PhD THESIS

ENVIRONMENTAL AND HEALTH RISK ASSESSMENT OF METAL POLLUTION IN DIFFERENT LAND USES

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Summary

Risk assessment of metals in soil must be based on both, classical and advanced analytical determinations, such as chemical and physical speciation of metals, microanalysis of particles etc., and a deep statistical treatment of the data, using multivariable analysis among others, combining these analytical and statistical tools objective conclusions can be reached. However, the metals impact on health and ecosystems vary with the source of metal, the land use and the soil physic-chemical properties. Therefore, in order to evaluate the impact of metals and metalloids in soils from Murcia Province, four land uses have been studied in this thesis: urban, industrial, mine and agriculture areas.

Urban areas were the first studied, this was because of the wide amount of people exposed to toxic elements. The objectives of this study were: to assess the population density as a key factor on the metal accumulation, to compare the efficiency of soil and road dust as metal pollution indicator and to develop a health risk assessment derived to the exposure of metals in soil and road dust. Results showed that population density is just a key factor in highly populated settlements, and that the metals are mainly accumulated in road dust. In addition, the accumulation of metals in fine particles and the high risk levels found for road dust make it potentially hazardous for human health, being necessary the development of monitoring and control plans in urban areas.

In the industrial area, three types of industrial activities have been compared: services, petrochemical and tannery industries. The goals on this study were: to elucidate the impact of each type of activity on soil pollution and human risk; and to compare the efficiency of soil and road dust as pollution indicators. Results highlight the larger ability of road dust as sink of metals in industrial areas while the type of industrial activity influences the concentration and behaviour of metals. In addition, the industrial activity has been proven as a key factor in the mobility and bioavailability of metals; hence understand the behaviour of each metal within each activity is crucial to develop preventive and monitoring plans.

In the mine area, two mining districts were selected, Cartagena-La Unión and Mazarrón, which included natural (soil and plants), urban, agricultural (soil and plants) and mine uses. Results suggested that both soil and road dusts of the towns (La Unión and Mazarrón) are enriched on metals from the mine wastes with the consequent risk for the human health. In addition, this enrichment was found in agriculture and natural soils near to mining ponds. High amount of metals was found in barley grains overreaching permissible levels for human feed. Furthermore, the behaviour of metals in an endemic plant, *Ballota hirsuta*, was studied in order to assess the potential risk for the wildlife and its potential use in phytoremediation.

Finally, in the agriculture area, the main objective was to establish which type of crop managements adds more metals to the soils, and the effect of this management in the behaviour of metals. Results obtained suggested that the management of all these crops enrich soils in Cd, Cu, Pb and Zn being the citrus management who adds the higher concentration of metals to the soil.

R esumen

La determinación del riesgo derivado de la presencia de metales en suelo se basa en el uso de métodos analíticos tanto clásicos como avanzados, tales como la especiación fisicoquímica de metales o el microanálisis de partículas, además necesita un adecuado tratamiento estadístico de los datos obtenidos siendo el más empleado el análisis multivariable. Esta combinación de herramientas analíticas y estadísticas es lo que nos permite alcanzar conclusiones objetivas para una investigación en este contexto. Sin embargo, el impacto generado por los metales sobre la salud y los ecosistemas variará en función del origen del metal, el uso del suelo y las propiedades fisicoquímicas del suelo. Por ello, y con el fin de estudiar el impacto ocasionado por los metales y metaloides en los suelos de la Región de Murcia se han propuesto para el desarrollo de esta tesis cuatro escenarios de estudio: urbano, industrial, minero y agrícola.

El primer escenario de estudio es el urbano debido a que presenta mayor volumen de población expuesta. Los objetivos de estudio dentro de este escenario han sido evaluar la variación en la densidad de población como factor clave en la contaminación por metales, comparar la eficacia de suelo y polvo sedimentado como indicadores de la contaminación por metales y evaluar el riesgo derivado de la exposición a los metales presentes en polvo y suelo. Los resultados han permitido concluir que la densidad poblacional solo es un factor a tener en cuenta en grandes núcleos de población y que además favorece la acumulación de metales en el polvo sedimentado. Además la mayor acumulación de metales en las partículas más finas del polvo sedimentado y los valores de riesgo más altos encontrados para el polvo hacen del mismo un peligro potencial para la salud humana que debe ser atendido en futuros planes de seguimiento y control.

En el escenario industrial se han comparado tres tipos de industrias: sector servicios, petroquímica y de curtido de pieles. El objetivo en este caso ha sido averiguar el impacto de cada una de ellas en la contaminación de los suelos por metales y el riesgo derivado para la salud humana, así como comparar la eficacia de suelo y polvo sedimentado como indicadores de la contaminación por metales. Los resultados resaltan de nuevo la mayor

capacidad del polvo sedimentado para acumular metales, mientras que el tipo de actividad industrial es la que condiciona qué metal se encuentra en mayor concentración y su comportamiento. Además se ha comprobado que la actividad industrial es un factor relevante en la movilidad y disponibilidad de los metales con lo que el conocer el comportamiento de cada uno de ellos en cada actividad específica es fundamental para elaborar planes de prevención y control.

Para el escenario minero se han seleccionado dos distritos mineros, Cartagena-La Unión y Mazarrón que incluyen los usos natural (suelo y planta), urbano, agrícola (suelo y planta) y minero. Los resultados sugieren que tanto el suelo como el polvo de ambos núcleos de población están enriquecidos en metales que provienen de la erosión de los residuos mineros con el consiguiente riesgo para la salud humana. Además este enriquecimiento también se ha encontrado en los suelos agrícolas y naturales cercanos a los depósitos, hallándose concentraciones de metales en granos de cebada superiores a los permitidos para el consumo humano. Así mismo, se ha estudiado el comportamiento de los metales en una planta endémica de ambos distritos mineros, *Ballota hirsuta*, también conocida como Marrubio, para evaluar tanto su peligro potencial para la fauna salvaje como su posible uso en labores de fitorremediación.

Finalmente, en el escenario agrícola este estudio ha pretendido determinar qué manejo de cultivo aporta mayor cantidad de metales al suelo así como el efecto de dicho manejo en el comportamiento de los metales. Los resultados obtenidos permiten concluir que las prácticas agrícolas en estos tipos de cultivos enriquecen el suelo en Cd, Cu, Pb y Zn siendo el manejo de los cítricos el que más contribuye a la contaminación de los suelos.

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Chapter

1

INTRODUCTION

AND

OBJECTIVES

Chapter 1

INTRODUCTION AND OBJECTIVES

1.1. Introduction

Soil contamination derived to the presence of metals and metalloids is a global concern in developed and undeveloped countries (Ferguson and Kasamas, 1999). Concerns about the accumulation of metals in soils are due to its persistence and potential toxicity (Ferreira-Baptista and De Miguel, 2005) that require a response by the responsible agencies to assess and reduce impacts on population and the environment.

But, when is a soil polluted by metals? In Spain, polluted soils are ruled by “Law 22/2011, of 28 July, of wastes and contaminated soils” and the “Royal Decree 9/2005 of 14 January which establishes a list of potentially soil contaminating activities and criteria and standards for declaring that sites are contaminated”. On this frame, the Region of Murcia is required to develop a list of polluted soils for an effectiveness protection against metal pollution. In accordance with existing legislation to declare a soil as polluted is necessary that a harmful element overreach a reference level or suppose an unacceptable risk for the protection of human health or ecosystems. However, these regulations do not include metals into the list of contaminants and generic reference levels for the protection of human health, however has been widely demonstrated that the accumulation of metals can produce health damages. In addition, the reference level for metals in soils is not specifically legislated, existing only a threshold level of metals in agriculture soils relative to sewage sludge application (Directive 86/278/CEE) and a calculated reference level for some metals in a regional scale for Region of Murcia (Martinez and Perez, 2007).

The risk assessment of metals on the population and ecosystems can be different according to the metal origin and place because it depends on the type, concentration and behaviour of metal and the specific conditions of each studied place.

The presence of metals and metalloids in soils depends primarily on the composition of parent materials and its pedogenic processes (Lu et al., 2012; Zhang et al., 2016), however a second source has been increasing on the last decades, the human activity. On the last decades a growing interest about the knowledge of metals concentration in soils has been propitiated by the ability of accumulation and persistence of metals on topsoil, making them potentially good indicators of pollution in contaminated environments (Yeung et al., 2003; Wong et al., 2006). On the same way, previous studies have reported that soils can also act as source of potentially harmful elements, as metals and metalloids (Burt et al., 2014) affecting population health if they reach toxic levels (Ahmed and Ishiga, 2006). First researches were mainly focused on the total metal content in soils (Caeiro et al., 2005; Ji et al., 2008; Shi et al., 2008; Sun et al., 2010) being the main indicator of pollution and the base for soil reclamation (Ljung et al., 2005). However, other researchers (Gupta et al., 1996; Maiz et al., 2000; Lu et al., 2003; Sahuquillo et al., 2003; Filgueiras et al., 2004; Guillen et al., 2012) concluded that the total content of metals is not enough to determine successfully the human and environmental risk, since this risk depends mostly of metals mobility and their ability to be uptake by plants, absorbed by organism and accumulate in their bodies. Thus, started perform studies on metals mobility which reported information about the solubility and bioavailability of metals in soils.

The bioavailability is defined as the fraction of metal that is available to the organisms. In soil eluates the chemically available fraction is generally the concentration in the interstitial water (water-soluble phase). However, the chemical available mobile fraction of a contaminant must not be equated to the available fraction of an unpolluted soil because relatively insoluble contaminants can be bound to fine soil particles that remain separated during the eluate collection (Kördel and Hund-Rinke, 2001). It was solved with the use of chelating agents as Diethylenetriaminopentaacetic acid (DTPA) or Ethylenediaminetetraacetic acid (EDTA) that are chemical organic substances that establish binds with metal ions from polluted soil solubilizing and keeping them in solution (Kabata-Pendias and Pendias, 1992; Schenkeveld et al, 2017). The effectiveness

and efficiency of chelating ligands in mobilizing metals has been widely studied and estimated based on results from extraction studies (Schenkeveld et al., 2017). Therefore, EDTA and DTPA chelates are commonly used agents forming strong complexes with divalent and trivalent metals such as Cd, Cu, Fe, Ni, Pb and Zn (Bloem et al., 2017). However, this treatment is not enough to know where the metal is exactly bound in soil due to chelating agents adsorb metals from different phases of soil, making impossible differentiate where the metal was located after the chelation process.

On this ways, researchers started to study other ways to know the soil constituents-metal association considering that metals can be found in nature associated with organic matter, iron, aluminium and manganese oxy-hydroxides, phyllosilicates, carbonates, etc. (Filgueiras et al., 2002) and therefore the mobility of metals and metalloids will depend on their affinity with the different soils phases. The chemical partition or sequential extraction procedures allow get information about the releasing of metals and later derived migration processes and toxicity (Rauret et al., 1998; Usero et al., 1996). These procedures consist in the addition of selective reagents on multiple steps to obtain a specific metal-soil bound to each soil phase. There are a variety of sequential extraction procedures in the literature being the most common that involves 6 steps (Ma and Rao, 1997), 5 steps (Tessier et al., 1979) or 3 steps as the BCR-three stage extraction (Thomas et al., 1994) although the most used is the Tessier procedure.

The binding between metals and soils constituents are affected by soils properties (Filgueiras et al., 2004) since variations in chemical or physical conditions can vary the associations causing an increase on the risk; hence the importance to study the concentration and phases of metals in soils, especially in soils affected by activities that can change the normal conditions.

