity is stimulated. This leads to a higher decomposition rate, realising metals bound to the organic matter, and finally resulting in metal mobilization (Bespalova et al., 2002).

An option to prevent the sorption of the metals to the solid phase is the addition of chelating agents, which stimulate the formation of metal-chelate complexes. Certain chelates additionally increase the translocation of metals into the shoots. In contrast, chelates can reduce the occurrence of microorganisms in the rhizosphere (Marques et al., 2009). However, a fundamental premise on contaminated sites is to immobilize contaminants and to lower their dispersion. Therefore, soil amendments, such as lime and organic fertilizers, can be used to increase soil pH and thus immobilization, reducing metal concentrations in the soil solution and thereby reducing their bioavailability (Epelde et al., 2006).

1.2 State of Art: Approach for Soil Contamination Assessment

Soil contamination can be distinguished between natural and anthropogenic origin and perceived as a site-specific, local, regional or global environmental problem. Depending on its magnitude assessment methods differ (Desaules, 2012). Generally, site-specific and local contamination is more severe and easier to identify than at bigger scale. According to Liedekerke et al. (2014) four management steps are defined for the management and control of local soil contamination, namely site identification, preliminary investigations, main site investigations, and implementation of risk reduction measures. The first management step refers to the mapping of sites where contaminating activities have taken place or are still in operation. Preliminary investigations and main site investigations considers the development of inventories and soil contamination assessment. Inventories of contaminating activities and contaminated sites are indispensable for the monitoring of local soil contamination. However, their nature and level of detail can take many forms, with regard to their geographical coverage (Liedekerke et al., 2014).

Due to great spatial variability of natural soil metal contents and the ability to appoint pristine metal contents, the major methodological problem of correctly assessing soil contamination is to define an appropriate geochemical background with reliable reference values for uncontaminated soil conditions (Desaules, 2012; Matschullat et al., 2000; Reimann and Garrett, 2005). Desaules (2012) recommends one approach for contamination assessment, consisting of geochemical and statistical analysis (Table 1). With geochemical methods the contamination in the field is assessed, supplemented by statistical methods to analyse and describe the collected data.

Geochemical Methods

Geochemical methods involve soil measurement to assess contamination levels and abnormal chemical patterns. Applying geochemical methods, geochemical knowledge such as soil science is used to discriminate natural and anthropogenic contamination. The reliability of this method is strongly dependent on the interpretation of the user, magnitude of sampling errors and the knowledge of the study area. Geochemical methods have a stronger reference to the location, compared to the statistical method (Desaules, 2012). For example the sequential extraction method provides information on the origin, mode of occurrence, biological and physiochemical availability, mobilization and transport of metals in the soil, by identifying the geochemical fractions and extractability of the metals (Desaules, 2012).

Statistical Methods

Statistical methods are of descriptive nature and summarize, describe and interpret data that is mostly accumulated in a database. This is particularly useful in communicating results of a research. Different statistical methods are available depending on the information a researcher wants to provide. **Univariate analysis** is carried out by describing a single variable, it is considered as the simplest form of quantitative analysis and it is commonly used in the first stages of research for describing the data. Identifying outlier values to distinguish between pristine and contaminated data, quantitatively separate normal data from anomalous positive outliers by using threshold levels, can be a reason to apply univariate statistics (Reimann et al., 2005). Furthermore, data differences over time and location can be analysed by applying univariate statistics. **Multivariate analysis** involves more than one variable at a time by taking into account the effects of all variables. Multivariate data analysis is rather qualitative and only of indicative nature and therefore according to Facchinelli et al., (2000), Manata et al., (2002) and Lee et al., (2006) it is appropriate for data treatment, allowing the identification of parameters controlling the metal variability in the soil. With a correlation analysis, relationships between variables for example between pH and bioavailable metal concentrations can be explored, while with a cluster analysis for example similarities between different years and locations can be defined. **Geostatistics (GIS)** is focusing on spatial or spatiotemporal datasets, and can be used to construct contamination distribution maps, comparing to other landscape information such as land use or lithology, by applying GIS software. Its application is specifically used for interpreting spatial variability at regional scale and for evidencing non-point-source contamination (Facchinelli et al., 2000; Lee et al., 2006).

Table 1 developed by Desaules (2012) gives an overview of existing assessment methods. "There is no correct soil contamination assessment method but only more or less appropriate site-specific approximations" (Desaules, 2012).

Table 1: Approaches for soil contamination assessment comprise statistical and geochemical methods (Desaules, 2012)

Assessment methods
Geochemical methods
a) Geochemical relationships (GR); b) Sequential extractions (SE); c) Enrichment factors (EF); d) Soil profile balance (SPB); e) Geochemical mapping (GM); f) Regulatory reference values (RRV)
Statistical methods
1) Univariate analysis
a) Standard deviation (STD); b) Median absolute deviation (MAD); c) Off-site Percentiles; d) Whisker and boxplots; e) Probability plots
2) Multivariate analysis
a) Factor analysis (FA); b) Cluster analysis (CA); c) Principle component analysis (PCA); d) Correlation analysis (CA); e) Regression analysis (RA); f) Analysis of variance (ANOVA)
3) Geo-statistics (GIS)

In a majority of studies for assessing the degree of metal contamination in soils, different methods are combined. Geochemical methods are used to collect soil data from the field, while statistical methods are used to describe, interpret and communicate the soil data. For assessing soil contamination in the soils of the Guadiamar Green Corridor we apply a combination of different methods. Soil sampling was used to obtain new data for assessing the present situation, standard deviation analysis (univariate analysis) to analyse the range of data, correlation analysis (multivariate analysis) to define the dependency between soil parameters and metal contamination, regression analysis to estimate the relationships among variables, and geo-statistics for spatial analysis.

1.3 The Guadiamar Green Corridor (South Spain)

The Guadiamar Green Corridor is introduced by giving information on the institutional context and by describing the case study.

1.3.1 RECARE Project

Between 2007 and 2012 the EU-funded DESIRE project was exploring the potentials of Sustainable Land Management (SLM) strategies to prevent and combat degradation and desertification in dry land areas around the world. DESIRE designed a global methodological framework to identify, prioritize, test, evaluate and disseminate SLM strategies in close collaboration with local stakeholders (Schwilch et al., 2012). The DESIRE methodology can also be applied to other soil threats than desertification and consequently will be used in the RECARE project, which is starting largely in 2014. A wide range of European soil threats have been identified by the European Soil Thematic Strategy, including soil erosion, salinization, compaction, desertification, floods and land-slides, loss of organic matter, contamination, sealing and loss of biodiversity (van Lynden et al., 2013). Soils have to be adequately monitored, protected and conserved to ensure important soils functions. The RECARE project is focusing on the above mentioned European soil threats, aiming to develop effective prevention, remediation and restoration measures by designing and applying targeted land management strategies in close collaboration with local stakeholders in 17 case study sites across Europe (van Lynden et al., 2013). In doing so, a wide range of bio-physical and socio-economic environments are covered. Furthermore, it aims at giving policy recommendations and improving the understanding of soil functioning in relation to land management, to achieve an impact with regard to preserving the environment. To overcome the complexity of soil systems and to understand the interactions between human activities and the multiple functions of a soil system, it requires a trans-disciplinary, integrated research approach as proposed by RECARE (van Lynden et al., 2013).

Alterra and Wageningen University are coordinating the RECARE project. This master study is written for the Soil Physics and Land Management chair group of Wageningen University, as part of the International Land and Water Management master program. For the Guadiamar case study, South Spain, local participants of the RECARE project are Evenor-Tech and the Institute for Natural Resources and Agrobiology of Seville (IRNAS). IRNAS is a research centre of the Spanish National Research Council (CSIC), while Evenor-Tech is a technology based company that is a spin-off from CSIC, and together they support this research with working facilities and supervision.

1.3.2 Case Study Description

The Study area, “Guadiamar Green Corridor”, is located in Southern Spain (Figure 3). In 2003 the “Guadiamar Green Corridor” was declared as protected landscape, occupying about 4500 ha including all land inundated by the toxic sludge released during the mind spill accident, covering the left and right banks of the Guadiamar river. It stretches from the Sierra Morena Mountains in the North to the costal Doñana National Park in the South (Figure 3). Alluvial soils are dominating the river basin and are vegetated nowadays with native species. Before the mine spill accident the land was used for agricultural production with cropland and pasture as main land use types. Nowadays, riparian forests and open grassland are under natural protection. According to Olías et al. (2006) the prevailing climate is typical Mediterranean, with mild wet winters and hot dry summers. Mean annual precipitation is 700mm, whereof 85% of the rainfall occurs between October and April. As a result, mean annual flow of the Guadiamar river shows high variability, with low discharge values of 0.2 $m^3 S^{-1}$ in summer and high values of 20 $m^3 S^{-1}$ in winter. Mean annual temperature is close to 17 ^oC, with maximum temperatures in July (35 ^oC) and minimum temperatures in January (5 ^oC) (Olías et al. 2006).

The Guadiamar drainage basin extends over two geologic features; the Palaeozoic massif (Sierra Morena) and the lower Guadalquivir basin. The Palaeozoic rocks consist of plutonic rocks (granites, diorites and gabbros), metamorphic rocks (slates, schists and hornfels), volcanic rocks (dacites and basalts) and volcano-sedimentary rocks (Salvany, 2004). The lower Guadalquivir basin consists of Miocene, Pliocene and Quaternary deposits. The Mio- and Pliocene deposits form a thick layer of marine deposits, which cover some parts of the Palaeozoic massif. These marine deposits consist of carbonate-silicate layers, marl layers, basalt silts and sands. The Quaternary deposits consists of marsh formations and alluvial deposits, covering the Mio- and Pliocene formations unconformable (Salvany, 2004). The Guadiamar river flows over a continuous alluvial deposit consisting of four main terraces, with varying thickness of 6 to 25 m. Each terrace is fining upward from coarse gravels to sand into silt and clay (Salvany, 2004).

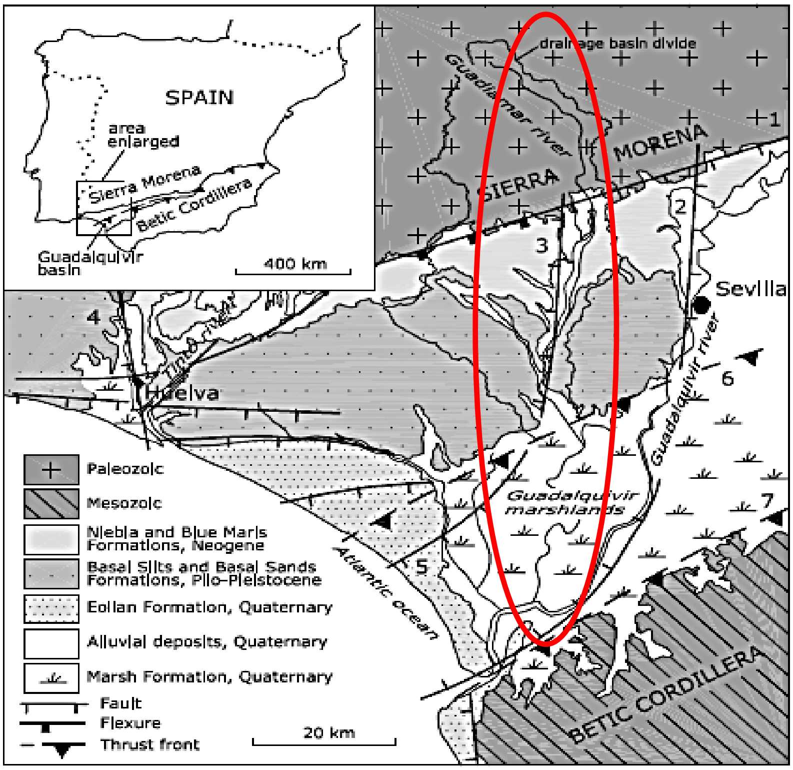

Figure 3: Geological map of the lower Guadalquivir basin, showing the location of the Guadiamar Green Corridor → red ellipse (Salvany, 2004)

The Mine Spill Accident

In the early morning of the 25th April 1998 a tailing-dam dike of an open-pit pyrite *(FeS_2)* mine breached and released acid water and toxic sludge into the nearby Agrio river which discharges into the Guadiamar river (Cabrera et al., 1999). These mines were poly-metallic deposits, consisting mainly of pyrite, also called fool's gold (Cabrera et al., 2008). Approximately 4.5 million m^3 of toxic sludge composed of acidic water and full of metals and other toxic elements flooded the riverbanks of the Agrio and Guadiamar rivers and threatened the Doñana National Park (Cabrera et al., 1999). A strip of 40 km length and approximately 300m width was covered by a layer (2-30 cm) of black sludge, contaminating about 4500ha of alluvial soils used for agriculture (Cabrera et al., 2008).

The first action taken was to remove all accumulated sludge as complete as possible from the soil surface mechanically, which started directly after the catastrophe and was completed in 1999. After removing the sludge, organic material and calcium-rich amendments have been applied giving priority to the immobilization of the contaminants, to reduce plant uptake and leaching and any further negative effects on human and ecosystem (Madejón et al., 2009; Aguilar et al., 2007). The third phase was the purchase of the affected land in 1999 and the implementation of the "Guadiamar Green Corridor" as a mean of restoring the Guadiamar basin and its ecosystem, with the aim to create an ecological buffer zone having a continuous vegetation belt between the Doñana National Park and the Sierra Morena Mountains. Re-vegetation started in 1999 by planting native tree and shrub species and restricting food production to minimize health risk, being one of the largest soil remediation operations in Europe (Hernández et al., 2004; Madejón et al., 2009).

However, in the superficial layer (0-20 cm) of the sludge affected soil severe metal contamination was measured after removal of the sludge (Cabrera et al., 2008). The mean metal concentrations are higher in the superficial layer of sludge covered soils than in unaffected soils (Cabrera et al., 1999). In general, soil profiles with higher clay content were contaminated less deep since metals are strongly absorbed by clay, indicating a lower metal mobility in clayey soils compared to sandy soils. In soils with more than 25% of clay, metal concentrations decreased after 20 cm depth, while in coarser soils the metals penetrated below this depth, down to a depth of 50 to 80 cm (Cabrera et al., 1999). The less mobile elements such as Cu and Pb indicate higher values in the first kilometres from the tilling dam, while the contamination caused by more mobile elements such as Cd and Zn is more similar along the whole river basin (Cabrera et al., 2008).

Threshold Values

According to Aguilar et al. (2004), the metal bioavailability in the soils of Guadiamar decreased markedly between 1998 and 1999 after mechanical sludge removal and applying soil amendments, indicating a quick change to precipitated forms. No big changes were observed anymore in the years between 1999 and 2001. However, in the study of Aguilar et al. (2004), the bioavailable fraction (extracted with EDTA) of Cu, Zn, Cd and Pb still exceeded the threshold values in 2001.

Threshold values have been defined in the Council Directive 86/278/EEC from 1986, which applies to all countries from the European Union. These values are defining the threshold for pseudo-total metal concentrations in mg kg^{-1} for soils with a pH of 6 to 7 (see Table 2). The method for soil analysis is defined in the Council Directive 86/278/EEC as following: "Analysis for heavy metals must be carried out following strong acid digestion. The reference method of analysis must be that of atomic absorption spectrometry and the limit of detection for each metal should be no greater than 10 % of the appropriate limit value". From a study by Gawlik and Bidoglio (2006) conductd for the Joint

Research Centre (JRC) and the European Comission, threshold values for pseudo-total metal concentrations have been defined using aqua regia extraction in soils with different pH. In Table 2 the proposed threshold values for pseudo-total Cd, Pb, Zn and Cu concentrations from the Council Directive 86/278/EEC (1986) and from Gawlik and Bidoglio (2006) for soils with a pH between 6 and 7 are presented.

Table 2: Threshold values in mg kg^{-1} for pseudo-total Cd, Pb, Zn and Cu concentrations for soils with a pH of 6 to 7 (Council Directive 86/278/EEC, 1986; Gawlik and Bidoglio, 2006)

Metals	**Threshold values**	
	Directive 86/278/EEC, 1986	Gawlik and Bidoglio, 2006
Cd	1 to 3	1
Pb	50 to 300	70
Zn	150 to 300	150
Cu	50 to 140	50

The proposed threshold values increase with higher soil pH, because the solubility of metals tend to decrease with increasing pH (Gawlik and Bidoglio, 2006). Therefore, we use the values for soils with a pH between 6 and 7, since the soils of the selected sampling area are close to 7. The values presented by Gawlik and Bidoglio (2006) are at the lower range of the values listed in the Council Directive 86/278/EEC from 1986. This is particularly driven by the fact that over the past decades the control of release of metals has been improved (Gawlik and Bidoglio, 2006). In the upcoming discussion the values presented by Gawlik and Bidoglio (2006) will be used.

Research Conducted in Guadiamar

Since the mine spill catastrophe the Guadiamar Green Corridor is a strongly investigated area, having national and international attention. Different research institutes and Universities from Spain and research groups from foreign countries have been working in the Green Corridor for few years, while especially IRNAS has been present for all the time over last 15 years. Topics about almost everything have been analysed, from fish, mammals, birds, microorganisms, invertbrates, plants, water, sediments, soil, atmospheric pollution, health risks for humans, socioeconomic impact etc. When putting “Guadiamar” into literature search engines, high amounts of published papers appear over a variety of topics. In Scopus 600 papers are available referring to Guadiamar.

Chapter 2: The Framework of the Guadiamar Green Corridor

Since so far no harmonized soil database for the Guadiamar case study exists, Evenor-Tech, as partner of the RECARE project, is assigned to create a soil database by collecting and incorporating available bio-physical and socio-economic data. This master research is initiating the starting face of the collaboration between Evenor-Tech, IRNAS and the RECARE project, and as the first step existing physiochemical soil data from 1999 to 2002 has been organized to create a harmonized Guadiamar database, spatially limited to the Guadiamar Green Corridor. Additionally, a spatial analysis has been carried out, dividing the Guadiamar Green Corridor into land units. Based on the land units soil sampling areas have been selected to define the current situation of a selected area around the village of Aznalcázar. The most important soil properties (pH, SOC, soil texture) together with the pseudo-total and bioavailable metal concentrations of Cd, Pb, Cu and Zn have been analysed. For evaluating long term changes and fate of metal contamination (temporal evolution) the current situation of a selected sampling area is compared with data from the past 15 years, which is derived from previous research conducted by the IRNAS research group. Finally, potential environmental risks are defined and discussed considering the current situation of a selected area taking the prevailing soil remediation measures and threshold values into consideration.

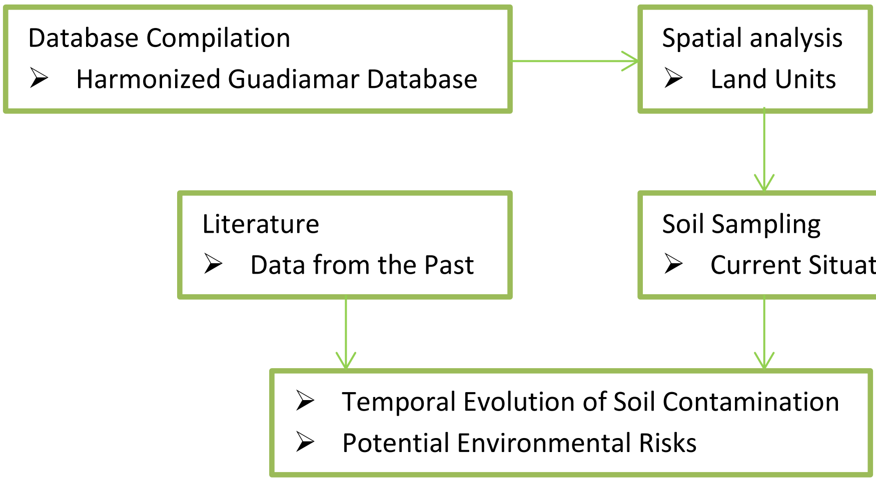

Figure 4: Schematic display of the Guadiamar framework applied in this study

2.1 Material and Methods

2.1.1 Database Compilation

Collecting Existing Biophysical Data

Initially, available physiochemical soil and land use data for Andalucía and the Guadiamar region has been collected. The following data has been provided by the “Red de Información Ambiental de Andalucía. Consejería de Medio Ambiente y Ordenación del Territorio. Junta de Andalucía”:

1) Peodological soil maps of Andalucía (2005); Scale 1:400’000
2) Analysis of affected soils by the toxic sludge (2002); Scale 1:50’000
3) Biochemical and ecological soil analysis (2002); Scale 1:10’000
4) Analysis of contaminated soils (2001); Scale 1:10’000

5) Cartography of remaining pyritic sludge (1999); Scale 1:10’000.
6) Applied soil amendments to conatminated soils (2002); Scale 1:10’000
7) Evaluation of contamination in the river basin of Guadiamar as reference for possible declaration as contaminated soil (2002); Scale 1:10’000

This data includes geographic and descriptive information originating from different investigations conducted after the mechanical sludge removal, between 1999 and 2002. They are saved and accessible in shape and excel files in http://www.juntadeandalucia.es/medioambiente/site/rediam. The geographic and descriptive information can be viewed in ArcGIS, while for each dataset an excel file is available. Additionally, a Land Use and Land Cover Map of Andalusia (Moreira, 2007) was available.

Limiting Data to Case Study Site

To reduce data size and focus exclusively on the contaminated area the “Guadiamar Green Corridor” (see Figure 5) has been selected as case study boundary and clip feature. All data has been clipped prior to analysis, using Arc GIS.

Assembling Data from 1999 to 2002 into a Single Database

For the necessity of having a harmonized database, enabling to conduct a biophysical analysis of the case study, a new Guadiamar database has been developed. The data has been re-codified according to the JRC methodology (JRC, 2013), contributing to the European Hydropedological Data Inventory (EU-HYDI). In the context of the European Soil Data Centre (ESDAC), the European Environmental Agency (EEA) and the Joint Research Centre (JRC) agreed jointly to harmonize soil related data in Europe (Liedekerke et al., 2014). Apart from general information regarding the soil profiles, the Guadiamar database contains attributes describing physiochemical soil data and metal contamination values for topsoil. The new Guadiamar database consists of an excel sheet containing data for all soil attributes, an excel sheet explaining the methodology and a correspondence sheet between original datasets and the Guadiamar database (see Appendix 2). The data is statistically analysed and discussed consulting literature.

The Guadiamar database integrates data of 872 soil profiles distributed over the whole Green Corridor including metal contamination values of Cd, Pb, Cu and Zn for topsoil (0-15 cm). For each soil profile one soil sample has been taken, resulting in 872 different sampling points across the Corridor giving content of metal contamination.

In addition, 18 sampling areas located across the Green Corridor have been integrated containing physiochemical soil data and metal contamination values for topsoil (0-15 cm). For each of the 18 sampling areas, between 9 and 21 soil samples have been taken, analysing the different attributes irregularly.

2.1.2 Land Units and Land Use Change of the Guadiamar Green Corridor

To develop a spatial understanding of the Green Corridor, a spatial analysis consulting geographic data from the Land Use and Land Cover Map of Andalusia (Moreira, 2007) in combination with the Guadiamar database has been carried, out using ArcGIS.

Land Units

The bio-available and the total amount of metals in a soil largely depend on soil properties, such as pH, soil organic matter and clay mineralogy (Alloway, 1995; Hesterberg, 1998). Therefore, we decided to create land units and as a next step to extrapolate the soil properties derived from the 18 sampling areas to the entire land units. In doing so, in the follow up of the RECARE project to bring the contamination values from the 872 soil profiles in relation to soil properties from the 18 sampling areas.

According to Zonneveld (1989) a land unit is an expression of the landscape by simultaneously using characteristics of the most obvious mappable land attributes such as landform, soil and vegetation. In this specific case we use geomorphology as an indicator representative of landform, lithology as an indicator representative of the soil and land use as an indicator representative of the vegetation. Land units have been created, dividing the landscape in similar zones. The land units are based on lithology, geomorphology and the land use before the mine spill accident, which have been generalized as presented in Appendix 1. The new classification of lithology is based on the consolidation of the material (Anaya-Romero, 2003), distinguishing between consolidated and not consolidated. This choice has been taken since the original classes did not allow classifying according to other criteria such as pH or origin, because several lithologies have undefined categories. Geomorphology is classified in fluvial area, wetland, hill and sand area. The land use classification is derived from the Land Use and Land Cover Map of Andalusia (Moreira, 2007) for the period before the mine spill at a scale 1:25,000 and a minimum map unit 0.5 ha. These maps are a result of the Coordination of Information on the Environment (CORINE) project, promoted by the European Commission in 1985, which provides consistent information on land cover and land cover changes across Europe (Neumann et al., 2007). Negligible classes, due to their size, relevance or lack of soil profiles, have been classified as not applicable.

Land Use Change

Additionally to the land use map before the mine spill accident which was used to create land units, a land use map of 2007 has been created for exploring land use changes within the Guadiamar Green Corridor, using the Land Use and Land Cover Map of Andalusia (Moreira, 2007).

2.1.3 Current Situation of Metal Contamination in Comparison with the Past 15 Years

For describing the current situation of a selected area, the region around the village of Aznalcázar has been selected due to organizational criterias. The current state of the whole region, including all 6 soil sampling areas, is defined by analysing the topsoil (0-15 cm).

Selecting Soil Sampling Areas

To be able to identify the current situation of a selected area and to conduct a comparison with the past 15 years, in other words to define the temporal evolution of soil contamination, soil sampling in similar locations like in the past is essential. Derived from the Guadiamar database, 18 sampling areas located across the whole Green Corridor having physiochemical soil data to compare with and which have been sampled in the past between 1999 and 2002, are therefore possible sampling areas of interest. From these 18 sampling areas 6 areas have been selected as benchmark areas situated in the Southern part of the Green Corridor. In Table 3 the coordinates of the 6 areas sampled in 2014 for this current study are presented, which correspond to the 6 sampling areas from the Guadiamar database. Additionally, in Figure 5 the localization of the 6 areas sampled in 2014 are presented.

Table 3: Coordinates of selected soil sampling areas; areas correspond to Figure 5

Sampling Area	Longitude	Latitude
Area 1	W 06 ° 15’’	N 37 ° 19
Area 2	W 06 ° 15.5’	N 37 ° 18.5’
Area 3	W 06 ° 15.7’	N 37 ° 17.4’
Area 4	W 06 ° 15.6’	N 37 ° 17.4’
Area 5	W 06 ° 15.6’	N 37 ° 16.7’
Area 6	W 06 ° 15.7’	N 37 ° 16’

Considering the created land units around the village of Aznalcázar, we have two main land units to differentiate. Three sampling areas are situated on fluvial pasture (1-3) and three on fluvial cropping (4-6) (Figure 5). We collected 18 soil samples from the topsoil (0-15 cm), for each sampling area three replications.

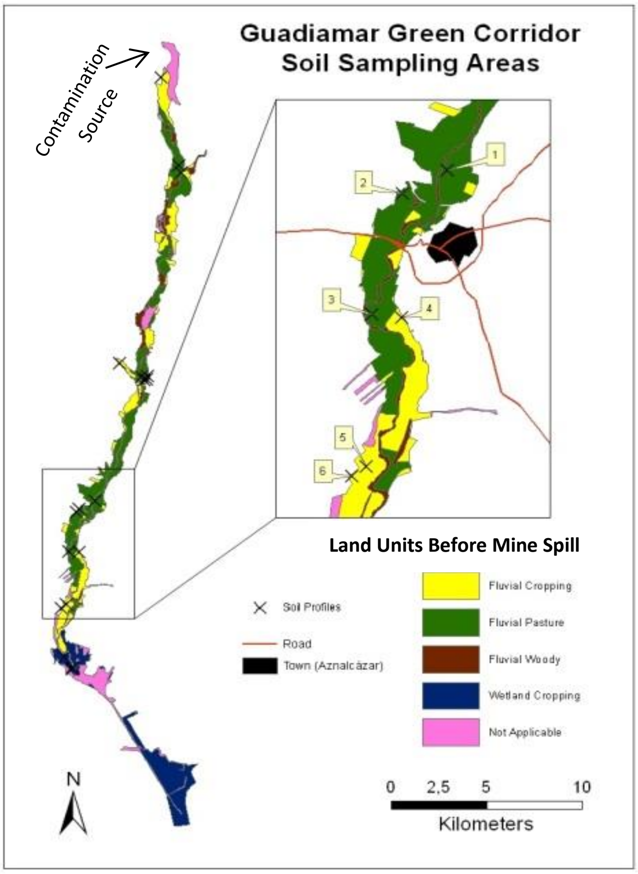

Figure 5: Location of the 18 sampling areas (named as soil profiles) distributed across the whole Green Corridor whereof 6 sampling areas around the village of Aznalcázar are selected for soil sampling (image enlargement) situated in the South of the Green Corridor; the land units are based on the land use before the mine spill accident, lithology and geomorphology

Soil Sampling

The soil sampling has been done on the 23th of January 2014 on a sunny day on moist soil. For each soil sampling area three soil samples have been taken within a distance of less than 50 meter. The soil samples, having a depth of 15 cm, have been taken with an auger and kept in plastic bags for transportation (Figure 6).