For the human risk assessment, the particle size distribution of soils and pollutants is also interesting because some studies have reported that metals and metalloids are more prone to be bound to fine particles than coarse ones due to the larger specific surface to adsorb metals (Wang et al., 2006; Cao et al., 2011). Fine particles of soils can be easily resuspended by wind erosion or the action of human activities, hence contributing to particulate matters in the air such as total suspended particulates (TSP, $<100\text{ }\mu\text{m}$), particles with an aerodynamic diameter $<10\text{ }\mu\text{m}$ (PM₁₀), and particles with an aerodynamic diameter $<2.5\text{ }\mu\text{m}$ (PM_{2.5}) (Luo et al., 2011) which are particularly

dangerous because of the inhalation exposure (Cao et al., 2011). Also, small particles are soluble, being more likely to traverse the gastric barrier and more efficiently adsorbed in human tissues than coarse fractions (Acosta et al., 2009). Based on fine particles, a new concept appeared related to urban and industrial environments: the road or street dust. It originates from natural sources (e.g., re-suspension of soil and weathered materials) and various anthropogenic activities (e.g., vehicular traffic, industrial plants, power generation facilities, residential fossil fuel burning, construction and demolition activities) and is deposited in soils and other surfaces, representing an important environmental indicator with a significant contribution to metal pollution in both environments (Han et al., 2008; Zhang et al., 2012). A long-term exposure to the polluted dust would cause chronic damage through inhalation or ingestion ways and dermal contact (Du et al., 2013).

Many studies has been focused on determining the total amount of metals in the bulk road dust samples (Christoforidis and Stamatis, 2009) instead on the distribution of metals in each particle size of dust and its association with main components of the dust even though is well known that fine particles are more dangerous for the human health.

For this reason, it is important not only to know if the soils or/and road dust are polluted but also assess the potential risks for population and environments. This information will be useful to government agencies and technicians for develop future monitoring plans to prevent health and environmental damages.

Currently major activities in Murcia Region can be divided in urban, industrial and agricultural activities. In addition mining activity is an abandoned industrial practice that has reported environmental risks in previous researches (Martínez-Lopez et al., 2008; Zhuang et al., 2009; Martínez-Pagán et al., 2011; Acosta et al., 2011; Castillo et al., 2013) and whose influence in human health could be interesting to be studied. The scenes for the development of this thesis have been carefully selected to perform a risk assessment connecting to the major activities of the Region. Thus, an urban area was selected due to the amount of potentially harmful activities daily developed in a city that release metals to the environment (Bi et al., 2013) (e.g. gas combustion, tyre and brakes abrasion, wastes from commercial activities, buildings materials, pesticides, fungicides in public gardens, etc.). Metals mainly associated to urban environments are Cd, Cu, Pb and Zn while Co, Cr, Mo and Ni are considered as secondary metals (Widinarco et al., 2000; Li et al., 2001; Lu et al., 2003; Marjorie et al., 2009).

Urban areas are usually highly populated, therefore a widely amount of people could be exposed to potentially harmful elements by inhalation and ingestion via and dermal contact. On this way, it was demonstrated that children are more susceptible to pollutants than adults (De Miguel et al., 2007). Metal concentration in urban soils and street dusts can be increased by nearby industrial activities and mine wastes.

Industrial areas were selected for this study because mostly of industrial processes produce metal usually spread to the environment and finally deposited in soils or road dust (Duong and Lee, 2009). Workers from industrial complexes are permanently exposed to a potential contamination (Duong and Lee, 2009) although not all industrial activities are equally pollutant. Hence, it will be necessary to know which ones pose higher risk for humans and the environment. Chemical activity in Region of Murcia is actually linked to oil refineries, chemical and fertilizers companies, thermal power plants, wastes management plants, etc. which are catalogued as potentially pollutants activities (Espejo-Marín, 2005) Nevertheless, companies from other sectors are also potential sources of pollution and should be taking account for evaluation. For this reason on this study were selected three different industrial activities representative of the Region: a petrochemical complex, a tannery industry and a service industry.

Mining activity is one of the more ancient industries in the Region developed from Romans and Phoenicians times until the latest nineties. The two main mining districts in the Region of Murcia, Cartagena-La Unión and Mazarrón, were selected for the mining scene. The principal mined ores in these districts were Blende (ZnS), Galena (PbS) and Pyrite (FeS).

The mining activity produced a huge volume of wastes from metallurgical and exploitation processes that were often dumped on the vicinity of metal treatment plants in structures known as tailing ponds (Penman, 1996). Mine wastes are rich in Fe-oxyhydroxides, sulphides, sulphates and metals (mainly Cd, Pb and Zn) (Conesa et al., 2007) being a strong potential source of metal pollution. Unreclaimed tailing ponds may pose a high risk especially under semiarid conditions because the lack of vegetation and scarce but torrential precipitation favour its erosion promoting acid mining drainage and dust spread to near natural, agriculture and populated areas, pollution of surface and groundwater and visual impact on natural surroundings (Zanuzzi and Faz, 2005; Li et al.,

2006; Liao et al., 2005; Song et al., 2013; Liao et al., 2016). Both selected mining district are less than a kilometre away from populated areas and many ponds are also surrounded by agriculture lands increasing the potential risk of toxicity by inhalation and ingestion via. These quality aspects of environmental health make the mine scene a priority area of study in order to support future restoration plans for the mining district to avoid potential health risk.

Finally the agriculture scenery is linked to the developing of the agriculture activity through the time. It is well known that the use of agrochemical in the crop management is one of the major sources of metal and metalloids in agricultural soils, together the parent material and atmospheric deposition (Nicholson et al., 2003; Franco-Uría et al., 2009). Adriano (2001) described phosphate fertilizers as the major anthropic source of metals in farmlands, but other fertilization practices as the use of livestock wastes, organic amendments or sewage sludge can also add a huge amount of metals to agriculture soils (Rodriguez et al, 2008). Once metals are in soil, they can be up taken by plants causing a risk for population and crops quality (Gitet et al., 2016 ;Nicholson et al., 2003) by the accumulation of metals on their tissues. However, this ability will depend to some factors as the plant species, the physicochemical soil properties and weather condition (Chopra and Patak, 2012). The knowledge of the actual metals sources on the main type of cultivated crops in the Region of Murcia is essential to be in agreement with the latest agriculture policies at European Union. They has been looking for a more sustainable way of crop management which develop more efficiency and eco-friendly fertilizing programs in order to minimize the environmental and health risk derived to the management of arable lands along the latest decades. The study of the agriculture scene will report to agriculture managers, technicians and govern responsible which crop management is more prone to accumulate metals in soils supporting their future decision on developing the best practices.

For a better quality of this study we should have a reference frame to compare obtained results from each studied scene to reach objective conclusions. According to Alloway (1990) and Kabata-Pendias and Pendias (1992) the main source of metals and metalloids in non-disturbed soils is the parent material making necessary the selection of a natural scene for each anthropic scene (urban, industrial, agriculture and mine). Both, natural and

anthropic scenes should share the same geological origin allow to know the behaviour of metals in natural soils and elucidate the differences with the anthropic environment.

1.2. Objectives

The main objective of this thesis is to give an overview about the current metal content of soils and road dust through the Region of Murcia and its pollution level. A second goal is to develop a risk assessment for the environment and human health derived to the exposure to metal and metalloids contained in soils and road dusts from the urban, industrial, mine and agriculture areas.

For these purpose, the following specific objectives are proposed:

- Study of each land use proposed (urban, industrial, mining and agriculture) and selection of sampling areas within each scene.
- Assess the metal pollution degree in soils and road dust affected by urban, industrial and mining activities.
- Develop a health and environmental risk assessment using multivariate analysis and metal partitioning.
- Compare the pollution and metal behaviour among the different scenes proposed.
- Evaluate the metal behaviour in soil and road dust in order to know their relative risk to population and environment.
- Elucidate if the population density could be an important factor in metal concentration in urban soil and road dust.
- Evaluate the impact of industrial activity in soils and the risk for human health.
- Develop a metal dispersion assessment from mining districts to near populated areas, natural zones and agriculture lands.
- Determine which crop management (cereal, fruit, citrus or horticultural) is more prone to accumulate metals in soils and the behaviour of these metals depending of the kind of crop.

1.3. Relevance of the thesis

Results and conclusion of this study can provide to the regional competent agencies useful information about the present contamination of soils to help them on the developing the list of polluted soils required by the State soil legislation, as well as support information relative to the contribution of urban, industrial, mining and agriculture activities to the metal soil pollution and its impact on human and environmental health.

Other relevant aspect of this thesis is the joint research of the road dust and soil metal content in urban and industrial scenes that have usually been studied separately on previous researches and the use of chemical partitioning and size particle fractionation for the better understanding of metal behaviour and a thorough risk assessment.

1.4. Structure of the thesis

Chapter 1 of this thesis aims to introduce the reader on the conceptual framework of the soil contamination and the need to research the potential risk for human health and the environment; based on previous experience of other researchers which support the actions done to achieve the objectives proposed.

Within this first chapter is also explained the relevance of this thesis as well its structure in different scenes governed by the different anthropic activities: urban, industrial, mining and agriculture.

The experimental results obtained during the development of this study are presented in Chapters 2, 3, 4, 5, 6, 7 and 8 of this document. Chapters 2 and 3 correspond to studies developed in the urban scene where the influence of population in metal concentration and chemical speciation and the risk of exposure to metals in soil and road dust are explained. Chapters 4 and 5 correspond to the industrial scene. In Chapter 4 an explanation about the influence of different industrial activities in the behaviour of metals can be found, while Chapter 5 is focus on identification of metal-enriched areas and metal behaviour by different depths for a specific industrial complex.

Results for mine scene are presented in Chapters 6 and 7. In Chapter 6 the spread of mine wastes to population settlements is studied, whereas Chapter 7 is focus on the influence of

mine wastes in natural and agriculture lands nearby. Chapter 8 presents results from the agriculture scene where the increase of metals in soil by the crop management was studied. Each chapter is written as a scientific paper and consist of the following sections: abstract, introduction, material and methods, results and discussion and conclusion.

Finally, the last part of this work includes Chapter 9 that sum up the main scientific conclusions of the study and Chapter 10 that includes the references list.

The background of the slide is a photograph of a park. It shows a paved path leading through a dense forest of tall trees. On the left side of the path, there is a wooden bench and a trash can. The lighting is bright, suggesting a sunny day, with sunlight filtering through the leaves.

Chapter

2

**INFLUENCE OF
POPULATION
DENSITY ON THE
CONCENTRATION
AND SPECIATION OF
METALS IN THE SOIL
AND ROAD DUST
FROM URBAN AREAS**

Chapter 2

INFLUENCE OF POPULATION DENSITY ON THE CONCENTRATION AND SPECIATION OF METALS IN THE SOIL AND ROAD DUST FROM URBAN AREAS

Abstract

Road dust and soil from high, medium and low populated cities and natural area were analyzed for selected physical-chemical properties, total and chemical speciation of Zn, Pb, Cu, Cr, Cd, Co, Ni to understand the influence of human activities on metal accumulation and mobility in the environment. The pH, salinity, carbonates and organic carbon contents were similar between soil and dust from the same city. Population density increases dust/soil salinity but has no influence on metals concentrations in soils. Increases in metal concentrations with population density were observed in dusts. Cu, Zn, Pb, Cr can be mobilized more easily from dust compared to the soil. In addition, population density increase the percentage of Pb and Zn associated to reducible and carbonate phase in the dust. The behaviour of metals except Cd in soil is mainly affected by physico-chemical properties, while total metal influenced the speciation except Cr and Ni in dusts.

2.1.Introduction

Population growth, traffic emissions, municipal waste disposal and industrial activities are major causes of environmental pollution in urban areas (Saeedi et al., 2012; Bi et al., 2013). Soils serve as sources and sinks for trace elements and such has been used as a key indicator of human disturbance (Burt et al., 2014). Surface soil and road dust are possible good indicators of accumulation of heavy metals (Yeung et al., 2003; Sezgin et al., 2004), because they are not biodegradable and can remain in the environment over long periods of time. Human exposure to metal pollutants in soils and road dust causes health hazards such as those affecting nervous, renal, cardiovascular and reproductive systems (Christoforidis et al., 2009), growth retardation in children or cancer (Jiries, 2003). Recent studies deal solely with soils (Imperato et al., 2003; Sun et al., 2010; De Miguel et al., 1998; Acosta et al., 2010; Loska et al., 2004; Acosta et al., 2011) or road dust (Lu et al., 2009; Baptista and De Miguel, 2005; Saedi et al., 2012; Du et al., 2013; Li et al., 2013). Only limited studies are available that compare both soils and road dust (Ordoñez et al., 2003; Al-Khashman, 2007; Christoforidis and Stamatis, 2009) to predict human and ecological risk upon exposures to heavy metals.