Figure 6: Soil sampling using an auger, collecting the top soil (0 -15 cm)

Soil Laboratory Analysis

Preparation of Soil Samples

Firstly, the soil has been dried in an oven at $40\ C^{o}$ for 48 hours, enabling to work the soil for further analysis. Secondly, with a mortar the soil has been broken up and sieved using a 2mm sieve (Chapman and Pratt, 1978). 50g of soil has been kept for texture analysis, 10g for pH, 1g for organic matter, 2.5g for EDTA extraction and 0.5g for pseudo-total metal analysis.

pH Analysis

As described by Thomas (1996), in small centrifugation tubes 10g of dry soil was mixed with 25ml of a 1M KCL solution. For 30min the tubes were put in a shaker to agitate and after that for another 30min left to decant. Finally, the pH was measured using a pH-meter from CRISON, type micro CM 2201.

Soil Organic Carbon (SOC) Analysis

To determine the oxidizable soil organic carbon content in $g\ 100g^{-1}$, the method of Walkley and Black (1934) was used. This method basically consists in the oxidation of the SOC with potassium dichromate ($K_2Cr_2O_7$) in presence of acidic sulfur (H_2SO_4). The excess of dichromate is then valorized with Mohr's Salt (0.5M sulfate-iron-ammonium solution). The SOC content is expressed in volume (ml) of Mohr's Salt. Finally, to get the amount of SOC in the soil the following formula needs to be applied:

$$(1) \qquad \text{SOC} \ (g\ 100g^{-1}) = \ (\text{ml of control} - \text{ml of Mohr's Salt}) * 3.9 / 20\text{ml (control set value)} * 1.724$$

Soil Texture Analysis

The hydrometer method by Day (1965) was used to determine particle fraction. 100ml of a 0.5 M sodium solution and 300ml of distilled water was added to 40g of soil and agitated for at least 8 hours. To determine the coarse sand fraction, the agitated solution was filtered with a 0.2mm sieve and dried over night by $105\ ^{o}C$. The lime and clay fraction was determined using a hydrometer at different time intervals (30s, 60s, 90min and 20h). Finally, the fine sand was washed and dried over night for weighing. To achieve complete dispersion it is necessary to eliminate the materials that cement particles in the aggregate, such as organic matter and carbonates. This is only done when there are high amounts of organic matter and carbonates, which was not the case in this research.

Metal Analysis

To determine the **pseudo-total** metal content in the soil the method of metal extraction with agua regia (HCL + HNO_3) was used (Ure et al., 1993). Agua regia is a mixture of nitric acid (HNO_3) and hydrochloric acid (HCL) in the ratio of 1:3. 0.5g of dried soil was weighted in centrifugation tubes and 3ml of HCL and 1ml of (HNO_3) was added. The samples were agitated for 3h before being centrifuged (10,000 rpm) for 10 min and filtered on Whatman n°1 filters (pores diameter < 11µm). The filtrate was collected and kept in PVC bottles until its immediate analysis. The trace elements determination was carried out by ICP-OES.

The **bio-available** metal contents were determined by extraction with a 0.05 M EDTA solution (Quevauviller et al., 1996). 25ml of the EDTA solution was added to 2.5 g of dried soil, agitated for 1h before being centrifuged (5000 rpm) for 5 min and filtered on Whatman n°1 filters (pores diameter < 11µm). The filtrate was collected and kept in PVC bottles until its determination by ICP-OES.

Statistical Analysis

For analysing the data from the **Guadiamar database**, univariate analysis was performed, more precise the Mean Value and the Standard Deviation (STD) was determined to define the data range, using SPSS 20.0 software for Windows.

For developing **land units and land use maps** of the study area a geo-statistical (GIS) analysis was performed using ArcGIS 10 software.

For describing the **current situation** of a selected area, multivariate analysis was performed, more precise a Correlation Analysis (CA) between bio-available metal concentration and soil parameters considering a significance level of $p<0.05$ has been conducted to analyse the data collected from soil sampling, using SPSS 20.0 software for Windows.

Continuation of this Study

Firstly, it has to be clarified and repeated that the soil samples taken for this master study do not correspond to the exactly same location as the data presented in the Guadiamar database, because of a lower GPS precision in the year 2000. Therefore, differences in soil properties and metal contamination due to spatial inconsistency are expected.

Secondly, different laboratory methods have been used in the Guadiamar database compared to the current study for analysing the soil (see Table 4) and the methodologies are not harmonized. According to Quevauviller et al. (1998) DTPA extracts less than EDTA, what is also reflected when comparing the data from the Guadiamar database (DTPA) with data from literature (EDTA). Furthermore, Kasozi et al. (2009) argues that there is no universal conversion factor between the Walkley and Black (1934) method and thermo-gravimetric methods, such as the ignition method, and that the ignition method is not very reliable. The ignition at 550 ^{o}C for 24h method by Schulte and Hopkins (1996) is expected to give higher SOC values because it also burns inorganic carbon, while the oxidation method by Walkley and Black (1934) only measures organic carbon. The only soil attribute which has been analysed with a similar method is the soil pH, using the pH-meter.

The reader might ask himself the question why for this current study not the same methods like in the Guadiamar database have been applied. Since the soil analysis has been conducted in the laboratory facilities of the IRNAS research group, and these methods have been applied over the last

15 years to study the Green Corridor it is necessary to continue with similar methods. Therefore, for comparing the current situation with the past, we will not further work with the Guadiamar database.

Table 4: Laboratory methods used in Guadiamar database and the current study to determine soil parameters and metal contamination

	Guadiamar Database	Current Study
PH-KCL	PH-meter (Thomas, 1996)	PH-meter (Thomas, 1996)
SOC	Ignition at 550 °C for 24h (Schulte and Hopkins, 1996)	Oxidation of SOC with potassium dichromate (Walkley and Black, 1934)
Soil Texture	Pipette method (Gee and Bauder, 1986)	Hydrometer method (Day, 1965)
Bioavailable Metals	Extraction with DTPA (Lindsay and Norvell, 1978)	Extraction with EDTA (Quevauviller et al., 1996)
Pseudo-total Metals	No Data	Extraction with agua regia (HCL + HNO_3) (Ure et al., 1993)

2.1.4 Comparison of Extraction with DTPA and EDTA for Assessing Bioavailable Metals

Since differing laboratory methods is one of the main tasks in the standardization of the Guadiamar database, but as well within the RECARE project, a subsequent analysis and attempt to come up with a conversion factor between DTPA and EDTA will be carried out. Data on bioavailable metal concentrations included in the Guadiamar database have been determined with extraction by DTPA while the current European method and the one used in this study to define the current situation of a selected area is extraction by EDTA. Furthermore, all other studies conducted within the Guadiamar Green Corridor present values determined by EDTA. If data wants to be compared we need harmonized methods or reliable conversion factors to standardize data. Enabling to compare bioavailable metal contamination extracted by DTPA and EDTA we need a conversion factor between both methods. Therefore, literature has been searched for that is comparing and discussing the differences between these two methods.

2.1.5 Potential Environmental Risks

To assess potential environmental risks for a selected area within the Guadiamar Green Corridor, all knowledge acquired during this research is consulted in combination with existing literature. Analysing the current situation by considering data on soil properties and metal contamination and linking this knowledge to the prevailing remediation measures, is the approach used to define potential environmental risks.

2.2 Results and Discussion

2.2.1 Database Compilation

In Table 5 the Guadiamar database structure is presented, including data from the years 1999 to 2002. Apart from general information about the soil profile, the database contains attributes describing physiochemical soil data and metal contamination (see also Appendix 2).

Table 5: List of attributes included in the Guadiamar database

Guadiamar database structure		
Description	**Unit**	**Label**
PROFILE_ID	-	Profile identification
SAMPLE_ID	-	Sample identification code
LOC_COOR_X	-	Local coordinates X or longitude
LOC_COOR_Y	-	Local coordinates Y or latitude
YEAR	-	Year of sampling
MONTH	-	Month of sampling [1,12]
SAMPLE_DEP_TOP	cm	Sample depth top
SAMPLE_DEP_BOT	cm	Sample depth bottom
HUMIDITY	%	Humidity
SOC	g 100g^{-1}	Soil organic carbon content
BD	g/cm^{3}	Bulk density
HUMIDITY_ATM	%	Humidity at 1/3 atmospheric pressure
PH_H2O	-	pH in soil-water suspension
PH_KCL	-	pH in soil-KCL suspension
AMMONIUM	mg N-NH4/g	Amount of ammonium
NITRATE	mg N-NO2/g	Amount of nitrate
P_INORG_AVAILABLE	mg P/g DM	Available inorganic phosphate
P_ORG_AVAILABLE	mg P/g DM	Available organic phosphate
SAND	%	Sand content
CLAY	%	Clay content
SILT	%	Silt content
COARSE	>2 mm	Coarse fragments
CADMIUM	mg/kg^{-1}	Cadmium content DTPA extracted
LEAD	mg/kg^{-1}	Lead content DTPA extracted
COPPER	mg/kg^{-1}	Copper content DTPA extracted
ZINC	mg/kg^{-1}	Zinc content DTPA extracted
TREATMENT	-	Application of amendment [0,3]
CLAY_AMENDMENT	t/ha	Amount of clayey red soil applied between 1999 and 2001
ORGANIC_AMENDMENT_1	t/ha	Amount of compost applied in 1999
ORGANIC_AMENDMENT_2	t/ha	Amount of dung applied in 1999
LIME_AMENDMENT_1	t/ha	Amount of sugar lime applied in 1999
LIME_AMENDMENT_1	t/ha	Amount of sugar lime applied in 2001

In Table 6 data of the 18 sampling areas and in Table 7 data of the 6 sampling areas are presented. The 18 sampling areas are distributed over the whole Green Corridor while the 6 sampling areas are part of the 18 areas but located in the South of the Green Corridor, situated around the village of Aznalcázar. The 18 sampling areas are an important part of the Guadiamar database and therefore discussed further, while the 6 sampling areas spatially coincide with a selected area which has been sampled for this research to define the current situation. Furthermore, comparing the data of the whole Green Corridor (Table 6) with an area in the South of the Corridor (Table 7), soil contamination and its distance to the source can be discussed. For the spatial view of the sampling area see also Figure 5.

In general, higher variability and standard deviations are received for the 18 sampling areas compared to the 6 sampling areas due to the higher sample size and higher spatial spreading (higher landscape variability).

Table 6: Soil properties and bioavailable metal fraction for the 18 sampling areas distributed over the whole Guadiamar Green Corridor with a sample depth of 0 -15 cm collected in the years 1999 to 2002 (SOC in g 100g^{-1}; CLAY, SILT and SAND in %; DTPA extracted Cd, Pb, Cu and Zn in mg kg^{-1}); *the sample size are different due to irregular number of analysis made

	Soil Properties					Metals			
	pH_KCL	**SOC**	**CLAY**	**SILT**	**SAND**	**Cd**	**Pb**	**Cu**	**Zn**
Sample size*	277	278	44	44	44	149	199	198	202
Mean	6.18	6.70	19.37	33.38	47.25	0.92	6.94	25.83	188.79
Minimum	1.25	1.09	5.27	7.181	1.625	0.18	0.19	0.192	0.38
Maximum	9.62	29.85	45.76	84.11	86.68	5.21	85.69	184.11	1857.06
STD	1.86	5.48	10.56	19.46	25.00	0.87	9.98	34.90	260.03

Table 7: Soil properties and bioavailable metal fraction for the 6 sampling areas situated in the South of the Guadiamar Green Corridor with a sample depth of 0 -15 cm collected in the years 1999 to 2002 (SOC in g 100g^{-1}; CLAY, SILT and SAND in %; DTPA extracted Cd, Pb, Cu and Zn in mg kg^{-1}); *the sample size are different due to irregular number of analysis made

	Soil Properties					Metals			
	pH_KCL	**SOC**	**CLAY**	**SILT**	**SAND**	**Cd**	**Pb**	**Cu**	**Zn**
Sample size*	78	78	12	12	12	36	60	60	60
Mean	7.44	4.14	19.39	26.36	54.28	0.29	5.77	7.67	69.78
Minimum	6.14	1.09	12.22	7.77	41.21	0.19	0.93	1.89	0.95
Maximum	8.16	8.70	27.14	35.77	68.62	0.58	27.04	16.30	133.44
STD	0.36	1.74	4.99	8.10	9.20	0.13	5.31	4.34	37.84

pH

There is basically one striking value which indicates a pH of 1.25 (Table 6), representing an incredibly acid soil. From expert knowledge of IRNAS staff and discussed by Ciadamidaro et al. (2014) there exist areas in the Green Corridor which are characterized by very low pH values around 3. Nevertheless, a soil pH of 1.25 has never been reported in this area and therefore the only explanation for this low value could be that it originates from soil samples taken in sludge. There are still remaining areas along the whole Corridor where the sludge has not been completely removed. However, in a study of Lacal et al. (2003) the pH of sludge was determined at lowest around 2.5.

Therefore, this low pH cannot be explained and if used for statistical analysis it should be deleted as outlier.