Most trace metals settle down as surface dust from atmospheric depositions before its incorporation into the soil matrix. Thus, the extent of atmospheric contamination may be better revealed by road dust than by bulk soils (Bi et al., 2013). In contrast, road dust is easily re-suspended or adhered to human skin, being an advantage to assess environmental quality and health risk. However, road dusts are often removed by the municipal road cleaning, making it difficult to collect appropriate dust samples, and compounded by the short residence time to incorporate high concentration metals.

The principal objective of this study was to determinate the influence of the population density in the physico-chemical properties including the total concentration and the chemical speciation of metals in soils and dusts. This information is expected to help environmental scientists and regulators to better understand the behaviour of metals in soils and dusts to manage the human and environmental risks of metals in the environment.

2.2. Material and methods

2.2.1. Study area and sampling collection

The study area includes three urban settlements and a natural land as control site located in Murcia Region (SE Spain). The climate of this Region is Mediterranean semiarid with 18°C annual mean temperature and 350 mm annual mean rainfall. Murcia city represents high density ($HD = 498 \text{ person/km}^2$) while Totana and Abaran cities have medium ($MD = 106 \text{ person/km}^2$) and low ($LD = 27.8 \text{ person/km}^2$) population densities, respectively (Fig. 2.1).

Fig.2.1. Location of the selected cities

The main economic activity of the three cities is an intense agricultural cultivation of lemons, oranges, cereals, and vegetables in the areas surrounding the cities. In addition, only in Murcia city there are two industrial areas located 5 km far away from the city, one

in the northwest and the other in the southwest of the city, including concrete plants, automobile services, manufactories of paints, steel products and electrical materials. However, previous studies (Acosta et al., 2009) have reported that heavy metals generated from these industrial areas do not reach Murcia city, therefore it is not expected any effect in urban soils or dust come from these sources.

A total of 40 soil and 18 road dust samples were collected (figures 2.2, 2.3 and 2.4); 18, 8, 4, 10 soils and 6, 4, 3, 5 dust samples at HD, MD, LD cities and natural area, respectively.

Fig. 2.2. Location of soil and road dust samples in HD city (top left), MD city (top right), LD city (bottom left) and natural area (bottom right). Black speckles are soil samples and white triangles are dust samples

Soil samples were taken in the topsoil from urban parks with a soil spade while dust samples were collected by sweeping an area of 1 m² using a polyethylene brush. The

sweep action was very gentle and directly into the plastic collection bag to avoid the re-suspension of dust (Acosta et al., 2011; Zhang et al., 2012; Du et al., 2013).

Fig. 2.3. Soil Samples from HD city (a,b), MD city (c,d), LD city (e,f) and natural area (g,h)

Fig. 2.4. Dust Samples from HD city (a,b), MD city (c,d), LD city (e,f) and natural area (g,h)

2.2.2. Analytical methodology

Soil and dust samples were dried for 48 hours at 45°C and passed through a 2 mm sieve. A split of each sample was ground using an agate mortar (RetschRM 100). The pH was measured in a solution of 1:1 water/soil ratio (Soil Survey Staff, 2004) while the electrical conductivity (EC) was measured in a 1:5 soil/water suspension (Andrades, 1996). The equivalent calcium carbonate was determined using the Bernard's calcimeter. Organic carbon was determined by the dichromate method (Soil Survey Staff, 2004). For total metal content, samples were digested using HNO_3 and H_3ClO_4 (Risser and Baker, 1990). Bioavailable metals were measure using DTPA (Lindsay and Norvell, 1978). Soluble metals were measured according to Buurman et al. (1996) and Frau (2000). The amounts of Zn, Pb, Cu, Cd, Cr, Ni and Co were determined by Atomic Absorption Spectrometer (AAnalyst 800, Perkin Elmer).

Chemical speciation of metals was estimated by a sequential digestion procedure adapted from Tessier et al. (1979) and modified by Li et al. (1995). The extraction was carried out in order to obtain the following fraction: 1: exchangeable; 2: carbonate-bound; 3: bound to Fe-Mn-oxides; 4: bound to organic matter and sulphide and 5: residual.

Certified reference material (BAM-U110) from the Federal Institute for Materials Research and Testing and reagent blanks were used as quality control samples during the analyses. We obtained recoveries of 92-109% for Cd, 91-98% for Cu, 94-105% for Pb and 91-99% for Zn.

2.2.3. Statistical analysis

Microsoft Excel was used to perform a descriptive statistical analysis of the data. Spearman correlation coefficient was used to estimate the relationship between chemical speciation and properties of soil and road dust. ANOVA test was used to identify differences among groups of variables using Tukey test. Principal Component Analysis was used to understand the correlations by grouping the variable into a few factors.

2.3. Results and discussion

2.3.1. Effect of population density on physical-chemical characteristics of soil and road dust

pH of the soil and dust samples ranged from neutral to moderately basic (Table 2.1), due to the presence of high carbonate of $> 300 \text{ g kg}^{-1}$ (Acosta et al., 2010). Salinity ranged between 0.5 to 1.5 dS m^{-1} and soils and road dusts are categorized as non-saline materials (Andrades, 1996). Organic carbon (OC) content was high in most of the soils, ranging from 13.2 to 37.1 g kg^{-1} and slightly lower in dust samples between 5.9 and 29.8 g kg^{-1} .

No statistical differences were found between pH value, salinity, carbonates and OC contents among soil and dust samples collected from similar population density areas. However, pH in natural soils and dust were higher than pH from the cities, which indicates that some urban activities (e.g. use of fertilizers/organic amendments in urban parks or traffic emissions) can acidify the dust/soil in urban areas. However, no

differences in pH were found between cities; indicating that an increase of population density does not affect the soil/dust pH.

In contrast, salinity in soils and dust from HD and MD cities was higher than natural area. The use of poor quality irrigation water and fertilizers in urban parks are likely the sources of salts in soils in cities (Vidal, 2002; Acosta et al., 2009). In addition, an increase in soil salinity with the population density was observed in the study. In urban parks in HD and MD cities, the trend can be due to high disturbance of vegetation and, therefore, high amount of fertilizers and water are necessary to maintain a good cover and vegetation health leading to increased salinity.

No differences were found between carbonate contents in soils and dust from cities and natural area, except for soils from MD where the carbonate content was low, this difference is likely due to geological background and not to the human activities, because carbonates is one of the most stable constituents in the soil under arid and semiarid climate.

Organic carbon content was higher in soils from the LD than soils from the others sites which can be related to the management of urban parks, where the organic matter accumulation are promoted by the application of organic amendments (Edmonson et al., 2014).

Table 2.1. Mean and (standard deviation) of physico-chemical properties of soil and road dust samples

	High density population		Medium density population		Low density population		Natural (no population)	
	Soil	Dust	Soil	Dust	Soil	Dust	Soil	Dust
pH	7.8(0.23)ab ^a	7.8(0.14)ab	7.69(0.44)a	7.51(0.31)a	7.76(0.33)ab	7.92(0.04)ab	8.36(0.3)c	8.27(0.28)b
Salinity (ds/m)	1.54 (1.68)d	0.52 (0.24)bc	1.36(0.98)c	0.49(0.44)bc	0.41(0.37)ab	0.29(0.07)ab	0.11(0.01)a	0.13(0.03)a
Carbonates (mg/kg)	345 (54)ab	421.4 (47)bc	283(64)a	336(22)ab	440(18)c	477(60)c	395(28)bc	404(52)bc
Organic carbon (mg/kg)	29.5 (9.5)bc	29.8 (6.8)bc	23.7(23.9)abc	25.8(11.4)abc	37.1(11)c	15.4(3.7)ab	13.2(2.7)ab	5.9(6.4)a
Total Zn (mg/kg)	75.2 (17.8)ab	203 (72)d	80.4(25.9)ab	149(21)cd	71.7(0.33)ab	105(10)bc	67(4.4)ab	50.3(25.3)a
Total Pb (mg/kg)	38.3 (23.6)ab	117 (19)c	57.2(27.2)abc	85.7(9.4)bc	41.2(9.8)ab	75.3(14.3)b	34.5(6.2)ab	27.8(15.9)a
Total Cu (mg/kg)	52.6 (39.4)b	134 (39)d	31.8(9.9)abc	75.4(22.9)cd	43.5(21.7)abc	68.7(21.1)bc	28.7(3.6)ab	19.5(9.1)a
Total Cd (mg/kg)	2.21 (0.76)b	1.07 (0.19)ab	1.08(0.23)a	1.55(0.24)ab	1.55(0.31)ab	1.28(0.12)ab	1.78(0.65)ab	1.19(0.63)ab
Total Cr (mg/kg)	23.9 (5)a	39.3 (10.8)c	24.2(7.6)a	28.7(3.6)ab	29(2)ab	23(2.8)a	30(9.7)ab	20.4(8.2)a
Total Ni (mg/kg)	46.4 (11.6)	41.7 (8.3)	40.9(12.4)	37.1(2.7)	37.9(2.8)	38.4(4.5)	46.7(4.8)	33(13.9)
Total Co (mg/kg)	26 (4.1)	23.3 (1)	20.9(2.9)	22.9(1.5)	21.4(0.7)	26.6(1.9)	24.3(1.3)	19(7.4)
DTPA Zn (mg/kg)	4.40(2.89)b	20.08(4.63)c	4.72(4.41)b	19.43(3.13)c	3.91(0.67)b	12.74(1.82)c	0.42(0.12)a	1.03(0.64)a
DTPA Pb (mg/kg)	4.26(2.99)ab	10.06(7.46)b	5.09(4.95)ab	4.93(2.26)b	1.51(0.43)ab	5.4(2.59)b	2.11(0.3)ab	1.47(1.95)a
DTPA Cu (mg/kg)	2.57(1.52)abc	16.20(6.74)d	2.72(2.39)abc	8.58(2.53)cd	23.4(41.5)cd	6.32(4.44)bcd	1.33(0.06)ab	0.71(0.37)a
DTPA Cd (mg/kg)	0.07(0.02)	0.03(0.01)	0.05(0.02)	0.04(0.01)	0.09(0.02)	0.04(0)	0.08(0.04)	0.05(0.01)
DTPA Cr (mg/kg)	0.16(0.06)	0.34(0.25)	0.2(0.05)	0.25(0.02)	0.13(0.03)	0.18(0.02)	0.19(0.05)	0.26(0.04)
DTPA Ni (mg/kg)	0.91(0.15)	0.67(0.2)	0.76(0.62)	0.49(0.13)	0.85(0.08)	0.42(0.1)	0.52(0.06)	0.36(0.19)
DTPA Co (mg/kg)	0.32(0.06)	0.27(0.1)	0.27(0.17)	0.25(0.04)	0.2(0.03)	0.15(0.03)	0.29(0.07)	0.18(0.1)
Soluble Zn (mg/kg)	0.21(0)ab	0.46(0.49)c	0.15(0.03)ab	0.35(0.14)c	0.12(0.04)a	0.17(0.01)ab	0.13(0.03)a	0.2(0.04)ab
Soluble Pb (mg/kg)	0(0)	0(0)	0(0)	0.04(0.08)	0(0)	0(0)	0(0)	0(0)
Soluble Cu (mg/kg)	0.38(0.1)a	0.9(0.61)c	0.29(0.06)a	0.81(0.3)c	0.31(0.09)a	0.45(0.11)ab	0.33(0.12)a	0.37(0.03)ab
Soluble Cd (mg/kg)	0.04(0.02)ab	0.01(0.01)a	0.02(0.01)a	0.02(0.01)a	0.07(0)b	0.01(0.01)a	0.06(0.03)b	0.03(0.01)a
Soluble Cr (mg/kg)	0.12(0.04)ab	0.18(0.06)bc	0.13(0.04)ab	0.21(0.02)c	0.09(0.01)a	0.16(0.03)bc	0.1(0.03)ab	0.14(0.02)abc
Soluble Ni (mg/kg)	0.3(0.14)abc	0.16(0.07)abc	0.24(0.1)abc	0.22(0.1)abc	0.37(0.13)bc	0.16(0.13)ab	0.38(0.11)c	0.15(0.09)a
Soluble Co (mg/kg)	0.21(0.1)c	0.12(0.07)ab	0.12(0.07)ab	0.13(0.07)ab	0.06(0.07)a	0.14(0.03)ab	0.09(0.04)ab	0.04(0.02)a

^aMeans(standard deviations) followed by different letters are significantly different ($p < 0.05$).

2.3.2. Population density and total metal concentrations in soil and road dust

Significant statistical differences were observed for total Zn, Pb, Cu and Cr concentrations between the soil and dust at HD city. Total Zn content at MD city was higher in dust than the soil, while metals in soil and dust were similar to natural area in LD site. The above observations suggest that if the same source of metals for both materials is considered, dust is more prone to accumulate metals than soils, especially in HD city. This may be due to that road dust is more close to the pollution sources (e.g. traffic emissions) than soil; in addition the dust's finer particle composition and the higher surface-to-mass ratio promote heavy metals retention in dust (Duong and Lee, 2011). These results are in agreement with other relevant studies (Wei et al., 2010; Saeedi et al., 2013) which reported that Pb and Zn concentrations in road dust were higher than those in urban soils.

In addition, no differences were observed in the concentrations of Zn, Pb, Cd, Cu and Cr in natural soils compared with urban soils, indicating that the urban activities and the density of population from the studied cities do not increase the metal concentrations in soils. In contrast, significant differences were found between road dust collected in natural and urban areas, indicating that road dust is a sink for metals in urban environments (Shi et al., 2008; Kumar et al., 2013; Du et al., 2013).

Total concentrations of Zn, Pb, Cu and Cr in dust from HD city are significantly higher than the concentrations of these metals from LD city, however MD city has concentrations statistically similar to the reported for both HD and LD cities (Table 2.1). Therefore, the effect of population density in the accumulation of these metals in road dust is only observable when the population density is highly increased. It has been reported that Zn and Cu comes from car components and corrosion of metallic parts, tyre abrasion or lubricants (Markus and McBratney, 1996; Wickle et al. 1998; Jiries et al., 2003; Al-Khashman, 2004) while Cr comes from chrome-plating of some motor vehicles (Al-Shayep and Seaward, 2001) and atmospheric deposition (Shi et al., 2008).

No differences were found in the total concentrations of Ni and Co between soils and dust between cities and natural area, suggesting that the source of these metals is the geological material of the area studied.

2.3.3. Effect of population density on chemical speciation of trace metals

Single extraction procedures

Statistical differences were observed for DTPA extractable Zn between soil and dust in each city, and for DTPA extractable Cu in the HD city (Table 2.1). These observations indicate that there is a higher risk of Zn and Cu uptake from dust than from soil. However, although urban activities increase the bioavailability of metals, especially in dust and for Zn, Pb and Cu, the population density is not a factor in increasing the bioavailability of metals (Table 2.1). In contrast, no differences were found in the DTPA extractable concentrations of Cd, Cr, Ni and Co between soils and dust between cities and natural area.

Concentrations of water soluble Cu and Zn were statistically higher in the dust than soils from HD and MD cities, and therefore higher risk of metals mobility is expected from road dust. In addition, in urban sites an increase of the Cu and Zn mobility in dust compared with natural areas was reported (Shi et al., 2008), however no effect of population density was found.

Sequential extraction procedure

Copper dominated in the residual fraction of soils from the three cities, while dust samples were dominated by oxidizable fraction in HD city, and oxidizable and residual fractions in both MD and LD cities (Fig. 2.5 and Table 2.2). These observations indicate that Cu can be mobilized after organic matter mineralization (Ma and Rao, 1997; Gupta and Chen, 1975; Harrison, 1981; Hickey and Kittrick, 1984; Li et al., 2013).

Fig. 2.5 Chemical partitioning of soil and dust samples of the three cities and natural area

Table 2.2. Concentration of metal (mg kg⁻¹) from sequential extraction procedure

		HD city		MD city		LD city		Natural area	
		Soil	Dust	Soil	Dust	Soil	Dust	Soil	Dust
Copper	Exchangeable	0.94	1.46	0.93	1.97	0.91	1.48	0.78	0.93
	Carbonates	1.96	9.16	1.71	4.51	1.64	4.74	2.00	1.33
	Reducible	3.89	17.52	3.13	5.03	3.81	5.11	3.30	3.01
	Oxidizable	6.92	65.07	7.52	30.90	9.22	29.76	1.02	1.64
	Residual	39.92	36.59	18.12	32.93	24.67	31.68	21.94	14.61
	Recovery (%)	102	96	99	100	93	106	101	110
Zinc	Exchangeable	0.21	0.92	0.33	0.91	0.18	0.75	0.24	0.80
	Carbonates	3.56	59.41	3.67	28.75	2.44	16.54	1.35	1.80
	Reducible	25.97	97.07	27.76	77.72	23.37	42.48	5.44	10.76
	Oxidizable	3.34	12.26	3.10	7.52	2.69	3.49	0.85	1.40
	Residual	39.65	49.31	44.67	35.57	43.03	43.57	57.53	36.51
	Recovery (%)	97	103	99	100	100	102	98	102
Chromium	Exchangeable	1.14	0.48	0.70	1.04	0.82	0.80	1.40	0.77
	Carbonates	2.22	2.50	2.27	2.27	1.75	2.23	2.72	1.89
	Reducible	7.76	16.60	7.23	15.19	10.27	12.35	8.97	7.74
	Oxidizable	2.80	3.31	2.59	3.28	5.14	1.68	2.90	1.05
	Residual	10.72	17.38	11.42	8.17	11.26	8.30	16.27	9.51
	Recovery (%)	103	105	100	104	101	110	108	103
Lead	Exchangeable	0.00	0.00	0.54	0.20	0.25	0.12	0.73	0.44
	Carbonates	7.86	12.66	5.90	8.15	4.63	7.89	6.07	5.98
	Reducible	15.36	61.28	12.45	40.39	14.02	16.97	12.87	7.03
	Oxidizable	0.89	0.86	0.76	1.22	1.51	1.27	0.54	0.53
	Residual	16.16	42.98	39.33	39.40	21.08	51.38	14.34	14.81
	Recovery (%)	105	98	103	104	101	103	100	104
Nickel	Exchangeable	0.93	1.57	1.13	2.54	0.26	2.35	1.37	1.79
	Carbonates	5.04	4.44	4.81	4.65	4.44	4.69	5.55	4.19
	Reducible	8.84	10.82	8.41	8.73	10.15	9.85	9.79	8.54
	Oxidizable	4.79	3.51	4.12	3.60	5.20	3.02	4.53	2.46
	Residual	26.01	23.77	22.01	16.83	16.37	21.15	26.23	16.97
	Recovery (%)	98	106	99	98	96	107	102	103
Cobalt	Exchangeable	0.41	0.95	0.55	1.35	0.34	1.31	0.64	1.04
	Carbonates	3.43	3.12	3.45	3.51	3.24	3.55	3.69	3.33
	Reducible	5.87	7.02	5.64	6.07	6.61	7.23	6.31	5.99
	Oxidizable	1.25	1.59	1.51	1.29	1.44	0.88	1.15	0.90
	Residual	15.34	11.03	10.77	10.39	10.72	14.66	12.34	9.84
	Recovery (%)	101	104	105	99	105	104	99	111
Cadmium	Exchangeable	0.13	0.16	0.21	0.19	0.19	0.18	0.08	0.14
	Carbonates	0.39	0.07	0.13	0.08	0.12	0.24	0.13	0.11
	Reducible	0.65	0.27	0.47	0.44	0.70	0.55	0.57	0.18
	Oxidizable	0.29	0.11	0.13	0.13	0.17	0.05	0.20	0.06
	Residual	0.88	0.52	0.20	0.48	0.38	0.25	0.84	0.61
	Recovery (%)	107	106	106	86	100	99	102	93

In addition, Cu distribution in the organic phase in natural soil/dust were lower than those reported in the urban soils/dusts, which can be related to the higher amount of organic matter in urban areas and indicates that Cu in natural areas come from geological material, because the highest concentrations of Cu were reported in the residual phase.

Zinc was dominant in the residual phase in soils from the three cities, while for dust samples the reducible phase was the most important fraction in HD and MD cities, whilst at LD city had obtained similar contents for reducible and residual phases (Fig. 2.5 and Table 2.2). Therefore, zinc is immobilized more in the soil than dust and more in LD than HD and MD sites. This indicates that Zn can be easily mobilized from dust in cities with higher population density. Zn bound to reducible phase in the soil and dust and bound to carbonates in dust were higher in urban areas than those reported in natural areas. These results suggest that Zn in natural areas originates from geological material due to its highest concentration in the residual phase.

The largest fraction of Pb in soils was observed in the residual and reducible phases in HD city while MD and LD cities solely showed major association with residual phase. Lead in the road dust was dominantly associated with reducible phase in HD city while the reducible and residual had the highest Pb content in MD city. However, Pb was primarily associated with residual phase in LD city. These results suggest that an increase in population density is proportional to Pb associated with the more reducible phase. A comparison of urban and natural soils revealed that the metal fractionations in HD and natural sites were very similar; while residual phase at MD and LD cities were higher than natural area. In contrast, 55% of Pb was associated with the residual phase in dust from natural areas while in HD, Pb in residual fraction was less than 40 %. In addition more than 50 % and 20% of Pb were bound to Fe-Mn oxides in dust from HD and natural areas, respectively (Fig. 2.5). These results suggest that soil is not a good material to predict potential risk of Pb mobilization associated with population density in urban areas, as no differences were observed in the chemical distribution among cities and natural areas.

Residual phase dominated the distribution of Cr, Ni and Co in both soils and dusts in all study sites, except for Cr in MD and LD which dominate the reducible phase (Fig. 2.5). In addition, the distribution of these metals in the different phases of natural soils and dust

are similar to those reported in urban areas, indicating that the distribution of these metals are not affected by population density, suggesting a geological origin of these elements (Hickey et al. 1984 and Li et al. 2013). Metals bound to residual phase usually suggest a non-anthropogenic source as they are incorporated in the lattice of minerals (USEPA, 2000; Shi et al., 2008).

In the soil samples, Cd in the residual phase at HD city was about 37%, 41 % and 45% at MD and LD cities, respectively. For dust samples, chemical partitioning was dominated by the residual phase in HD city and reducible phase in LD city. In MD city both residual and reducible phases had similar dominance with 36% and 33% respectively. Cadmium bound to reducible phase can become easily mobile and more available than oxidizable and residual phases, under pH and Eh variations, and therefore higher risk of mobility is expected in MD and LD cities than HD city. In addition, only the HD city had the similar Cd fractionation to those of the natural areas. These results suggest that population density does not affect the distribution pattern of Cd in soils and dust, and therefore other factors such as physico-chemical properties could influence the behaviour of this element (Ma and Rao, 1997; Osakwe, 2013).