SOC

The SOC content of the soil has as well a very high variation ranging 1.09g $100g^{-1}$ to 29.85g $100g^{-1}$ (Table 6). SOC content around 1g $100g^{-1}$ is nothing unusual on arable land in a Mediterranean climate (Ganuza and Almendros, 2003). In the study of Ganuza and Almendros (2003) on organic carbon storage in Spanish soils, describes that cropland has the lowest values slightly above 1g $100g^{-1}$, forests and scrub land around 3.5g $100g^{-1}$, and pastures showing SOC values of up to 7g $100g^{-1}$. The SOC value of 30g $100g^{-1}$ is found in the wetlands of the Guadiamar Green Corridor and according to Murillo-Rodriguez et al. (2011) this reflects and extremely high value, nevertheless such high values have been measured before in Spanish wetlands. Another reason for this high value can be that the soil sample has been taken at a spot with accumulation of fresh organic matter, probably even partly consisting of the applied compost amendments. According to Darlington (n.d.) average compost consist of at least 50 g $100g^{-1}$ organic matter. Average values for wetlands are ranging between 3g $100g^{-1}$ and 10g $100g^{-1}$ (Murillo-Rodriguez et al., 2011; Powell, 2008; Ahn and Jones, 2013). As stated in a technical report of the European Commission by Gobin et al. (2011), SOC contents in the topsoil of wetlands are highest, followed by grassland and lowest under arable land.

Soil Texture

Soil clay fraction varies between 45% and 5%, while silt and sand contents have even higher variation (Table 6). Soil texture is largely determined by parental material and the amount of weathering and can differentiate within small areas (Saglam and Dengiz, 2012). This high variation could be due to the fact that the Green Corridor extends over two geologic features, the Palaeozoic massif and the lower Guadalquivir basin.

Metals

Comparing the bioavailable metals from the 18 sampling areas, which are spread over the whole Green Corridor (Table 6) with the ones from the 6 sampling areas, which are situated in the South of the Green Corridor (Table 7), gives an indication that areas further away from the source of contamination have lower contamination values. Areas closest to the source are most contaminated. This indication matches for all mean values of the bioavailable metal fraction. In other studies on the soils of Guadiamar for example conducted by Cabrera et al. (2008) and Carreira de la Fuente et al. (2002), this trend of lower contamination further away from the source has been proven before. Two factors can be responsible for that, either the spatial deposition of the toxic sludge or the mobility of the metals. Cabrera et al. (2008) discusses that metal mobility plays an important role on how far away from the source and in which concentrations metals can be found. According to Cabrera et al. (2008) there is a considerable difference between less mobile elements such as Pb and Cu and strongly mobile elements such as Cd and Zn. The concentration of Pb and Cu in the soil is much higher in the upper part of the Guadiamar river close to the mine, with decreasing concentrations downstream. Cd and Zn show similar contamination levels along the whole river, from north to south (Cabrera et al., 2008).

2.2.2 Land Units and Land Use Change of the Guadiamar Green Corridor

Land Units

From the combination of lithology, geomorphology and the land use before the mine spill accident, land units have been developed, resulting in five different units, fluvial cropping, fluvial pasture, fluvial woody, wetland cropping and not applicable. Additionally, the location of the 18 sampling areas, in the map named as soil profiles, which contain important soil information are presented in Figure 7.

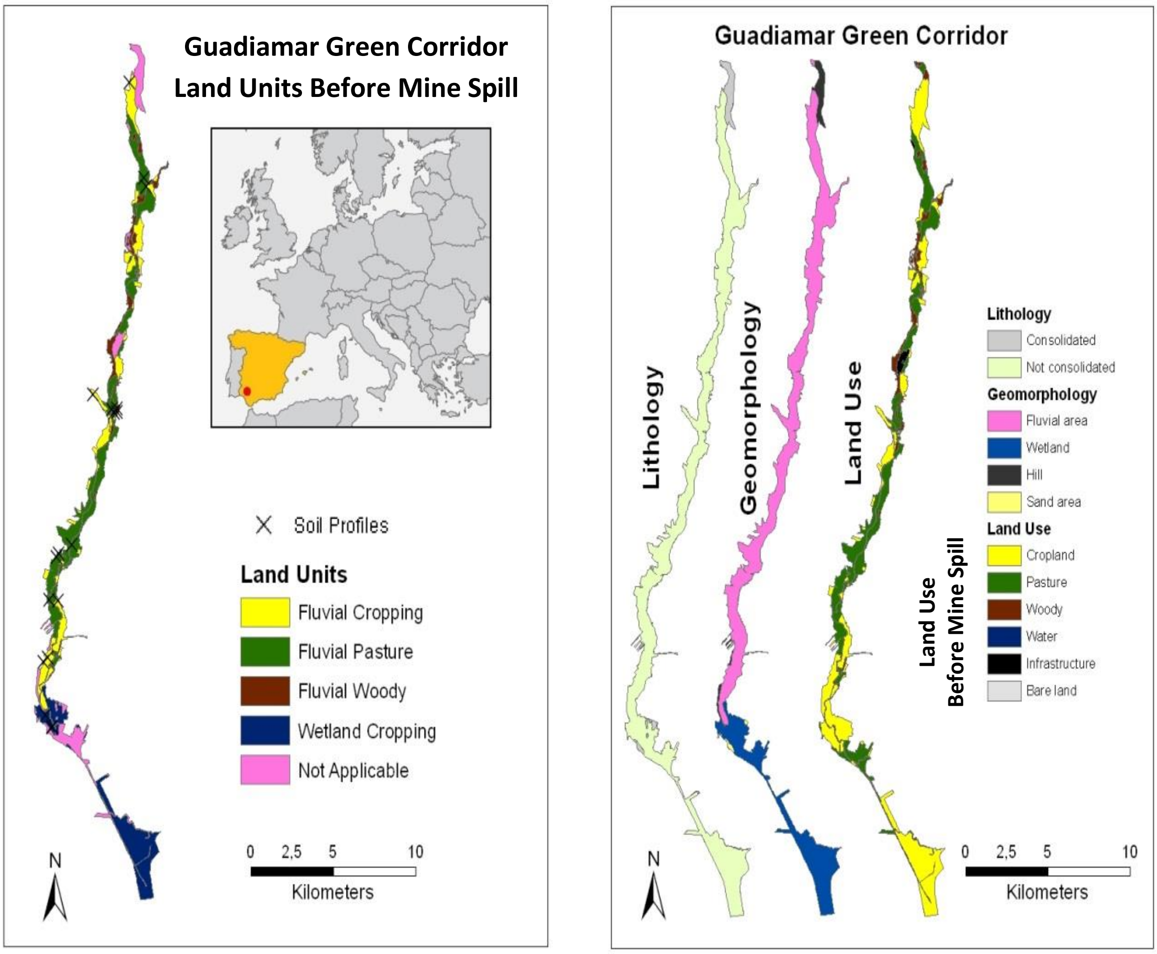

Figure 7: Left: Land units before the mine spill accident in the Guadiamar Green Corridor;
Right: Lithology, geomorphology and the land use before the mine spill for the Guadiamar Green Corridor

As result it is obtained a homogenous landscape with little diversity in lithology and geomorphology. Basically, the whole river bed consists of unconsolidated fluvial material, due to the natural evolvement of such river landscapes. Fluvial material, lose and unconsolidated sediments such as gravel, sand, silt and clay, predominate in a river bed (Ball and Teeple, 2013). To the northern end of the Green Corridor a small area with consolidated material exists, representing the start of a mountain range. The geomorphology of the study area simply comprises fluvial and wetland, whereof the lower parts of the Guadiamar river slowly flow into a floodplain. Since the prevailing soils do not differentiate much, having similar lithology and geomorphology, the main difference is found in the management, hence the land use. Before the mine spill catastrophe two main land use types were existing, pasture and cropland, with additionally some smaller woody plots decorating the landscape. According to Dunjo et al. (2002) and Parras-Alcantara et al. (2013) land use influences soil properties, mostly SOM, and therefore land use can have an effect on contaminant availability, since according to Alloway (1995) contamination of a soil highly depends on soil properties such as pH, SOM and texture.

Land Use Change

As presented in Figure 8, we can see the land use before the mine spill accident. The main land use types were cropland and pasture with few woody plots along the river banks. As well the land use of 2007 is presented, derived from the Land Use and Land Cover Map of Andalusia (Moreira, 2007). The methodology used to define land use was remote sensing, aerial photography. Remote sensing indicates a likewise land use before the mine spill and in 2007, but after soil sampling (ground truth) it becomes obvious that for 2007 cropland and pasture represent natural grassland. Also Cabello (2003) describes that in the years after the mine spill catastrophe all contaminated land, known as the Guadiamar Green Corridor, has been banned for agricultural production and re-vegetated with native species, and therefore the only land use nowadays is natural vegetation consisting basically of woody riparian areas and open grassland with scattered trees and shrubs on the flood areas (see also Figure 9). For woody area remote sensing is quite precise though and represents reality.

Therefore, after ground truth we have explored the main land use change within the Guadiamar Green Corridor, indicating a change from cropland and pasture to natural grassland. And some minor areas have changed from cropland and pasture to woody land (Figure 8).

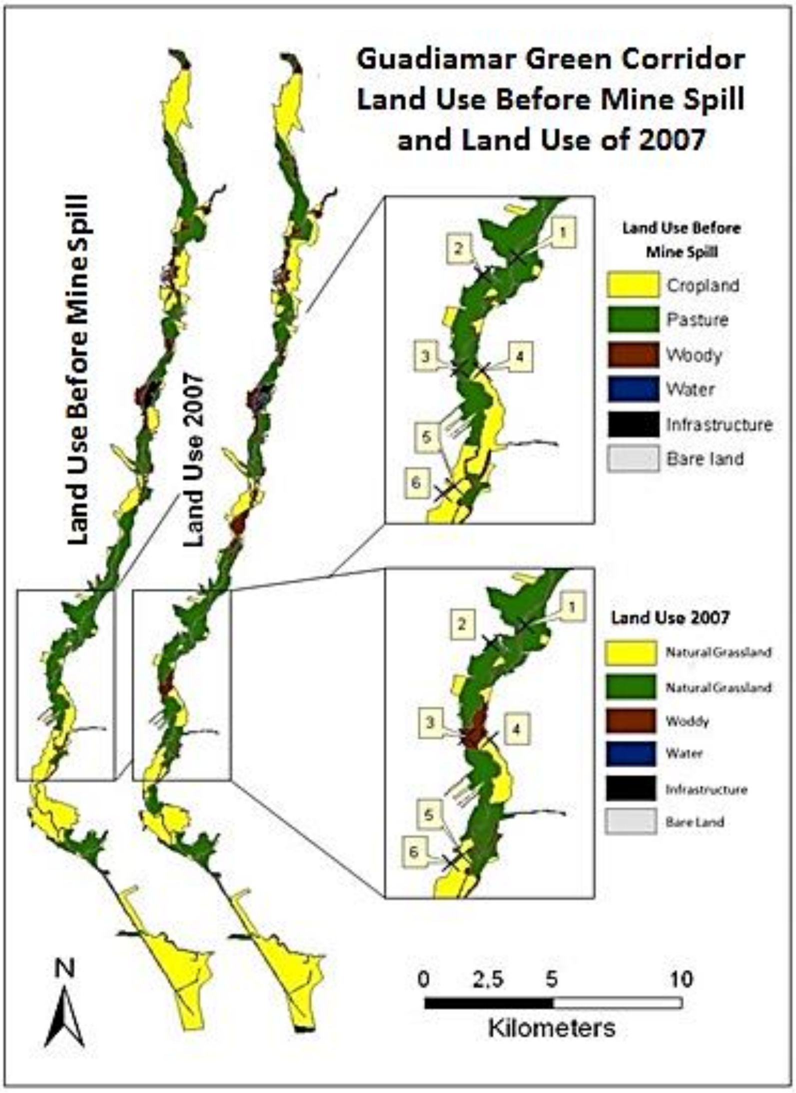

Figure 8: Land use maps from before the mine spill and of 2007; indicating the major land use change for the Guadiamar Green Corridor from cropland and pasture to natural grassland

Considering the land use change from agricultural area to natural vegetation we can expect some changes in soil properties. According to Acin-Carrera et al. (2013), land use change has the biggest effect on SOC content when transferring cropland into natural grassland. In the research of Muñoz-Rojas et al. (2011) it is discussed that the SOC content in the superficial layer (0–25 cm) on fluvial soils in Andalucía increase by 13.4 Mg/ha after a land use change from cropping land to forest, as it is the case for sampling are 3, and by 30.9 Mg/ha from cropping land to open grassland, as in the case for sampling area 5 and 6. Since a higher SOC content provides the soil with buffering capacity, this increases biodiversity and water holding capacity and improves soil structure and therefore aggregate stability. A soil with higher SOC content is according to Acin-Carrera et al. (2013) considered to be more fertile. A higher SOC content also stands for a stronger absorption of metals to organic compounds. Soils with SOC content lower than 1g $100g^{-1}$ can be considered as degraded (Acin-Carrera et al., 2013). Regarding the influence of land use change on the pH, Dunjo et al. (2002) argue that the pH seems not to depend directly on the land use, rather on the parental material. Nevertheless, land use especially if land manager interfere can influence pH significantly, for example amendments such as lime increase pH or fertilizers such as ammonium sulphate and urea creating acidic reactions in the soil decrease pH (Vossen, n.d.). Due to the fact that intensive actions have been undertaken in the area such as the application of amendments and mechanical cleaning, still soil properties are probably stronger influenced by anthropogenic activities than by the land use.

2.2.3 Current Situation of Metal Contamination in Comparison with the Past 15 Years

Description and Discussion of the Selected Soil Sampling Area

Figure 9: Pictures of soil sampling areas showing the land use at the time of soil sampling in January 2014

The soil sampling area in the South of the Guadiamar Green Corridor around the village of Aznalcázar is mostly open grassland with scattered shrubs and trees. They differ mainly in the grass density and the amount of fresh, green grass (Figure 9). Sampling area 3 is a riparian forest with a majority of white poplar. White poplar is known to accumulate Cd and Zn (Madejón et al., 2013) and therefore higher pseudo-total levels of Cd and Zn in the superficial layer are expected, since white poplars are absorbing contaminants from deep soil layers, accumulating them in the leaves and through litter fall spreading them to the superficial layer. Furthermore, due to the fact that the area is close to the river and strongly vegetated, the mechanical removal of the sludge was impeded and sludge residues are expected, resulting most probably as well in higher contaminant values. Agricultural use is banned in the whole Green Corridor. Nevertheless, horse droppings have been observed during the field visit, due to illegal grazing.