2.3.4. Behaviour of heavy metals in the soil and road dust

Zinc

In soils, positive correlations were found among OC, total, DTPA extractable metals and carbonate, reducible and oxidizable phases for soil samples, grouped in Factor 1 (Table 2.3). This suggests that an increase in organic matter will promote Zn-binding to oxidizable phase as well as the distribution of metals bound to carbonate, reducible and oxidizable phases are controlled by its total concentration. In contrast, Factor 2 includes pH, electrical conductivity and soluble metal. Negative value of pH indicates that if pH is increased the concentration of soluble metals will be decreased. For dust samples, the results indicate that distribution of Zn between the solid phases is not controlled by physico-chemical properties of dust, but it is affected by its total concentration (Table 2.3).

Table 2.3. Spearman correlation coefficients (**P<0.01 and * p<0.05; nd.: non-detected)

		Soil							Dust						
		pH	Electrical Conductivity	Carbonates	Organic Carbon	Total Metal	DTPA Metal	Soluble Metal	pH	Electrical Conductivity	Carbonates	Organic Carbon	Total Metal	DTPA Metal	Soluble Metal
Copper	Exchangeable	.018	.076	-.110	.073	.030	.038	-.205	-.789	.551	-.201	.525	.640	.569	.794
	Carbonates	.192	-.070	.024	-.201	.461	.495	.335	-.488	.605	.215	.592	.815	.856	.531
	Reduc ble	-.017	-.084	.237	.197	.451	.672	.048	-.409	.618	.203	.522	.767	.718	.466
	Oxidizable	-.620	.577	-.276	.674	.715	.778	.106	-.417	.787	.096	.828	.956	.838	.598
	Residual	-.208	.240	-.067	.262	.690	.370	.485	-.468	.838	-.123	.574	.836	.458	.436
Zinc	Exchangeable	.150	-.023	-.169	-.065	-.009	-.105	.101	-.096	.145	-.075	.093	.228	.191	-.002
	Carbonates	-.622	.714	-.464	.571	.534	.903	.344	-.436	.694	-.010	.551	.642	.654	.206
	Reduc ble	-.642	.685	-.411	.692	.721	.876	.327	-.473	.608	.037	.512	.647	.615	.251
	Oxidizable	-.692	.734	-.411	.814	.683	.887	.421	-.439	.699	-.037	.564	.652	.645	.193
	Residual	.247	-.441	.290	-.156	.078	-.395	-.172	.189	.230	-.071	.115	.002	-.086	-.321
Chromium	Exchangeable	.363	-.255	.107	-.166	-.022	-.187	-.200	-.311	-.174	-.498	-.194	-.257	.196	.330
	Carbonates	.463	-.468	.226	-.519	.154	.357	-.040	-.281	.630	.029	.611	.466	.075	.554
	Reduc ble	.346	-.451	.676	-.174	.286	-.243	-.327	-.436	.551	-.037	.647	.740	.005	.445
	Oxidizable	-.213	.032	.412	.525	.327	-.036	-.141	-.650	.740	-.150	.900	.659	-.157	.498
	Residual	-.064	-.038	.128	.043	.867	-.047	-.214	.105	.042	.032	.350	.627	-.081	-.373
Lead	Exchangeable	.448	-.537	.161	-.517	-.075	-.110	nd	.211	-.638	-.298	-.799	-.675	-.414	nd
	Carbonates	-.093	.246	-.077	.031	.533	.625	nd	-.292	.664	-.069	.696	.897	.831	nd
	Reduc ble	-.364	.314	-.094	.404	.737	.783	nd	-.473	.691	-.157	.765	.890	.647	nd
	Oxidizable	-.447	.381	-.218	.429	.312	.268	nd	-.422	.230	.098	.289	.368	.314	nd
	Residual	-.414	.268	-.162	.099	.833	.543	nd	-.456	.662	-.098	.505	.679	.694	nd
Nickel	Exchangeable	.523	-.414	-.072	-.356	.120	-.254	-.001	-.529	.128	-.379	-.036	-.042	-.110	.131
	Carbonates	.565	-.486	.358	-.596	.154	-.257	.288	-.004	-.385	-.072	-.298	.334	-.004	-.210
	Reduc ble	.162	-.229	.536	-.108	.077	.168	.220	.215	.159	.378	.071	.408	.450	-.162
	Oxidizable	-.380	.261	.134	.724	.142	.457	.110	-.627	.610	-.409	.637	.047	.485	.228
	Residual	.100	.002	-.179	.050	.816	.100	-.067	.032	.083	.355	.066	.740	-.069	-.270
Cobalt	Exchangeable	.428	-.256	.082	-.386	.050	.120	-.188	-.408	.094	-.303	.004	.264	.087	.262
	Carbonates	.436	-.407	.383	-.558	.054	-.104	-.262	0.000	-.502	.020	-.481	.097	-.479	-.399
	Reduc ble	.275	-.315	.536	-.238	.211	-.099	-.141	.031	-.029	.741	-.023	.480	-.592	-.234
	Oxidizable	-.413	.305	-.109	.578	-.079	.078	.109	-.323	.683	-.259	.816	-.130	.455	.177
	Residual	.081	.091	-.025	.198	.590	.164	.118	.064	.029	.110	-.272	.600	-.286	.228
Cadmium	Exchangeable	-.533	.498	-.286	.290	-.299	-.348	-.444	-.146	.263	-.335	.251	.402	.151	.079
	Carbonates	-.267	.428	-.185	.328	.598	.112	-.131	.170	-.066	.412	-.173	.279	-.110	-.206
	Reduc ble	.035	-.002	.041	.280	.812	.477	.240	-.458	.223	.033	.028	.476	-.367	-.278
	Oxidizable	-.068	.204	-.043	.224	.857	.440	.234	-.519	.293	-.221	.546	.207	-.057	-.058
	Residual	.303	-.192	.236	-.046	.910	.596	.367	-.087	-.013	.034	.032	.422	.013	.278

Table 2.4. Principal component analysis

	Zinc							Cadmium							Copper						
	Soil				Dust			Soil				Dust			Soil					Dust	
	1	2	3	4	1	2	3	1	2	3	1	2	3	4	1	2	3	4	5	1	2
pH	-.45	-.71	.01	.15	-.51	-.12	-.64	-.01	.33	-.84	-.79	-.37	.05	-.20	.01	-.74	-.49	-.16	.00	-.26	-.85
Electrical Conductivity	.05	.84	.30	-.18	.25	.44	.69	.14	-.49	.54	.70	.16	-.21	.02	-.02	.24	.83	.02	.02	.28	.79
Carbonates	-.28	-.22	-.70	.40	.03	.11	-.80	-.03	-.60	-.29	-.56	.13	-.58	.25	.00	-.02	-.80	.07	.18	.31	-.56
Organic carbon	.70	.44	-.24	.16	.84	.21	.33	.16	.20	.81	.78	.07	-.28	-.11	.09	.90	.05	-.01	.05	.68	.49
Total metal	.87	.08	.30	.17	.83	-.20	.23	.95	.24	-.07	.14	.64	.11	.72	.96	.11	.02	.14	.04	.84	.46
Extractable metal	.86	.24	.06	-.26	.89	.26	.27	.48	.80	.08	-.23	-.09	.85	-.01	.00	.19	-.11	.83	.08	.86	.12
Soluble metal	.19	.58	.03	-.09	.62	-.05	-.11	.18	.88	-.12	-.16	.05	.90	.25	.15	-.02	.05	.29	.73	.57	.44
Exchangeable phase	.10	.06	.87	.15	-.29	.82	.02	-.29	-.27	.66	.29	.82	.24	.03	.13	.01	.30	.23	-.76	.32	.79
Carbonates phase	.76	.07	.16	-.51	.55	.79	.06	.84	-.30	.07	-.52	.69	-.32	-.07	.31	-.54	.16	.65	.17	.93	.09
Reducible phase	.84	.18	.24	-.30	.57	.73	.04	.75	.27	.16	.14	.89	-.24	-.14	.50	-.07	-.10	.40	-.25	.87	.06
Oxidizable phase	.86	.38	.11	-.07	.53	.78	.12	.93	.04	.08	.72	-.11	.08	.32	.18	.60	.26	.55	-.14	.86	.33
Residual phase	-.09	-.25	.04	.87	-.17	.79	.06	.84	.28	-.26	.11	-.20	.06	.94	.97	.04	.02	-.05	.09	.30	.75

	Chromium							Lead							Nickel						
	Soil				Dust			Soil				Dust			Soil					Dust	
	1	2	3	4	1	2	3	1	2	3	1	2	3	1	2	3	4	5	1	2	3
pH	.64	.55	-.13	-.21	-.66	.27	.55	-.12	-.60	-.65	-.13	-.79	.38	-.60	.40	.12	-.43	.29	-.65	-.13	-.58
Electrical Conductivity	-.22	-.78	.08	.12	.79	-.38	.07	.06	.52	.53	.23	.65	-.49	.20	-.49	.07	.77	-.14	.79	-.12	.20
Carbonates	-.04	.78	.20	-.05	-.22	.64	.07	.19	-.61	-.23	-.07	.05	.93	-.05	.87	-.07	-.08	-.28	-.41	.38	-.34
Organic carbon	-.81	-.18	.10	.19	.85	.15	-.29	.24	.22	.67	.48	.76	-.11	.84	-.16	.15	-.06	-.30	.86	.22	-.07
Total metal	-.10	.16	.96	.00	.80	.49	.06	.69	.67	.08	.82	.53	-.07	.17	.03	.94	.15	-.03	.16	.94	.09
Extractable metal	.24	-.40	.14	.72	.41	-.30	.83	.76	.42	.27	.96	.13	-.06	.79	-.02	.04	.43	.24	.85	.32	-.14
Soluble metal	-.03	-.41	-.13	.78	.60	-.64	.17	nd	nd	nd	nd	nd	nd	-.03	.31	.07	.77	-.02	.59	-.33	.31
Exchangeable phase	.29	-.15	.04	-.63	-.15	-.79	-.24	-.05	.06	-.83	-.25	-.75	-.19	-.08	-.07	-.12	-.13	.93	-.04	.08	.94
Carbonates phase	.85	.06	.26	.10	.75	.02	.38	.84	-.13	.09	.90	.26	.02	-.58	.37	.19	.25	.46	.12	.77	.54
Reducible phase	-.10	.72	.19	-.17	.84	.17	.08	.87	.09	.30	.57	.63	-.06	.01	.76	-.04	.12	.17	.30	.83	.06
Oxidizable phase	-.75	.33	.14	-.03	.88	.01	-.34	.24	.10	.61	.15	.50	.21	.84	.22	.24	.00	.03	.75	.11	.06
Residual phase	.07	.06	.94	-.04	.42	.75	.00	.34	.87	-.08	.71	.23	-.11	.05	-.12	.96	-.04	-.07	-.15	.79	-.12

	Cobalt							
	Soil				Dust			
	1	2	3	4	1	2	3	4
pH	-.57	.57	.16	.23	-.40	-.56	-.42	.22
Electrical Conductivity	.78	-.11	-.13	-.43	.00	.61	.68	-.21
Carbonates	-.21	.01	.12	.77	.08	-.15	-.06	.92
Organic carbon	.09	-.86	.11	-.16	.01	.92	.12	-.03
Total metal	.23	.13	.83	.25	.89	.28	.13	.20
Extractable metal	.86	-.01	.08	.22	-.31	.53	.20	-.59
Soluble metal	.75	-.04	.28	-.31	.07	.10	.96	-.04
Exchangeable phase	.02	.43	-.47	-.09	.80	-.07	.20	-.39
Carbonates phase	.13	.78	-.05	.18	.95	-.03	-.18	.01
Reducible phase	-.02	.21	.05	.80	.76	.35	-.18	.44
Oxidizable phase	.20	-.68	-.16	.05	.13	.93	.07	-.11
Residual phase	-.05	.00	.92	-.04	.76	-.07	.22	.26

Cadmium

The distribution of Cd in the different solid phases in urban soils is controlled by its total concentration as shown in Table 2.4 (Factor 1) and Table 2.3. Factor 2 grouped carbonates, DTPA extractable and water soluble Cd, suggesting that carbonates enhance precipitation of Cd and its immobilisation (Porta et al., 1999). Factor 3 included positive correlations between Cd bound to exchangeable phase, pH and OC content; which suggests that a variation of pH can solubilise or immobilise Cd (Porta et al., 1999).