Current Situation (2014)

In Table 8 the mean values of all 6 soil sampling areas and the average value for the whole region, obtained from the field work of this master study are presented, to describe the current situation of the selected sampling area around the village of Aznalcázar. Additionally, threshold values for pseudo-total metal concentrations are given.

Table 8: Soil texture description and mean values of pH-KCL, SOC (g 100g^{-1}), pseudo-total and bioavailable (EDTA extracted) metal concentrations (mg kg $^{-1}$) for the 6 soil sampling areas in the South of the Guadiamar Green Corridor (Aznalcázar) with a sample depth of 0 -15 cm collected in the years 2014; Average values for the whole region around Aznalcázar and threshold values for pseudo-total metal concentrations (mg kg $^{-1}$) for soils with a pH between 6 and 7

Sampling Area	**pH_KCl**	**SOC**	**Texture**	**Fraction**	**Cd**	**Pb**	**Cu**	**Zn**
Area 1	6.81	3.17	Clay loam	EDTA	0.66	16.54	23.11	67.27
				Total	1.56	134.2	88.72	446.6
Area 2	6.95	3.09	Silty clay	EDTA	0.77	17.28	21.34	69.30
				Total	1.63	117.3	82.27	416.7
Area 3	6.98	3.37	Clay	EDTA	1.74	25.55	45.35	147.5
				Total	3.27	110.3	142.4	768.7
Area 4	6.91	3.25	Clay	EDTA	1.07	33.01	35.76	100.7
				Total	2.28	182.0	130.4	729.7
Area 5	6.98	2.98	Clay	EDTA	0.80	16.15	28.97	79.25
				Total	1.85	158.7	115.2	535.4
Area 6	6.82	2.49	Silty clay	EDTA	1.21	21.85	38.39	87.02
				Total	2.60	110.4	143.6	655.4
Average Values	*6.91*	*3.06*		*EDTA*	*1.04*	*21.73*	*32.15*	*91.84*
				Total	*2.20*	*135.5*	*117.1*	*592.1*
Threshold Values				*Total*	*1*	*70*	*50*	*150*

pH

The average soil pH of the selected sampling area is 6.91. It is well known that the metal solubility and therefore their bioavailability is mainly determined by the soil pH (Violante et al., 2010). According to Takáč et al. (2009) higher proportions of cationic metals such as Cd, Pb, Cu and Zn are bioavailable in acidic soils. As discussed by Evan et al. (1995) Pb and Cu already form strong complexes with organic matter and clay particles at a pH around 5, while Zn and Cd are completely absorbed at a soil pH of 6. In a study on metal leaching by Dijkstra et al. (2005) the pH dependency has been determined, proving lowest metal concentrations in the soil solution between pH 6 and 8, having the metals absorbed mainly to soil organic matter and partly to clay minerals. Therefore, having a soil pH of 6.91 supports a strong absorption of the studied metals to the solid phase, reducing the bioavailable metal fraction.

Since directly after the mine spill accident soil amendments such as lime have been applied to immobilize the metals, the influence of a decreasing effect of the lime amendment over time has to be understood. As discussed by Madejón et al. (2009), a slight decrease of the pH over the years after the lime application is a normal effect. However, 15 years after the lime application the soil pH is still neutral so that this effect of decreasing soil pH is rather low and probably mainly dependent on the naturally occurring soil pH.

SOC

The average SOC content of the selected sampling area is 3.06g $100g^{-1}$. According to Gobin et al. (2011) an average SOC content of 3g $100g^{-1}$ in the Mediterranean climate is considered as a good value. Ganuza and Almendros (2003) argue that SOC doesn’t drop much below 3g 100 g^{-1} under dense natural vegetation, not even in dry and hot climates. Soils with healthy SOC contents, as it is the case for the selected sampling area, have generally increased biological activity and improved soil structure, and are overall considered as more fertile (Acin-Carrera et al., 2013). In regard to metal contamination, a high SOC content stands for a stronger absorption of metals to organic compounds (Acin-Carrera et al., 2013). Therefore, the selected sampling area has a healthy SOC content providing absorption capacity for metals.

Additionally to lime, also compost has been applied resulting in an immediate increase of SOC directly after application. As the pH, also the SOC decreases over the years due to the degradation of the organic material until it reaches its natural level (Madejón et al., 2009). It seems that 15 years after the application, the SOC found its natural equilibrium at around 3g $100g^{-1}$ which is considered according to Ganuza and Almendros (2003) as a common value for soils under natural vegetation. However, if low SOC contents impede metal absorption promising technologies exist to add stable and nearly indecomposable carbon to the soil, in the form of biochar (Bolan et al., 2014).

Soil Structure

All soil samples contain high amounts of clay. The clay content varies between 35% and 55%, while the silt content varies between 30% and 45%. The soil texture is quite similar for all 6 sampling areas and therefore the selected sampling area can be identified having silty and clay soils (Figure 10). Clay particles form strong complexes with metals and with increasing clay content the immobilization of metals increase (Alloway, 1995; Takáč et al., 2009). In soils having 25% of clay the mobility of metals is already strongly reduced since metals are absorbed by clay particles (Cabrera et al., 1999). Therefore, having a soil with 35% to 55% of clay supports the absorption and immobilization of the studied metals.

Soil texture is a very stable soil parameter and hardly reacts on changing management (Gholami, 2013). On fluvial soils with seasonal flooding the river transports and deposits material and therefore soil particles can be rearranged frequently. Lime amendment mostly influences pH and additionally for some soils it can help stabilize soil aggregates, but does not directly influence the fraction of sand, silt and clay within a soil (Karcauskiene and Repsiene, 2009; Walworth, 2012).

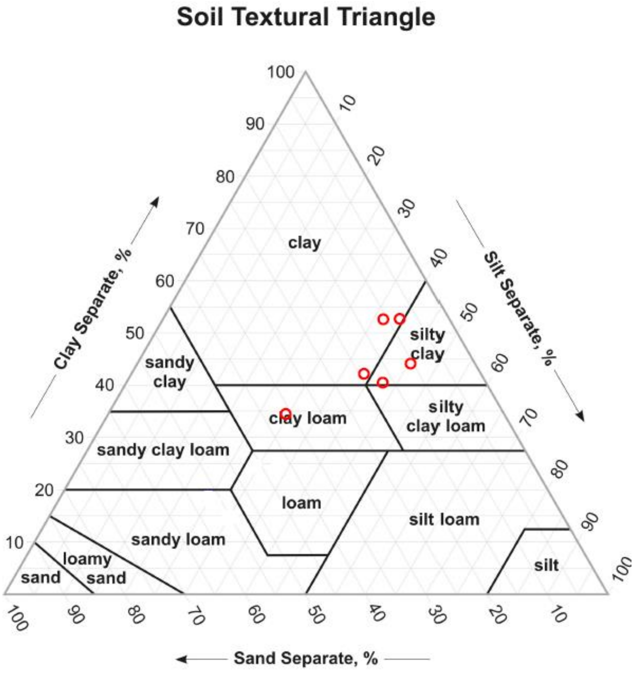

Figure 10: Soil texture triangle presenting the soil texture of the 6 sampling areas in the region of Aznalcázar

Pseudo-Total Metal Contamination

The average values of the total metal concentrations in the selected sampling area are clearly over the threshold values (Table 8). This indicates that the selected sampling area is exceeding the threshold for total metal concentrations as defined by the European Directive 86/278/EEC from 1986 and by Gawlik and Bidoglio (2006).

Evident from Table 8, higher Cd, Zn and Cu concentrations are found in sampling area 3 compared to the other areas. It is important to remark the presence of white poplar, that according to Madejón et al. (2013) accumulate Cd and Zn in its biomass, and from a two year field research conducted by Ciadamidaro et al. (2014) we know that soils vegetated with white popular do not change their total metal concentration in the soil over short term. Since the land use type is constant for the last 15 years it might be possible that through litter fall and its subsequent decomposition of leaves containing high levels of Cd and Zn the total metal concentration in the superficial layer can be increased in areas vegetated by white popular, when considering a longer time period. Another possibility could be that due to the existence of trees, sludge removal was impeded and less complete.

Bioavailable (EDTA extracted) Metal Contamination

The average values for the bioavailable fraction within the selected sampling area are likewise to other studies conducted in the region of Aznalcázar. Similar to the total metal concentrations, as well for the bioavailable fraction higher Cd and Zn concentrations are found in sampling area 3, probably for the same reasons.

Comparison over the Past 15 Years

In Table 9 existing data on soil metal contamination in the Guadiamar Green Corridor has been collected and presented to put the current master study in context with research from the past 15 years. In most of the research data has been collected over the whole Guadiamar Green Corridor (GGC) while only few studies have focused their investigation on the area around Aznalcázar (AZ).

Table 9: Mean pseudo-total (agua regia extracted) and bio-available (EDTA* extracted) metal concentrations (mg kg $^{-1}$) of sludge, unaffected and affected soils derived from literature and from the current master study; Studies were conducted either in the whole Guadiamar Green Corridor (GGC) or in the area of Aznalcázar (AZ), while the data originates from different sampling years and soil depth (cm) and characterized by different sample size (N)

Source	N	Location	Year	Prof.	Cd	Pb	Cu	Zn
Sludge								
Total								
Cabrera et al. 1999	12	GGC	1998	-	25.1	7888	1552	7096
Galan et al. 2002	4	GGC	1998	-	23.3	9552	1793	6460
Unaffected soils								
Total								
Cabrera et al. 2008	45	GGC	1998	0 - 20	0.33	38.2	30.9	109
Madejón et al. 2006	10	GGC	1999	0 - 25	1.19	41.9	43.8	83.8
Cabrera et al. 2008	45	GGC	2005	0 - 20	0.35	65.1	31	117
Galan et al. 2002	3	GGC	1998	0 - 25	0.5	30	30	70
Bio-available								
Madejón et al. 2004	10	GGC	1999	0 - 25	0.03	5.45	5.66	4.56
Affected soils								
Total								
Cabrera et al. 1999	12	GGC	1998	0 - 15	2.16	316	104	630
Galan et al. 2002	9	GGC	1998	0 - 25	1.9	147	109	538
Madejón et al. 2004	25	GGC	1999	0 - 25	4.29	305	179	583
Madejón et al. 2006	10	GGC	1999	0 - 25	3.46	201	146	618
Cabrera et al. 2008	45	GGC	2005	0 - 25	2.32	291	110	491
Domínguez et al. 2008	100	GGC	2005	0 - 25	1.44	210	115	457
Ciadamidro et al. 2014a	3	GGC	2009	0 - 20	1.6	167	132	476
Ciadamidro et al. 2014a	3	GGC	2011	0 - 20	1.9	149	131	501
Bio-available								
Madejón et al. 2006	10	GGC	1999	0 - 25	1.05	44.3	56.5	174
Madejón et al. 2004	25	GGC	1999	0 - 25	1.25	58	63.3	117
Cabrera et al. 2008	45	GGC	1999	0 - 25	2.0	53	66	140
Madejón et al. 2002	3	AZ	1999	0 - 25	0.96	28.6	38.3	74.9
Madejón et al. 2004	3	AZ	2000	0 - 25	1.72	13.7	116	225
Madejón et al. 2004	3	AZ	2001	0 - 25	0.76	21.8	28.5	70
Current Master Study								
Total	18	AZ	2014	0 - 15	2.20	135.5	117.1	592.1
Bioavailable	18	AZ	2014	0 - 15	1.04	21.73	32.15	91.84
Guadiamar Database								
Bioavailable (DTPA)	60	AZ	2000	0 - 15	0.23	5.77	7.67	69.78

Overall, the data has a huge variability most probably due to irregular sludge deposition and removal and due to natural variability.

Pseudo-Total Metal Concentrations

Comparing the pseudo-total values of the 6 soil sampling areas from this current master study with similar research conducted by Ciadamidaro et al. (2014); Madejón et al. (2004, 2006); Cabrera et al. (1999, 2008); Domínguez et al. (2008) and Galan et al. (2002) which is presented in Table 9, it is obvious that the values are in a likewise range. Only Pb has slightly lower values since Pb is characterized by very low mobility (Kabata-Pendias and Pendia, 2001; Cabrera et al., 2008). Because total metal concentrations in literature only exists for the whole Guadiamar Green Corridor, and therefore lower values for the region of Aznalcázar which is located further away from the source are expected for metals with low mobility. Quoting Table 9 and comparing the total metal concentrations from literature with the concentrations identified in this study, we can conclude that the variability of the total metal concentration did not change in the soils of the Guadiamar Green Corridor over the last 15 years. Comparing the field results with results derived from a long term monitored experimental plot "El Vicario", confirms that total metal concentrations in the soils of the Guadiamar Green Corridor are likewise over the past 15 years (Madejon et al., 2009; Xiong, 2012).

Comparing the total metal concentrations of unaffected soils, as well presented in Table 9, with affected soils, it becomes obvious that affected soils are considerably higher contaminated than unaffected soils. Affected soils are those which have been inundated with the toxic sludge. The total metal concentrations of all affected soils do exceed the threshold values clearly. On the other hand, the unaffected soils generally do not exceed the threshold values with some values close to the threshold. This indicates that the soils of Guadiamar by nature have high concentrations of the studied metals.

Bioavailable (EDTA extracted) Metal Concentrations

The bioavailable metal concentrations identified during this study are like the total concentrations within the data range from literature (Table 9). Likewise, the variability of the bioavailable fraction did not change over the last 15 years. However, the IRNAS and other research groups have been working in the last years with the $CaCl_2$ extraction that reflects better the amount of trace elements available for plants (Kabata-Pendias, 2004). Concentrations of trace elements in soils extracted with $CaCl_2$ 0.01 M have been decreasing in time showing a stabilization of the available trace elements in time (Madejón et al., 2009; 2010). As well different studies of plants in the Green Corridor are showing similar behaviors, a tendency to decrease trace element contents in aerial parts (Domínguez et al., 2008). Due to these interesting results, following some alternative extractants to EDTA and DTPA are discussed shortly.

Alternative Extractants to EDTA and DTPA

For remediation efforts and environmental risk assessment, estimating the metal bioavailability in soils is becoming more important, since the total metal concentration is not the best indicator for the degree of contamination (Menzies et al., 2007; Frische et al., 2003). To study the bioavailability a thorough understanding of processes in the soil but also at the soil-plant interface is required (Frische et al., 2003). According to Menzies et al. (2007) many methods, such as extraction by EDTA and DTPA, are chemically aggressive and generally to intensive to detect low levels of elements, while bioavailability can be estimated by various other chemical extractants such as mild acids, organic extractants or neutral salts. The usefulness of an extractant to predict the bioavailability depends on the ability to predict to which extent plants extract and accumulate a specific element, and this is as well very much dependent on the plant species (Menzies et al., 2007). Comparisons between different methods are not unproblematic since each extractant behaves different in changing environments, mostly depending on the soil type (Menzies et al., 2007; Frische et al., 2003). The majority of data on bioavailable soil metal concentrations in the Guadiamar Green Corridor has been determined with the EDTA extraction method by Quevauviller et al. (1998). According to Cajuste et al. (2000) and Menzies et al. (2007), both DTPA and EDTA provide poor prediction of actual metal bioavailability for plants. Both, extraction with DTPA and EDTA, use organic ligands capable to form strong complexes with metals. In studies on soil-plant interactions neutral salt solutions such as the extraction by $CaCl_2$ are more frequently used to determine the actual bioavailability of metals (Kabata-Pendias, 2004; Ciadamidaro et al., 2014). According to Kabata-Pendias (2004) and Menzies et al. (2007) neutral salt solutions tend to provide best relationships between soil extraction and plant tissue accumulation, representing best the extraction of the biosphere and therefore the actual metal bioavailability.

In a graph of Bolan et al. (2014) the different forms a metal exist in soil are presented. The metal can occur in the soil solution, in a non-specific or specific form, or precipitated (Figure 11). Plants do have the ability to extract metals from the soil solution and in certain conditions may even extract metals from non-specific forms, while metals bound in specific and precipitated forms are not available for plants. In the precipitated form the metal is completely immobilized (Bolan et al., 2014). Since EDTA and DTPA also extract metals bound in specific forms these methods do not represent the actual bioavailability instead overestimating bioavailability. Neutral salt solutions extracting less are more appropriate for estimating actual metal bioavailability.

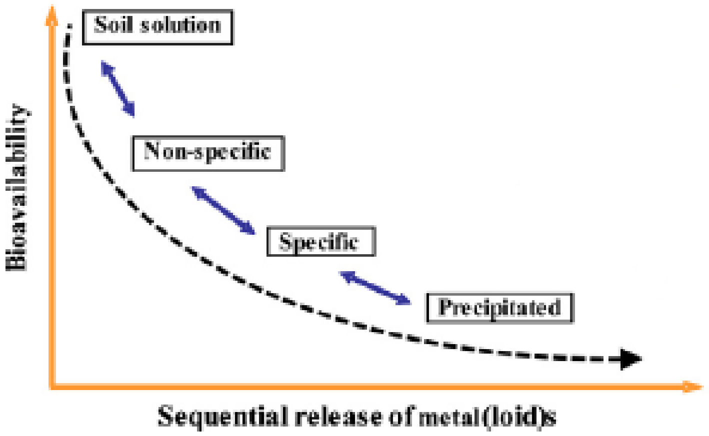

Figure 11: The interaction between adsorption of metals in soil and their bioavailability (Bolan et al., 2014)

Extractability

With the data collected during this master study the extractability of the four studied metals has been calculated. This describes the extracted fraction (with EDTA) from the pseudo-total soil metal fraction. In doing so, we discovered that Cd has the highest extractability with almost 47%, followed by Cu with 27%, Pb 16% and Zn 15%. This value cannot be generalized since the extractability or availability is very much depending on the environmental chemistry and the ecotoxicology (Frische et al., 2003), simplified this value varies between different environments.

2.2.4 Comparison of Extraction with DTPA and EDTA for Assessing Bioavailable Metals

According to an elaborate study of Haynes and Swift (1983) the extraction methods with DTPA (Lindsay and Norvell, 1978) and EDTA (Quevauviller et al., 1996) have been investigated and compared. Haynes and Swift (1983) showed EDTA to be more useful in indicating potential or actual bioavailability of metals than DTPA. According to Quevauviller et al. (1998) DTPA extracts less than EDTA. However, apart from the method used with its particular extractant, soil chemical characteristics such pH, SOC, soil texture but as well the pseudo-total concentration and stability of the metal complexes, influence strongly the quantity of a metal extracted from the soil (Haynes and Swift, 1983). Therefore, it is difficult to come up with a universal conversion factor applicable for different environments with different soils. Quevauviller et al. (1996) stress repeatedly that due to a lack of uniformity in the different procedures the results cannot be compared worldwide.

Nevertheless, comparing these two methods, especially since in this study data from both methods exist, and trying to find relations is an objective. Table 10 presents results from two studies by Quevauviller et al. (1998) and Haynes and Swift (1983). Identical soil samples have been analysed with DTPA and EDTA, investigating eight different soil types.

Table 10: Results derived from two studies by Quevauviller et al. (1998) and Haynes and Swift (1983); Cd, Pb, Cu and Zn extracted with EDTA and DTPA from eight different soil types; results from current master study added

Source	Method	Cd	Pb	Cu	Zn
Quevauviller et al. 1998	EDTA	2.68	59.7	57.3	383
	DTPA	1.34	15	32.3	142
	Ratio DTPA : EDTA	***0.5***	***0.25***	***0.56***	***0.37***
Haynes and Swift 1983	EDTA	-	-	1.3	2.95
	DTPA	-	-	0.7	1.8
	Ratio DTPA : EDTA	**-**	**-**	***0.54***	***0.61***
	EDTA	-	-	1.15	1.4
	DTPA	-	-	0.7	0.85
	Ratio DTPA : EDTA	**-**	**-**	***0.61***	***0.61***
	EDTA	-	-	1.05	1.3
	DTPA	-	-	0.37	0.6
	Ratio DTPA : EDTA	**-**	**-**	***0.35***	***0.46***
	EDTA	-	-	0.95	1
	DTPA	-	-	0.45	0.55
	Ratio EDTA : DTPA	**-**	**-**	***0.47***	***0.55***
	EDTA	-	-	0.95	0.6
	DTPA	-	-	0.17	0.25
	Ratio DTPA : EDTA	**-**	**-**	***0.18***	***0.42***
	EDTA	-	-	0.5	0.5
	DTPA	-	-	0.14	0.2
	Ratio DTPA : EDTA	**-**	**-**	***0.28***	***0.4***
	EDTA	-	-	0.35	0.2
	DTPA	-	-	0.23	0.15
	Ratio DTPA : EDTA	**-**	**-**	***0.66***	***0.75***
	Mean Ratio	**0.5**	**0.25**	**0.46**	**0.52**
Current master study	EDTA	1.04	21.73	32.15	91.84
Guadiamar Database	DTPA	0.23	5.77	7.67	69.78
	Ratio DTPA : EDTA	***0.22***	***0.27***	***0.24***	***0.76***

Defining the ratio between the two methods obviously a huge variability is obtained. For Pb and Cd unfortunately only one soil type has been analysed. However, for Pb the ratio fits pretty well while for Cd the ratio is unlike. The ratio (DTPA:EDTA) for Cu and Zn, derived from eight different soil types, varies for Cu between 0.18 and 0.66 and for Zn between 0.37 and 0.75. The ratios calculated for this current study, for Cu 0.24 and for Zn 0.76, are within the data range presented in Table 10. However, since the ratio variability is that huge and the ratio strongly depends on the soil type and the metal itself, a reliable conversion factor needs to be metal and soil specific and cannot be developed from such little data.

2.2.5 Potential Environmental Risks

After introducing the framework of the Guadiamar Green Corridor by assessing the past and present situation, potential environmental risks are presented in Figure 12.

The main objective for the Guadiamar Green Corridor is to keep metals immobilized and the soil vegetated to minimize erosion. According to Liedekerke et al. (2014) the management and control of contaminated sites consist of four steps: site identification, preliminary investigation, intensive site investigation and implementation of risk reduction measures. This has happened in Guadiamar over the last 15 years. Beside mechanical sludge removal, phytoremediation has been implemented and soil amendments applied to reduce environmental risks. Bolan et al. (2014) describe that the fate of metals in the environment depend mostly on the soil type. In the case of Guadiamar potential environmental risks are associated with soil pH, fluvial erosion and plant uptake. Thanks to the natural protection of the Guadiamar Green Corridor environmental risks are well managed and are not considered to be high, assuming that the protection status of the Guadiamar Green Corridor and the soil pH does not change.

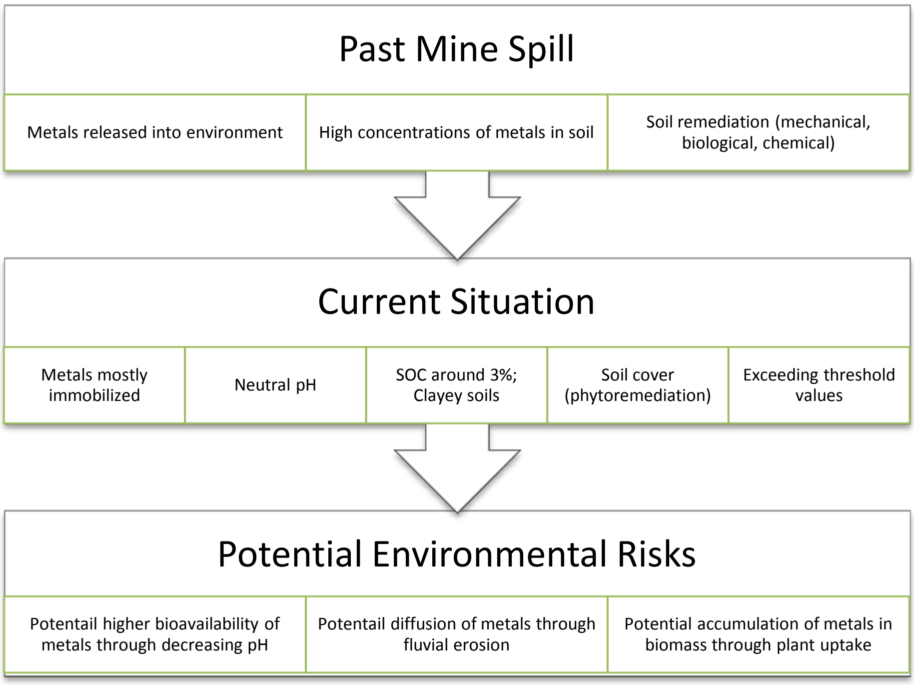

Figure 12: Schematic of the past and current situation and related environmental risks for the a sampling area around the village of Aznalcázar

Fluvial Erosion

Erosion is controlled and minimized due to the fact that the Guadiamar Green Corridor is a protected area, free of agricultural use having permanent vegetation cover. By reducing metal mobility through vegetation cover, risks for environmental degradation for example through leaching or erosion are minimized (Wen-sheng et al., 2004).

Plant Uptake

Plant uptake is according to Wen-sheng et al. (2004) limited because plants with the ability to accumulate metals are tending to be slow-growing and produce low biomass. If plants accumulate metals the harvestable biomass is preferable collected and disposed to avoid metal diffusion and possible food chain pollution. But since the Guadiamar Green Corridor is a natural area with minimal intervention and without food production, collecting contaminated biomass is not an objective. As well the diffusion of contaminated biomass is limited since the riparian poplar forests, which are accumulating most, are surrounded by low accumulating grassland.

Higher Bioavailability

A changing soil pH and its subsequent increase of metal bioavailability is probably the strongest risk for the environment of Guadiamar. The change of metal availability over time as effect of changing pH needs to be understood and monitored. According to Landner and Reuther (2005) only metal ions in the soil solution are bioavailable, particularly those acquirable by a root system. Due to a dynamic equilibrium between the soil solution and the exchange fraction, which is dominated by soil pH, a metal ion transfer occurs. According to Sauve et al. (2000) the most important factors influencing the equilibrium between dissolved metals (soil solution) and absorbed metals (exchange fraction) are apart from soil pH, the total metal concentration and the organic matter content. The soil solution and the exchange fraction are of major importance for the potential movement of metals in the soil (McLean and Bledsoe, 1992). In a study on metal leaching by Dijkstra et al. (2005) the pH dependency has been determined, proving lowest metal concentrations in the soil solution between pH 6 and 8.

The current situation of soil properties in a selected sampling area is supporting metal immobilization. Neutral soil pH, high SOC content and clayey soils prevail. SOC and clay minerals are strongly absorbing metal ions, especially under neutral soil pH (Alloway, 1995). The risk that high amounts of metal become bioavailable is minimized, as long as the pH stays neutral. Due to the fact that if metals become bioavailable it causes severe environmental problems, monitoring the bioavailable fraction in the soils of Guadiamar is essential. Igwe et al. (2005) define metals as very toxic posing a threat to man and the environment. As well considering that the total metal concentrations in the soils of the Green Corridor are exceeding the threshold values.

Since the application of soil amendments, 15 years ago, the pH level and SOC content is varying in little range. But there exist research by Madejon et al. (2009) that documents a slight decrease of pH and SOC over the years. Years after lime application, soil pH is moving towards the equilibrium with its natural state and therefore the naturally occuring soil pH can be a potential risk or not. In a study of Ciadamidaro et al. (2014) comparing neutral contaminated soil with acid contaminated soil under field condition, indicates that soil with very low pH around 3 exist in the Guadiamar Green Corridor. And therefore, areas with naturally acidic conditions need special attention, at its best they have to be identified and managed keeping neutral pH.