For dust samples, the results from PCA indicate that distribution of Cd in solid phases except oxidizable and residual phases is not controlled by any physico-chemical properties and its behaviour depends on other factors such as total Cd content. Metal bound to oxidizable phase is strongly affected by pH and OC content, therefore variation in these variables will cause a mobilization of Cd.

Copper

Factor 1 consists of total Cu with reducible and residual phases. In addition, Spearman correlation matrix indicates that Cu distribution in various chemical fractions depended on the total Cu content of soils (Table 2.3). As the total Cu concentration in soils increased, the concentration of Cu bound to reducible phase and bound to organic fractions increased (Ma and Rao, 1997). DTPA extractable Cu and Cu bound to carbonate phase are grouped into Factor 4, likely due to DTPA extraction of some Cu bound to carbonates and therefore an increase in Cu-carbonate promotes a higher Cu extraction by DTPA (Gupta, 1996).

For dust samples, Factor 1 includes OC content, total Cu, DTPA extractable Cu and concentrations of Cu bound to carbonate, reducible, and oxidizable phases. In contrast, Factor 2 includes pH, EC, carbonate content and Cu bound to exchangeable and residual phases. Correlation among these variables were pH-exchangeable phase, organic carbon-oxidizable phase, total Cu-Cu bound to carbonate; total Cu-Cu bound to reducible phase, etc. Therefore, copper behaviour is affected by both physico-chemical properties of dust and total concentration of Cu in this material.

Chromium

Factor 1 shows the influence of pH in the Cr bound to carbonate phase due to the precipitation of Cr-carbonates; and strong relationship between OC and oxidizable phase. Factor 2 includes carbonate content, Cr bound to reducible phase and electrical conductivity. In addition, total concentration of Cr controls the residual phase as shown in Factor 3. The relationship between total metals and residual fraction is included in Factor 4. Therefore, behaviour of Cr in urban soils is mostly affected by soil physic-chemical properties, although Cr bound to residual phase is directly controlled by its total concentration in the soil parent material.

For dust samples, positive correlations were found between total metal and reducible and oxidizable phase; OC and carbonate, reducible and oxidizable phase and between EC and carbonate and oxidizable phases (Factor 1). In addition, carbonate content and Cr bound to exchangeable phase are inversely associated in Factor 2, indicating that an increase in carbonates promotes a decrease in the exchangeable fraction of Cr. Similar to urban soils, distribution of Cr in solid phases of dust is mostly affected by physic-chemical properties.

Lead

A positive correlation was found between total Pb concentration and residual phase, followed by reducible and carbonate phases as indicated in Factors 1 and 2. In addition, pH, EC and OC content were closely related to residual, exchangeable and oxidizable phases in Factors 2 and 3.

The behaviour of Pb in urban dust is similar to that reported for the urban soil, where total Pb concentration controls the amount of Pb bound to carbonate, reducible and residual phases, and pH, EC and OC are the main properties affecting the concentration of Pb bound to exchangeable, reducible and oxidizable phases.

Nickel

For urban soil, Factor 1 included OC, pH, DTPA extractable Ni and Ni bound to carbonate and oxidizable phases (Table 2.4) which among others, indicates that increase in pH or OC in dust promotes Ni association with carbonates and organic matter through

precipitation or chelation. In contrast, total metal concentration controls the Ni concentration in the residual phase as indicated in Factor 3. Also, the results showed increase in the soil salinity could increase the water soluble Ni (Factor 4).

For dust samples, Factor 1 grouped pH, EC, OC, DTPA extractable and water soluble Ni, and Ni bound to oxidizable phase. Organic matter is positively correlated with oxidizable phase, while likely pH and EC are the responsible of water soluble Ni concentration (Table 2.3). Dust samples showed a positive correlation between the total Ni and residual phase, both include in Factor 2 together with the Ni concentrations bound to carbonate and reducible phases. According with PCA analysis, concentration of exchangeable Ni is not affected by any physical-chemical properties neither total Ni concentration because no other variable is grouped in Factor 3, however a negative correlation with pH was found (Table 2.3).

Cobalt

For urban soil, pH, EC, DTPA extractable and water soluble Co are associated with each other in Factor 1 (Tables 2.3 and 2.4). Positive correlations were found between pH and OC and Co concentration bound to carbonate and oxidizable phases (Factor 2). Factor 3 showed a strong relation between total metals and residual phase and Factor 4 between carbonate concentrations and reducible phase. These results show that Co concentration in most labile phases (water soluble and exchangeable) are controlled by pH, while most immobilize phase (residual) is associated with total concentration of Co.

For urban dust, the Co concentration bound to most of the phases (except oxidizable phase) is controlled by its total concentration (Factor 1). However, the positive correlation was found between OC and oxidizable phase (Factor 2), indicating that organic matter is a sink of Co in urban dust.

2.4. Conclusions

In urban areas a decrease of dust/soil pH and an increase salinity compared with natural areas was reported. However, an increase of population density does more affect the pH in studied urban areas. In contrast, an increase in soil salinity with the population density was observed.

Density of population does not increase Zn, Pb, Cu and Cr concentrations in soils. In contrast, increase in total metal concentrations in road dust was reported when the density of population was increased. This suggests that road dust is a sink of metals in urban environments.

Copper, Zn, Pb, Cr distributions were dominated by residual fraction in soils and by oxidizable fraction for Cu and reducible phase for Zn, Pb and Cr in dust samples, which indicates that these metals can be mobilized more easily from the dust than soil. However, the distribution of Ni and Co is not affected by population density. In soils and dusts, Cd was dominated by the residual phase at HD city while the reducible phase dominates for the MD and LD cities, therefore higher risk of Cd mobility is expected in MD and LD cities than HD city. Results suggest that an increase in the population density increase the percentage of Pb and Zn associated with the more labile phase in dust samples. However, fractionations of Cr, Cu, Co and Ni in the different phases were not affected by the population density in dust.

The behaviour of Zn and Co in soil is affected by both physic-chemical properties and total metal concentration while dust is mainly affected by its total concentration. Copper and Pb behaviour in the dust and soils are affected by both physical-chemical properties and total concentration. The behaviour of Cd in the soil and dust is mainly affected by its total concentration. In contrast, the behaviour of Cr and Ni in the soil and dust is mainly affected by physical-chemical properties.

Chapter 3

**SOIL OR DUST FOR
HEALTH RISK
ASSESSMENT
STUDIES IN URBAN
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Chapter 3

SOIL OR DUST FOR HEALTH RISK ASSESSMENT STUDIES IN URBAN ENVIRONMENT

Abstract

In order to identify the best material (soil or dust) to be selected for health risk assessment studies, road dust and urban soil from three cities with different population densities were collected, and size fractions were analysed for metal content (Pb, Zn, Cu, Cd, Cr, Co, and Ni). Results showed similar distribution of the size particles among cities, predominating fractions between 75µm and 2000µm in road dust and particles below 75µm in soil. Metals were mainly bound PM10 fraction in both soil and road dust increasing the risk of adverse health effects, overall through inhalation exposure. The risk assessment showed that the most hazardous exposure pathway was the ingestion via, followed by dermal absorption and inhalation routes. Values of hazard quotient showed that the risk for children due to the ingestion and dermal absorption was higher than adults, and slightly larger at PM10 comparing to <75µm fraction for the inhalation route. Higher risk values were found for road dust although any hazard index or cancer risk index value did not overreach the safe value of 10⁻⁶.

3.1.Introduction

Urban activities release a variety of potentially harmful pollutants to the environment, especially metals and organic compounds (Wong et al. 2006). Atmospheric particles deposition induces metal accumulation in surface soil and road dust causing environmental and health risk (Acosta et al. 2015). Recent researches are focused on the concentration of metals in bulk soil and road dust (Shi et al. 2008; Sun et al. 2010; Duong et al. 2011) however the concentration in different particles size fractions is critical to estimates the potential contributions to environment safety and health (Han et al. 2008).

Generally, trace metals are found associated to finer particles, especially to PM₁₀ and PM_{2.5}, causing serious risk on human health because of the incorporation of metals to the human body through the mouth and nose (Ljung et al. 2008; Kong et al. 2011; Cao et al. 2011; Boisa et al. 2014).

Human health risk assessment is the process to estimate the nature and probability of adverse health effects in humans who may be exposed to chemicals (US-EPA, 2016a). Human are exposed to pollutants by three main pathways: ingestion, inhalation and dermal absorption of soil and dust. The health risk assessment has usually been investigated separately for soil (Izquierdo et al. 2015; Teng et al. 2015; Huang et al. 2016; Chen et al. 2016) and dust (Ferreira-Baptista et al. 2005; Kong et al. 2011; Du et al. 2013; Li et al. 2013; Liu et al. 2014; Wang et al. 2016; García-Rico et al. 2016) and few authors have investigated both soil and dust (De Miguel et al. 2007).

The aim of this study was assessed the health risk of metal exposure for children and adults in three cities with different population densities and elucidate which material, soil or dust, contributes more to increase the health risk. In addition, inhalation hazard quotient from PM₁₀ and from <75µm fraction were calculated and compared between each other in order to evaluate the difference.

3.2. Materials and methods

3.2.1. Study area

The study area consists of three different populated urban settlement located in Murcia Region (SE of Spain). Murcia city represents high population density (HD = 498 person/km²) while Totana and Abaran cities have medium (MD = 106 person/km²) and low (LD = 27.8 person/km²) population densities, respectively.

The climate of the region is Mediterranean semiarid with 18°C annual mean temperature and 350 mm annual mean rainfall. The weather and the social habits invite people to spend time at streets and gardens, especially children.

Difficulty to collect soil samples in urban areas has limited the sampling to parks and urban gardens. Most of the parks from each city were sampled, which were selected taking into account their spatial distribution, size and use for the population. Concretely, thirty surface soil samples were collected for the three cities (Fig.3.1). Each soil sample was taken from the surface (0–5 cm) using a soil spade and was composed by 3 sub-samples collected 1 m apart from the vertices of a triangle to form a composite sample. We used surface soil because metal additions to soils in urban areas occur mostly on top soil (De Miguel et al. 1998; Porta et al. 1999).

During the sampling we tried to collect both materials, soils and dusts, as closer as possible, however sampling of dust was restricted to those roads where dust is accumulated in enough amount to be sampled, as is showed in Fig. 3.1, Specifically, thirteen street dust samples were collected by sweeping an area of 1 m² using a polyethylene brush and getting 3 sub-samples for each site. The sweep was slow and directly into the plastic bag in order to avoid dust re-suspension (Acosta et al. 2011; Zhang et al. 2012; Du et al. 2013).

Fig. 3.1. Sampling map. At the top of the figure HD city (left) and MD city (right) and at the bottom LD city; Black speckles represent soil samples and white triangles represent dust samples

3.2.2. Sample analysis

Soil and dust samples were dried for 48 hours at 40°C and passed through a 2 mm metal-free sieve. A subsample of bulk sample is separated for fractionating in three particle size fractions using two methodologies. For fine particles (PM₁₀), 50 g of soil/dust is dispersed with Na-polyphosphate for 8h by horizontal shaking (250 rpm), then a 1L glass column is filled with the soil dispersion and the fractions were separated by repeated sedimentation and decanting based in the Stokes' law (Ljung et al. 2008; Boisa et al. 2014; Li et al. 2017). For particles larger and smaller than 75µm, after oven-dry, a sieve of 75µm was used, shaking 10-minutes for each sample. The weight of each size fraction (<75 µm and >75 µm) is determined to calculate the distribution of each particle size fraction using a laser diffraction particle sizer (Mastersizer 2000).