Risk Assessment

A commonly used approach for assessing environmental risks of contaminated sites is the ecological risk assessment (ERA) with the purpose to ensure sustainable landuse by protecting ecological structure and functions (Ferguson et al., 1998). The common approach normally consists of a comparison of chemically analysed soil data or by monitoring with bio-indicator species. In many countries ERA is considered when setting soil quality objectives for policy formulation, mostly based on expert judgement, toxicity tests or models. The application of bio-indicators is rare (Ferguson et al., 1998) however for the Guadiamar case study it could be a possible approach to economically monitor metal availability. Ferguson et al. (1998) argue that ERA actions include remediation, restrictions on landuse and actions to prevent metal dispersion, all of them already applied to the Guadiamar Green Corridor. For monitoring the bioavailable fraction of the Green Corridor the use of bio-indicators (plants and animals) is highly promising according to Carreira de la Fuente et al. (2002).

Chapter 3: Conclusions and Future Perspectives

In this chapter the current study is synthesized by giving conclusions and by presenting future perspectives. In doing so, basically all existing information coming from this research, from literature and expert knowledge is combined. Soil science is used to understand the behaviour of metals in the soil, ecology to understand the interactions within the ecosystem, biology to understand the living organisms and therefore by combing different expertise an integrated view is reached.

3.1 Conclusions

- The Guadiamar database is difficult to compare with other soil research since laboratory methods to define physiochemical soil attributes are not harmonized. There is a strong need for standardisation of methodologies (sampling procedures and analytical methods) in soil research at European scale. The comparability of data depends on data harmonization, one of the key issues to obtain a Europe wide database on metal contamination.

- Physiochemical soil data originating form research conducted within the Guadiamar Green Corridor has a huge variability, due to irregular distribution of the toxic sludge and inaccurate cleaning as well as due to natural variability with the Green Corridor stretching from mountain ridges down to wetlands.

- With a neutral soil pH, a SOC content of around 3g 100 g^{-1} and clayey soils the current situation of a selected area in the region of Aznalcázar is supporting metal absorption and immobilization.

- Threshold values for soils with a pH between 6 and 7 are exceeded for pseudo-total metal concentrations, and this is not expected to change since metals are not biodegradable.

- Evaluating soil contamination over the last 15 years illustrates that the variability of the soil metal concentrations (pseudo-total and EDTA extracted) did not change in the soils of the Guadiamar Green Corridor.

- A reliable conversion factor between the extraction method by DTPA and EDTA for assessing bioavailable metal concentrations in the soil could not be identified. To further improve comparability of available data by applying conversion algorithms is a possibility since we cannot ignore existing data. However, focusing in further research on other extractants to assess metal bioavailability such as neutral salt solutions is more recommendable since it better represents the actual bioavailability and what effectively can be extracted by the biosphere.

- Even though if the studied metals are greatly immobilized, the huge stock of metals in the soils (exceeding threshold values) of the Green Corridor form a potential environmental risk, especially in soils with naturally low pH, so that long-term monitoring is essential. Only with a proper monitoring (using bio-indicators is highly promising) it can be ensured that the amazing and unique ecosystem with the Doñana Natural Park at the Southern end of the Guadiamar Green Corridor is sufficiently protected.

3.2 Future Perspectives

During the entire RECARE project the Guadiamar database will further be used to create a new model to assess the applicability and impact of prevention, remediation and restoration measures. Scaling-up contamination threats, modelling future scenarios and ecosystem service analysis are additional interests for which a comprehensive Guadiamar database is required. In a further step, the database will be complemented with socio-economic data so that effective prevention, remediation and restoration measures using an innovative trans-disciplinary approach become feasible. Knowledge of stakeholders and scientists from the 17 different case study sites, covering a range of soil threats, will provide an overview of different environments across Europe. The applicability and impact of such measures will be assessed using a new model, integrating bio-physical and socio-economic parameters. To ensure that project results are available and disseminated to stakeholders a web-based dissemination and communication hub will be developed. Finally, using the acquired knowledge to make a step forward in soil conservation, existing policies will be reviewed and hopefully new policies will be formulated considering European soils as a precious and non-renewable resource on which our future depends. European land use policies are strongly required giving soil the attention and protection it deserves.

Soil research across European is using existing data and contributing to the scientific world with new data. Consistent and standardized methodologies in soil research are strongly required to harmonize data. Similar sampling procedures and analytical methods facilitate the unification and comparison of data. Such an attempt has been started by the European Soil Data Centre (ESDAC) aiming to be the first contact point for all European soil information such as datasets, documents, reports, maps etc. The main objective is to make data access and use as simple as possible and accessible for public. This initiative needs to be further strengthened and supported by working together under the guidance of research agreements at European level.

Over the past 15 years, a river landscape completely degraded has been brought back to life. Remediation measures and successful re-vegetation transformed a devastated riverbed into a green corridor. An intensive site specific management and control of the contamination has been conducted. Now the time has come to define and agree on how to monitor the Guadiamar Green Corridor efficiently, economically and properly to guarantee that no other environmental catastrophe will happen. The possibility to use the affected soils for production again is not realistic, since the metal concentrations in the soil are relatively high and land use change would influence metal availability with potential release into the environment and into the food chain. The main focus is on environmental monitoring by keeping the current situation how it is, a permanent vegetation cover, a neutral pH and high SOC contents. Furthermore, protecting the Guadiamar Green Corridor as a natural area, serving as biological refugim and for recreation, is a positive side effect.

Detailed monitoring with an average sampling interval of 5 to 10 years seems to be an adequate compromise to measure changes in metal contamination, which are likely to be slow. Detailed monitoring including expensive soil sampling is only recommended in risk areas, hence areas with naturally low soil pH, where explicit identification of problem areas or risk zones is needed. For the biggest part of the Guadiamar Green Corridor, where the soil pH is naturally neutral, the use of bio-indicators might be the appropriate method to monitor the health of an environment.

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Appendices

Appendix 1

A) Generalization of lithology

Original Classes (LITOLOGIA)	New Code	New Classes
• PIZARRAS, ARENISCAS Y GRAUVACAS	1	Consolidated
• CONGLOMERADOS, ARENAS Y LIMOS ROJOS		
• CALIZAS CONGLOMERATICAS, CONGLOMERADOS Y ARENAS		
• MARGAS GRIS AZULADAS		
• LAVAS BASICAS Y ACIDAS, BRECHAS Y AGLOMERADOS DACITICOS		
• ALUVIAL: GRAVAS, ARENAS, LIMOS Y ARCILLAS	2	Not consolidated
• TERRAZA: GRAVAS, ARENAS, LIMOS Y ARCILLAS		
• LIMOS ARENOSOS CALCAREOS AMARILLENTOS		
• LIMOS Y ARCILLAS		

B) Generalization of geomorphology

Original Classes (AMB GEOMOR)	New Code	New Classes
• TERRAZAS	1	Fluvial area
• MODELADO DEL ZOCALO PLEGADO: AREAS CON PROFUSION DE CAUCES E INTERFLUVIOS		
• LLANURA ALUVIAL		
• MARISMA DESECADA	2	Wetland
• MARISMA VIVA		
• LOMAS Y LLANURAS MARGOSAS DE LA DEPRESION PERIFERICA	3	Hill
• LOMAS Y TALUDES DE LAS PLATATAFORMAS TABULARES MIOPLIOCENAS		
• MODELADO DE VERTIENTES DEL PIEDEMONTE		
• ARENALES	4	Sand area

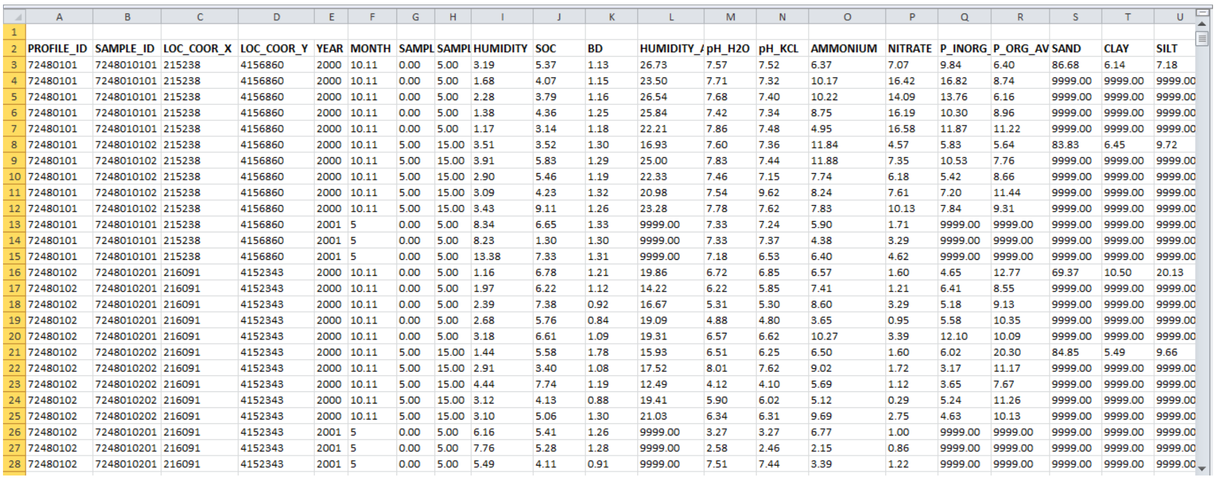
C) Generalization of land use

Original Code (UC99 N2)	Original Classes (DESC 99)	New Code	New Classes
11	• URBANIZACIONES RESIDENCIALES	1	Infrastructure
12	• AUTOVIAS, AUTOPISTAS Y ENLACES VIARIOS		
13	• OTRAS INFRAESTRUCTURAS TECNICAS		
13	• ESCOMBRERAS Y VERTEDEROS		
13	• ZONAS MINERAS		
22	• RIOS Y CAUCES NAT.:LAMINA DE AGUA	2	Water
22	• BALSAS DE RIEGO Y GANADERAS		
21	• MARISMA MAREAL CON VEGETACION		
21	• MARISMA RECIENTE SIN VEGETACION		
42	• MATORRAL DISPERSO CON PASTIZAL	3	Pasture
43	• PASTIZAL CONTINUO		
43	• PASTIZAL CON CLAROS (ROCA, SUELO)		
22	• RIOS Y CAUCES NAT.:OTRAS FORM. RIPARIAS	4	Woody
22	• RIOS Y CAUCES NAT.:BOSQUE GALERIA		
41	• MATORRAL DISP. ARBOLADO: EUCALIPTOS		
41	• MATORRAL DISP. ARBOLADO: QUERCINEAS. DISPERSO		
41	• FOR. ARBOL. DENSA: CONIFERAS+EUCALIPTOS		
41	• PASTIZAL ARBOLADO: QUERCINEAS. DENSO		

41	• PASTIZAL ARBOLADO: QUERCINEAS. DISPERSO		
41	• PASTIZAL ARBOLADO: EUCALIPTOS		
41	• PASTIZAL ARBOLADO: QUERCINEAS+CONIFERAS		
41	• PASTIZAL ARBOLADO: CONIFERAS. DISPERSO		
36	• CULTIVOS HERBACEOS Y PASTIZALES	5	Cropland
31	• CULTIVOS HERBACEOS EN SECANO		
32	• ARROZALES		
32	• CULTIVOS FORZADOS BAJO PLASTICO		
32	• OTROS CULTIVOS HERBACEOS REGADOS		
32	• CULTIVOS HERBACEOS EN REGADIO: REGADOS Y NO REGADOS		
32	• CULTIVOS HERBACEOS EN REGADIO: NO REGADOS		
32	• CULTIVOS LEÑOSOS EN REGADIO: PARCIALMENTE REGADOS O NO REGADOS		
32	• CULTIVOS LEÑOSOS REGADOS: CITRICOS		
31	• CULTIVOS LEÑOSOS EN SECANO: OLIVAR		
32	• OTROS CULTIVOS LEÑOSOS REGADOS		
32	• MOSAICO DE SECANO Y REGADIO CON CULTIVOS HERBACEOS Y LEÑOSOS		
44	• ROQUEDOS Y SUELO DESNUDO	6	Bare land

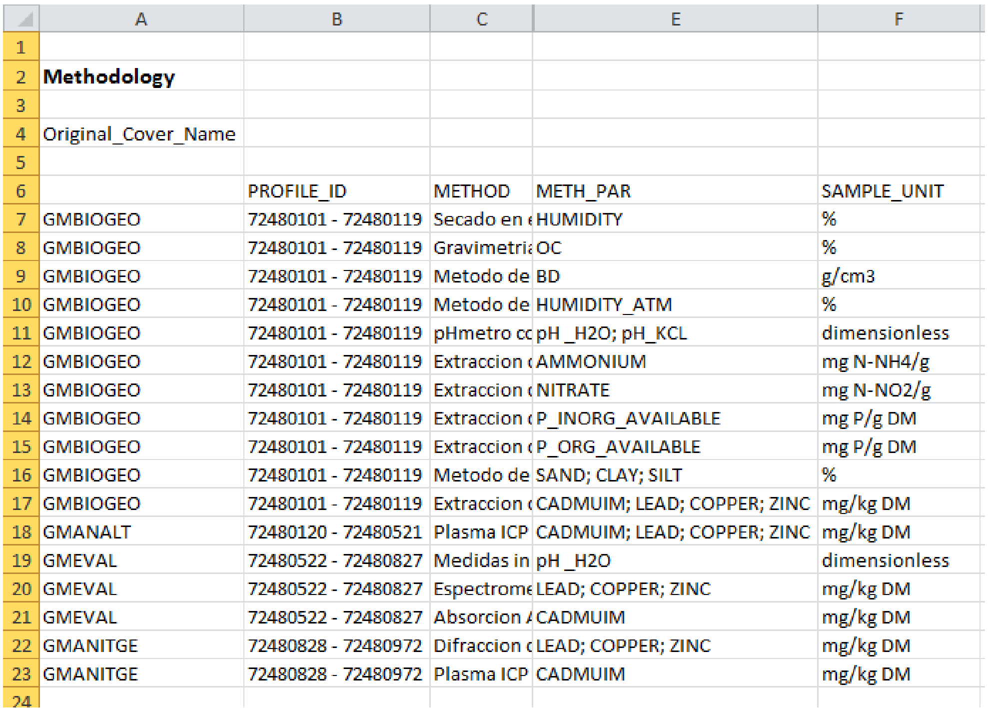
Appendix 2

A) Data sheet



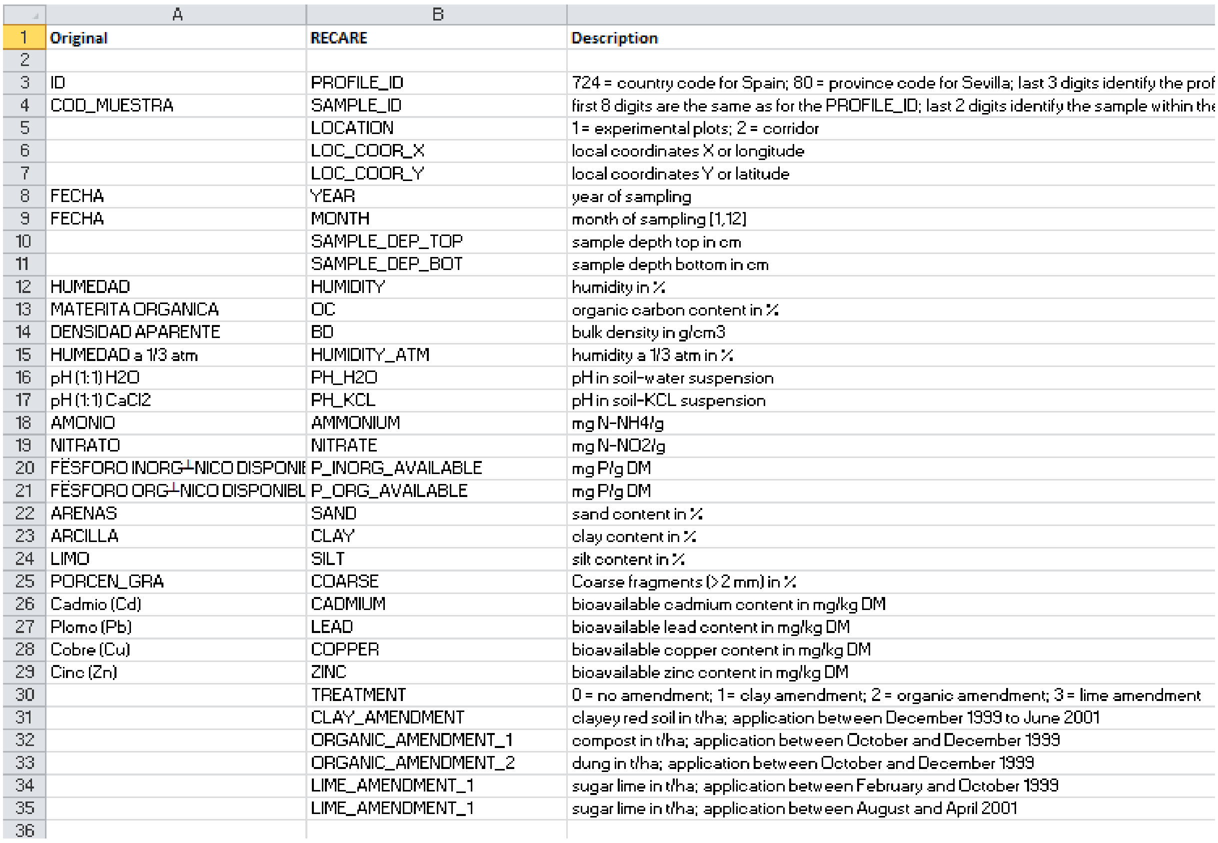
	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S	T	U
1																					
2	PROFILE_ID	SAMPLE_ID	LOC_COOR_X	LOC_COOR_Y	YEAR	MONTH	SAMPL	SAMPL	HUMIDITY	SOC	BD	HUMIDITY_	pH_H2O	pH_KCL	AMMONIUM	NITRATE	P_INORG_	P_ORG_AV	SAND	CLAY	SILT
3	72480101	7248010101	215238	4156860	2000	10.11	0.00	5.00	3.19	5.37	1.13	26.73	7.57	7.52	6.37	7.07	9.84	6.40	86.68	6.14	7.18
4	72480101	7248010101	215238	4156860	2000	10.11	0.00	5.00	1.68	4.07	1.15	23.50	7.71	7.32	10.17	16.42	16.82	8.74	9999.00	9999.00	9999.00
5	72480101	7248010101	215238	4156860	2000	10.11	0.00	5.00	2.28	3.79	1.16	26.54	7.68	7.40	10.22	14.09	13.76	6.16	9999.00	9999.00	9999.00
6	72480101	7248010101	215238	4156860	2000	10.11	0.00	5.00	1.38	4.36	1.25	25.84	7.42	7.34	8.75	16.19	10.30	8.96	9999.00	9999.00	9999.00
7	72480101	7248010101	215238	4156860	2000	10.11	0.00	5.00	1.17	3.14	1.18	22.21	7.86	7.48	4.95	16.58	11.87	11.22	9999.00	9999.00	9999.00
8	72480101	7248010102	215238	4156860	2000	10.11	5.00	15.00	3.51	3.52	1.30	16.93	7.60	7.36	11.84	4.57	5.83	5.64	83.83	6.45	9.72
9	72480101	7248010102	215238	4156860	2000	10.11	5.00	15.00	3.91	5.83	1.29	25.00	7.83	7.44	11.88	7.35	10.53	7.76	9999.00	9999.00	9999.00
10	72480101	7248010102	215238	4156860	2000	10.11	5.00	15.00	2.90	5.46	1.19	22.33	7.46	7.15	7.74	6.18	5.42	8.66	9999.00	9999.00	9999.00
11	72480101	7248010102	215238	4156860	2000	10.11	5.00	15.00	3.09	4.23	1.32	20.98	7.54	9.62	8.24	7.61	7.20	11.44	9999.00	9999.00	9999.00
12	72480101	7248010102	215238	4156860	2000	10.11	5.00	15.00	3.43	9.11	1.26	23.28	7.78	7.62	7.83	10.13	7.84	9.31	9999.00	9999.00	9999.00
13	72480101	7248010101	215238	4156860	2001	5	0.00	5.00	8.34	6.65	1.33	9999.00	7.33	7.24	5.90	1.71	9999.00	9999.00	9999.00	9999.00	9999.00
14	72480101	7248010101	215238	4156860	2001	5	0.00	5.00	8.23	1.30	1.30	9999.00	7.33	7.37	4.38	3.29	9999.00	9999.00	9999.00	9999.00	9999.00
15	72480101	7248010101	215238	4156860	2001	5	0.00	5.00	13.38	7.33	1.31	9999.00	7.18	6.53	6.40	4.62	9999.00	9999.00	9999.00	9999.00	9999.00
16	72480102	7248010201	216091	4152343	2000	10.11	0.00	5.00	1.16	6.78	1.21	19.86	6.72	6.85	6.57	1.60	4.65	12.77	69.37	10.50	20.13
17	72480102	7248010201	216091	4152343	2000	10.11	0.00	5.00	1.97	6.22	1.12	14.22	6.22	5.85	7.41	1.21	6.41	8.55	9999.00	9999.00	9999.00
18	72480102	7248010201	216091	4152343	2000	10.11	0.00	5.00	2.39	7.38	0.92	16.67	5.31	5.30	8.60	3.29	5.18	9.13	9999.00	9999.00	9999.00
19	72480102	7248010201	216091	4152343	2000	10.11	0.00	5.00	2.68	5.76	0.84	19.09	4.88	4.80	3.65	0.95	5.58	10.35	9999.00	9999.00	9999.00
20	72480102	7248010201	216091	4152343	2000	10.11	0.00	5.00	3.18	6.61	1.09	19.31	6.57	6.62	10.27	3.39	12.10	10.09	9999.00	9999.00	9999.00
21	72480102	7248010202	216091	4152343	2000	10.11	5.00	15.00	1.44	5.58	1.78	15.93	6.51	6.25	6.50	1.60	6.02	20.30	84.85	5.49	9.66
22	72480102	7248010202	216091	4152343	2000	10.11	5.00	15.00	2.91	3.40	1.08	17.52	8.01	7.62	9.02	1.72	3.17	11.17	9999.00	9999.00	9999.00
23	72480102	7248010202	216091	4152343	2000	10.11	5.00	15.00	4.44	7.74	1.19	12.49	4.12	4.10	5.69	1.12	3.65	7.67	9999.00	9999.00	9999.00
24	72480102	7248010202	216091	4152343	2000	10.11	5.00	15.00	3.12	4.13	0.88	19.41	5.90	6.02	5.12	0.29	5.24	11.26	9999.00	9999.00	9999.00
25	72480102	7248010202	216091	4152343	2000	10.11	5.00	15.00	3.10	5.06	1.30	21.03	6.34	6.31	9.69	2.75	4.63	10.13	9999.00	9999.00	9999.00
26	72480102	7248010201	216091	4152343	2001	5	0.00	5.00	6.16	5.41	1.26	9999.00	3.27	3.27	6.77	1.00	9999.00	9999.00	9999.00	9999.00	9999.00
27	72480102	7248010201	216091	4152343	2001	5	0.00	5.00	7.76	5.28	1.28	9999.00	2.58	2.46	2.15	0.86	9999.00	9999.00	9999.00	9999.00	9999.00
28	72480102	7248010201	216091	4152343	2001	5	0.00	5.00	5.49	4.11	0.91	9999.00	7.51	7.44	3.39	1.22	9999.00	9999.00	9999.00	9999.00	9999.00

B) Methodology sheet



	A	B	C	E	F
1					
2	**Methodology**				
3					
4	Original_Cover_Name				
5					
6		PROFILE_ID	METHOD	METH_PAR	SAMPLE_UNIT
7	GMBIOGEO	72480101 - 72480119	Secado en	HUMIDITY	%
8	GMBIOGEO	72480101 - 72480119	Gravimetri	OC	%
9	GMBIOGEO	72480101 - 72480119	Metodo de	BD	g/cm3
10	GMBIOGEO	72480101 - 72480119	Metodo de	HUMIDITY_ATM	%
11	GMBIOGEO	72480101 - 72480119	pHmetro c	pH _H2O; pH_KCL	dimensionless
12	GMBIOGEO	72480101 - 72480119	Extraccion	AMMONIUM	mg N-NH4/g
13	GMBIOGEO	72480101 - 72480119	Extraccion	NITRATE	mg N-NO2/g
14	GMBIOGEO	72480101 - 72480119	Extraccion	P_INORG_AVAILABLE	mg P/g DM
15	GMBIOGEO	72480101 - 72480119	Extraccion	P_ORG_AVAILABLE	mg P/g DM
16	GMBIOGEO	72480101 - 72480119	Metodo de	SAND; CLAY; SILT	%
17	GMBIOGEO	72480101 - 72480119	Extraccion	CADMUIM; LEAD; COPPER; ZINC	mg/kg DM
18	GMANALT	72480120 - 72480521	Plasma ICP	CADMUIM; LEAD; COPPER; ZINC	mg/kg DM
19	GMEVAL	72480522 - 72480827	Medidas in	pH _H2O	dimensionless
20	GMEVAL	72480522 - 72480827	Espectrom	LEAD; COPPER; ZINC	mg/kg DM
21	GMEVAL	72480522 - 72480827	Absorcion	CADMUIM	mg/kg DM
22	GMANITGE	72480828 - 72480972	Difraccion	LEAD; COPPER; ZINC	mg/kg DM
23	GMANITGE	72480828 - 72480972	Plasma ICP	CADMUIM	mg/kg DM
24					

C) Correspondence sheet between original datasets and the RECARE databse



	A	B	
1	**Original**	**RECARE**	**Description**
2			
3	ID	PROFILE_ID	724 = country code for Spain; 80 = province code for Sevilla; last 3 digits identify the prof
4	COD_MUESTRA	SAMPLE_ID	first 8 digits are the same as for the PROFILE_ID; last 2 digits identify the sample within the
5		LOCATION	1 = experimental plots; 2 = corridor
6		LOC_COOR_X	local coordinates X or longitude
7		LOC_COOR_Y	local coordinates Y or latitude
8	FECHA	YEAR	year of sampling
9	FECHA	MONTH	month of sampling [1,12]
10		SAMPLE_DEP_TOP	sample depth top in cm
11		SAMPLE_DEP_BOT	sample depth bottom in cm
12	HUMEDAD	HUMIDITY	humidity in %
13	MATERITA ORGANICA	OC	organic carbon content in %
14	DENSIDAD APARENTE	BD	bulk density in g/cm3
15	HUMEDAD a 1/3 atm	HUMIDITY_ATM	humidity a 1/3 atm in %
16	pH (1:1) H2O	PH_H2O	pH in soil-water suspension
17	pH (1:1) CaCl2	PH_KCL	pH in soil-KCL suspension
18	AMONIO	AMMONIUM	mg N-NH4/g
19	NITRATO	NITRATE	mg N-NO2/g
20	FËSFORO INORG┴NICO DISPONI	P_INORG_AVAILABLE	mg P/g DM
21	FËSFORO ORG┴NICO DISPONIBL	P_ORG_AVAILABLE	mg P/g DM
22	ARENAS	SAND	sand content in %
23	ARCILLA	CLAY	clay content in %
24	LIMO	SILT	silt content in %
25	PORCEN_GRA	COARSE	Coarse fragments (> 2 mm) in %
26	Cadmio (Cd)	CADMIUM	bioavailable cadmium content in mg/kg DM
27	Plomo (Pb)	LEAD	bioavailable lead content in mg/kg DM
28	Cobre (Cu)	COPPER	bioavailable copper content in mg/kg DM
29	Cinc (Zn)	ZINC	bioavailable zinc content in mg/kg DM
30		TREATMENT	0 = no amendment; 1 = clay amendment; 2 = organic amendment; 3 = lime amendment
31		CLAY_AMENDMENT	clayey red soil in t/ha; application between December 1999 to June 2001
32		ORGANIC_AMENDMENT_1	compost in t/ha; application between October and December 1999
33		ORGANIC_AMENDMENT_2	dung in t/ha; application between October and December 1999
34		LIME_AMENDMENT_1	sugar lime in t/ha; application between February and October 1999
35		LIME_AMENDMENT_1	sugar lime in t/ha; application between August and April 2001
36			