One gram of each fraction, >75 μ m, <75 μ m and <10 μ m, and the bulk soil/dust sample were grounded and digested using 20 mL nitric/perchloric acid at 210 °C during 90 minutes. After cooling, 0.1 N HCl is added to fill a 100 mL volumetric flask (Risser and Baker 1990) and the total amounts of metals (Cd, Co, Cr, Cu, Ni, Pb, and Zn) were measured with ICP-OES and ICP-MS. Samples were analysed in triplicate and reference material (BAM-U110) and reagents blanks were used as quality control during the analysis.

3.2.3. Health Risk Assessment

Human health risk assessment consists of four stages (1) hazard identification, (2) toxicity assessment, (3) exposure assessment and (4) risk characterization (Lim et al. 2008). The exposure assessment evaluates the type and magnitude of exposures to chemical of potential concern at a site (US-EPA 2004). In general, exposure duration, exposure frequency and contact rate are likely to be the most sensitive parameters in an exposure assessment (US-EPA 1989).

Direct ingestion, fugitive dust inhalation and dermal absorption are common routes of human exposure to contaminant in the residential setting (US-EPA 1996).

The methodology used to calculate the exposure risk of soil and road dust metals has been recently used in risk assessment studies (Dehghani et al. 2017; Gope et al. 2017; Li et al. 2017; Li et al. 2017b) and was based on the USEPA methodology for risk assessment. The daily dose received through ingestion (D_{ing}), dermal (D_{dermal}) and inhalation (D_{inh}) routes were calculated using the equations (1)-(3) adapted from the US Environmental Protection Agency (1989, 1992, 1996, 2002, 2004).

$$D_{ing} = C \times \frac{IngR \times EF \times ED}{BW \times AT} \times 10^{-6} \quad (1)$$

$$D_{dermal} = C \times \frac{SL \times SA \times ABS \times EF \times ED}{BW \times AT} \times 10^{-6} \quad (2)$$

$$D_{inh} = C \times \frac{InhR \times EF \times ED}{PEF \times BW \times AT} \quad (3)$$

For carcinogens elements (Cd, Cr, Ni and Co), the lifetime average daily dose (LADD) was calculated for the inhalation route in order to assess the cancer risk (eq. 4) (Li et al. 2013; Lu et al. 2014; Dehghani et al. 2017).

$$LADD = \frac{C \times EF}{AT \times PEF} \times \left(\frac{InhR_{child} \times ED_{child}}{BW_{child}} + \frac{InhR_{adult} \times ED_{adult}}{BW_{adult}} \right) \quad (4)$$

where D ($\text{mg kg}^{-1} \text{ day}^{-1}$) is the daily dose intake through ingestion (D_{ing}), dermal absorption (D_{dermal}) and inhalation (D_{inh}). C is the concentration of metal (mg kg^{-1}) in the soil or dust. The ingestion rate (IngR) for this study is estimated in 100 mg day^{-1} for adults and 200 mg day^{-1} for children (US-EPA 2002), the inhalation rate (InhR) is estimated in $20 \text{ m}^3 \text{ day}^{-1}$ for adults (US-EPA 1986) and $7.6 \text{ m}^3 \text{ day}^{-1}$ for children (Lu et al. 2014). Exposure frequency (EF) is $122 \text{ day year}^{-1}$, the exposure duration (ED) is 24 years for adults and 6 years for children (US-EPA 2002). Standard body weight (BW) from US-EPA (1986) is 70 kg for adults and 15 kg for children. Data for dermal dose were recovered from RAGS part E (US-EPA 2004) being SL the skin adherence factor, that for this study is 0.07 mg cm^{-2} for adults and 0.2 mg cm^{-2} for children; SA is the exposed skin area, in this study 5700 cm^2 for adults and 8000 cm^2 for children. The ABS is the dermal absorption factor which was 0.001 (unitless) for all metals of this study.

The particulate emission factor (PEF) relates the concentration of contaminant in soil with the concentration of dust particles in the air. The default value calculated by US-EPA (1996) $1.32 \cdot 10^9 \text{ m}^3 \text{ kg}^{-1}$ has been used for this study. The average time (AT) for non-carcinogens is calculated as $ED \times 365$ days and for carcinogens 70×365 days (US-EPA 1989).

The concentration term (C) in the intake equation is an estimate of the arithmetic average concentration for a contaminant based on a set of site sampling results. Because of the uncertainty associated with estimating the true average concentration at a site, the 95% upper confidence limit (UCL) of the arithmetic mean should be used (USEPA 1992b). For this study we have used a non-parametric UCL method, the Chebyshev Inequality (US-EPA 2002b).

Risk characterization was assessed from the hazard quotient (HQ) for each metal at each site for non-carcinogens (eq.5) and cancer risk (CR) for carcinogens (eq.6).

$$HQ = \frac{D}{RfD} \quad (5)$$

$$CR = D \times SF \quad (6)$$

where D is the ingestion, dermal or inhalation calculated dose from equations 1 to 3; RfD is the corresponding reference dose that is defined as the intake or dose per unit of body weight ($\text{mg kg}^{-1} \text{ day}^{-1}$) that is unlikely to result in toxic (non-carcinogenic) effects to human populations, including sensitive subgroups. For carcinogenic metals, the dose (D) has been calculated as the lifetime average daily dose (LADD) that is multiplied by the corresponding slope factor (SF). It is used to express the cancer risk as an estimate of the upper-bound probability of an individual developing cancer as a result of exposure to a particular carcinogen.

Reference doses and slope factors (Cd, Co, Cr, Cu, Ni, and Zn) used in the study were taken from the Risk Assessment Information System (RAIS, accessed April 2016) and lead (Pb) values from De Miguel et al. (2007). Toxicity values for dermal absorption were calculates multiplying oral reference dose by gastrointestinal absorption factor. The inhalation reference dose for Cd, Co, Cu, Pb, and Zn were substituted by oral reference dose because of after inhalation, the absorption of the particle bound toxicants will results similar health effects as if the particles have been ingested (Van der Berg 1995; Ferreria-Baptista and De Miguel 2005; Li et al. 2013; Li et al. 2017; Li et al. 2017b).

The Hazard Index (HI) was the sum of the Hazard Quotient (HQ) from each pathway. Hazard Index values <1 means that there is no significant risk of non-carcinogenic effects while HI values >1 suggests that adverse effects may occur (US-EPA 2001 in Lu et al. 2014). For cancer risk, the acceptable value to ensure no risk ranges from 10^{-4} to 10^{-6} (Lu et al, 2014) that means from one additional case in a population of 1 million to one in 10,000 people is acceptable (Lim et al. 2008).

3.3. Results and discussion

3.3.1. Particle size distribution and metal concentration in the soil and road dust

Particle distribution was focused in three specific particles sizes: (1) $>75\mu\text{m}$ (coarse fraction), (2) $<75\mu\text{m}$ (fine fraction) and (3) particulate matter $<10\mu\text{m}$ (PM₁₀).

The mass proportion for each particle size fraction is referred to the total mass of particles in the soil or road dust samples. Thus, a similar pattern distribution was found for HD, MD and LD cities (Fig.3.2).

Fig.3.2. Particle size distributions (%) of soil and dust samples

Among the fractions, the highest percentages in the soil were obtained for fractions below $75\mu\text{m}$ in the HD city, while the coarse fraction ($75-2000\mu\text{m}$) ranges on 35-50% of the total particles. Contrary, road dust samples were governed by the coarse fraction, overreaching 70% of the total particles in the three cities.

Figure 3.3 shows the concentration of metals (Cd, Co Cr, Cu, Ni, Pb, and Zn) in different particle size fractions and the bulk sample for both soil and road dust. The percentages of metals loadings in different size fractions were calculated by multiplying metal concentrations with the mass percentage of each size fraction (Li et al, 2017b).

Highest metal concentration in the bulk soil was found at MD city for Pb, HD city for Co and HD and LD cities for Cu while Zn, Cd, Cr and Ni showed similar values for soils of the whole studied cities. Contrary, Pb, Cu, Cd and Cr of dust samples reported the highest

values at HD city and Co and Ni for HD and LD cities. Metal values obtained for the bulk soil were mostly higher than obtained by Acosta et al. (2011) and Chen et al. (2016) and lower those reported by Shi et al. (2008) for urban soil of Spain, Beijing and Shanghai.

Focus on differences among particles larger and smaller than $75\mu\text{m}$, highest concentrations of Pb, Zn, Cu and Cr were observed in fine particles ($<75\mu\text{m}$) for soil and dust, except for Pb in HD city and Cu in LD city dust where both metals are mainly bonded to the coarse fraction ($>75\mu\text{m}$). The same has been observed with Co for dust in the three cities and Ni in HD and MD cities dust.

Fig.3.3. Metal concentration by particle size in soil and dust

Highest metal concentration in the fine fraction ($<75\mu\text{m}$) of soil was found at MD city for Pb (75.5 mg kg^{-1}), Co (35 mg kg^{-1}) and Cr (43 mg kg^{-1}) and at HD city for Cu (123 mg kg^{-1}) while Zn, Cd, and Ni showed similar values for soils of the whole cities studied. Those values were higher than reported by Tang et al. (2017) for urban soils of Beijing and Dehghani et al. (2017) for urban soils of Teheran.

Contrary, the highest metal concentrations in the fine fraction of the road dust were reported for the HD city, whose dust values of Cu, Co and Ni were higher than reported by Tang et al (2017) and Li et al (2017) for road dust of Beijing and Chengdu (China).

Particles below $10\mu\text{m}$ (PM10) represented about 20% of weight in the bulk soil samples and about 10% in the road dust samples. The impacts of PM10 on human health are acknowledged to reduce cardio-pulmonary function and increase mortality from cardiovascular disease, the occurrence of asthma in children, and the risk of cancer (Hou et al. 2016). As consequence this fraction could become more hazardous for human health than the amount of harmful elements bound to others fractions.

Highest concentrations of trace metals were reported for dust samples in the fine fraction, especially in PM10, suggesting that road dust is a more interesting media than soil to understand the risk assessment for human health in urban environment, especially on this particle fraction. The accumulation of metals in fine particle fractions might be contributed to the increased surface area and negative charges (Luo et al., 2015; Qin et al., 2016).

The HD city showed the highest values of Pb and Cu for the soil and road dust samples within the PM10 fraction ($91/170 \text{ mg kg}^{-1}$ and $146/217 \text{ mg kg}^{-1}$, respectively) while in HD and MD cities the values of Zn reach 130 mg kg^{-1} in soil and 450 mg kg^{-1} in dust samples of PM10. Similar values among cities were found for Cd (0.4 mg kg^{-1}) and Cr (45 mg kg^{-1}) in soil while for dust HD city showed the highest values for both metals Cd (0.97 mg kg^{-1}) and Cr (85 mg kg^{-1}). Results obtained were higher those reported by Acosta et al. (2009) but lower than obtained by Amato et al. (2009) at different Mediterranean regions.

3.3.2. Human Risk assessment

After the particle size distribution analysis has shown that mostly of metals were bound to the finer fraction ($<75\mu\text{m}$), the potential adverse effect to the human health was assessed. The Upper Confidence Limit (UCL) from total metal in the fraction below $75\mu\text{m}$, toxicity values and results from Hazard Quotient (HQ), Hazard Index (HI) and Cancer Risk (CR) are shown in Table 3.1.

Results of Hazard Quotients (HQs) for non-carcinogenic effects showed the ingestion route as the main contributor to the total risk, followed by dermal absorption and inhalation of particles from the soil and road dust samples. Similar results has been found in previous studies for soil and road dust samples (Ferreira-Baptista and De Miguel; 2005, De Miguel et al. 2007; Du et al. 2013; Li et al. 2013; Lu et al. 2014; Gope et al. 2017) in urban environments.

Conversely, the inhalation route for Ni in soil and road dust showed an HQ ten to hundred times higher than dermal suggesting higher contribution of the inhalation route to the total risk for Ni. The contribution of the particulate matter could reach more than 50% of importance for some metals as Ni while for others is under 1% (Boisa et al. 2014).

Observed children risk values for trace metals were one order of magnitude higher than for adults from ingestion and dermal absorption routes in the three studied cities (Table 1), as same as observed Li et al. (2017b). Children may ingest significant quantities of the soil due to their tendency to play on the ground outdoors and to mouth objects or their hands while adults may also ingest soil or dust particles adhere to food, cigarettes, or their hands (US-EPA 2011).

Table 3.1. Risk indexes for carcinogenic and non-carcinogenic metals in urban soil and road dust

		Pb	Zn	Cu	Cd- non can	Cd-can	Cr- non can	Cr-can	Co- non can	Co-can	Ni- non can	Ni-can
Oral RfD		3,50E-03	3,00E-01	4,00E-02	1,00E-03		3,00E-03		2,00E-02		2,00E-02	
Dermal RfD		5,25E-04	6,00E-02	1,20E-02	1,00E-05		6,00E-05		5,40E-03		1,60E-02	
Inhal. RfD		3,50E-03	3,00E-01	4,00E-02	1,00E-03		2,86E-05		2,00E-02		6,00E-06	
Inhal. SF						6,10E+00		4,10E-01		8,40E-01		9,80E+00
High Density City												
C (95% UCL)	Soil	7,74E+01	1,35E+02	2,43E+02	4,80E-01	4,80E-01	4,39E+01	4,39E+01	3,75E+01	3,75E+01	1,30E+02	1,30E+02
	Dust	2,16E+02	6,14E+02	2,93E+02	1,50E+00	1,50E+00	1,15E+02	1,15E+02	6,23E+01	6,23E+01	1,25E+02	1,25E+02
Adults												
HQ ing	Soil	1,23E-04	1,84E-02	2,90E-03	2,29E-04		6,99E-03		8,95E-04		3,11E-03	
	Dust	3,44E-04	8,38E-02	3,50E-03	7,15E-04		1,83E-02		1,49E-03		2,99E-03	
HQ dermal	Soil	2,46E-06	4,89E-04	3,86E-05	9,14E-05		1,40E-03		1,32E-05		1,55E-05	
	Dust	6,86E-06	2,23E-03	4,65E-05	2,85E-04		3,65E-03		2,20E-05		1,49E-05	
HQ inhal	Soil	1,60E-06	3,25E-08	4,40E-07	3,47E-08		1,11E-04		1,36E-07		1,57E-03	
	Dust	4,47E-06	1,48E-07	5,30E-07	1,08E-07		2,91E-04		2,25E-07		1,51E-03	
HI	Soil	1,27E-04	1,89E-02	2,94E-03	3,20E-04		8,50E-03		9,09E-04		4,70E-03	
	Dust	3,55E-04	8,60E-02	3,55E-03	1,00E-03		2,22E-02		1,51E-03		4,51E-03	
CR	Soil					1,05E-10		6,45E-10		1,13E-09		4,58E-08
	Dust					3,27E-10		1,69E-10		1,87E-09		4,39E-08
Children												
HQ ing	Soil	1,15E-03	1,71E-01	2,71E-02	2,14E-03		6,53E-02		8,35E-03		2,91E-02	
	Dust	3,21E-03	7,82E-01	3,26E-02	6,67E-03		1,71E-01		1,39E-02		2,79E-02	
HQ dermal	Soil	1,61E-05	3,20E-03	2,53E-04	5,98E-04		9,14E-03		8,66E-05		1,02E-04	
	Dust	4,50E-05	1,46E-02	3,05E-04	1,87E-03		2,39E-02		1,44E-04		9,76E-05	
HQ inhal	Soil	2,84E-06	5,76E-08	7,80E-07	6,15E-08		1,97E-04		2,41E-07		2,79E-03	
	Dust	7,92E-06	2,63E-07	9,4E-07	1,92E-07		5,16E-04		4,00E-07		2,68E-03	
HI	Soil	1,17E-03	1,75E-01	2,74E-02	2,74E-03		7,46E-02		8,44E-03		3,20E-02	
	Dust	3,26E-03	7,96E-01	3,30E-02	8,54E-03		1,95E-01		1,40E-02		3,07E-02	
CR	Soil					1,05E-10		6,45E-10		1,13E-09		4,58E-08
	Dust					3,27E-10		1,69E-10		1,87E-09		4,39E-08
Medium Density City												
C (95% UCL)	Soil	1,24E+02	1,73E+02	1,00E+02	4,85E-01	4,85E-01	6,16E+01	6,16E+01	4,91E+01	4,91E+01	7,49E+01	7,49E+01
	Dust	1,99E+02	4,99E+02	1,50E+02	3,97E-01	3,97E-01	5,96E+01	5,96E+01	2,52E+01	2,52E+01	5,38E+01	5,38E+01
Adults												
HQ ing	Soil	1,97E-04	2,37E-02	1,19E-03	2,32E-04		9,81E-03		1,17E-03		1,79E-03	
	Dust	3,17E-04	6,81E-02	1,79E-03	1,89E-04		9,48E-03		6,01E-04		1,29E-03	
HQ dermal	Soil	3,92E-06	6,29E-04	1,59E-05	9,24E-05		1,96E-03		1,73E-05		8,91E-06	
	Dust	6,33E-06	1,81E-03	2,38E-05	7,56E-05		1,89E-03		8,89E-06		6,41E-06	
HQ inhal	Soil	2,55E-06	4,18E-08	1,81E-07	3,51E-08		1,56E-04		1,78E-07		9,03E-04	
	Dust	4,12E-06	1,20E-07	2,71E-07	2,87E-08		1,51E-04		9,11E-08		6,49E-04	
HI	Soil	2,03E-04	2,43E-02	1,21E-03	3,24E-04		1,19E-02		1,19E-03		2,70E-03	
	Dust	3,28E-04	6,99E-02	1,81E-03	2,65E-04		1,15E-02		6,10E-04		1,94E-03	

Table 3.1. (Continuation)

		Pb	Zn	Cu	Cd- non can	Cd-can	Cr- non can	Cr-can	Co- non can	Co-can	Ni- non can	Ni-can
CR	Soil					1,06E-10		9,05E-10		1,48E-09		2,63E-08
Children	Dust					8,66E-11		8,74E-10		7,57E-10		1,89E-08
HQ ing	Soil	1,84E-03	2,21E-01	1,11E-02	2,16E-03		9,16E-02		1,09E-02		1,67E-02	
	Dust	2,96E-03	6,36E-01	1,67E-02	1,77E-03		8,85E-02		5,61E-03		1,20E-02	
HQ dermal	Soil	2,57E-05	4,12E-03	1,04E-04	6,05E-04		1,28E-02		1,13E-04		5,84E-05	
	Dust	4,15E-05	1,19E-02	1,56E-04	4,95E-04		1,24E-02		5,82E-05		4,20E-05	
HQ inhal	Soil	4,53E-06	7,42E-08	3,21E-07	6,22E-08		2,76E-04		3,15E-07		1,60E-03	
	Dust	7,31E-06	2,13E-07	4,81E-07	5,09E-08		2,67E-04		1,62E-07		1,15E-03	
HI	Soil	1,87E-03	2,25E-01	1,12E-02	2,77E-03		1,05E-01		1,11E-02		1,83E-02	
	Dust	3,01E-03	6,47E-01	1,68E-02	2,26E-03		1,01E-01		5,67E-03		1,32E-02	
CR	Soil					1,06E-10		9,05E-10		1,48E-09		2,63E-08
Low Density City	Dust					8,66E-11		8,74E-10		7,57E-10		1,89E-08
C (95% UCL)	Soil	6,45E+01	1,37E+02	8,49E+01	6,36E-01	6,36E-01	6,08E+01	6,08E+01	4,70E+01	4,70E+01	7,13E+01	7,13E+01
	Dust	1,21E+02	3,09E+02	1,55E+02	6,69E-01	6,69E-01	6,95E+01	6,95E+01	5,84E+01	5,84E+01	9,29E+01	9,29E+01
Adults												
HQ ing	Soil	1,03E-04	1,87E-02	1,01E-03	3,04E-04		9,67E-03		1,12E-03		1,70E-03	
	Dust	1,92E-04	4,22E-02	1,85E-03	3,20E-04		1,11E-02		1,39E-03		2,22E-03	
HQ dermal	Soil	2,05E-06	4,97E-04	1,35E-05	1,21E-04		1,93E-03		1,66E-05		8,48E-06	
	Dust	3,83E-06	1,12E-03	2,46E-05	1,28E-04		2,21E-03		2,06E-05		1,11E-05	
HQ inhal	Soil	1,33E-06	3,31E-08	1,54E-07	4,60E-08		1,54E-04		1,70E-07		8,59E-04	
	Dust	2,50E-06	7,46E-08	2,81E-07	4,84E-08		1,76E-04		2,11E-07		1,12E-03	
HI	Soil	1,06E-04	1,92E-02	1,03E-03	4,25E-04		1,18E-02		1,14E-03		2,57E-03	
	Dust	1,99E-04	4,33E-02	1,88E-03	4,47E-04		1,34E-02		1,42E-03		3,35E-03	
CR	Soil					1,39E-10		8,92E-10		1,41E-09		2,50E-08
Children	Dust					1,46E-10		1,02E-09		1,76E-09		3,26E-08
HQ ing	Soil	9,58E-04	1,75E-01	9,46E-03	2,83E-03		9,03E-02		1,05E-02		1,59E-02	
	Dust	1,79E-03	3,94E-01	1,73E-02	2,98E-03		1,03E-01		1,30E-02		2,07E-02	
HQ dermal	Soil	1,34E-05	3,26E-03	8,83E-05	7,93E-04		1,26E-02		1,09E-04		5,56E-05	
	Dust	2,51E-05	7,35E-03	1,61E-04	8,35E-04		1,45E-02		1,35E-04		7,24E-05	
HQ inhal	Soil	2,36E-06	5,86E-08	2,72E-07	8,16E-08		2,73E-04		3,02E-07		1,52E-03	
	Dust	4,43E-06	1,32E-07	4,98E-07	8,59E-08		3,12E-04		3,75E-07		1,99E-03	
HI	Soil	9,74E-04	1,78E-01	9,55E-03	3,63E-03		1,03E-01		1,06E-02		1,75E-02	
	Dust	1,82E-03	4,01E-01	1,74E-02	3,82E-03		1,18E-01		1,32E-02		2,28E-02	
CR	Soil					1,39E-10		8,92E-10		1,41E-09		2,50E-08
	Dust					1,46E-10		1,02E-09		1,76E-09		3,26E-08

The Hazard Quotient (HQ) from inhalation route was in the same order of magnitude for adults and children although higher values for children were observed. The inhalation HQs for Pb and Ni were hundred times lower than HQs for dermal and ingestion routes (Table 1). A similar behaviour was observed for the other non-carcinogenic metals. Thus for adults, the HQ_{inh} value of Zn range from 10⁻⁴ to 10⁻⁶ times lower than dermal and ingestion HQs, Cu among a hundred and ten thousand times, Cd from 10⁻³ to 10⁻⁴, Cr range from 10 to 100 and Co from a hundred to a thousand time lower than the others HQs.

For children, the difference of the HQ inhalation with the ingestion and dermal HQs of non-carcinogenic metals was increased one or two order of magnitude than adults mainly due to the higher values of the ingestion quotient. Similar results have been observed in Gope et al. (2017).

Hazard Index (HI) soil values for adults and children in HD, MD and LD cities decreased as follow Zn>Cr>Ni>Cu>Co>Cd >Pb. Highest soil risk values, for adults and children were found for Cu (2.94E-03/2.74E-02) and Ni (4.70E-03/3.20E-0) in HD city; Zn (2.43E-02/ 2.25E-01), Cr (1.19E-02/ 1.05E-01), Co (1.19E-03/ 1.11E-02) and Pb (2.03E-04/ 1.87E-03) in MD city, and Cd (4.25E-04 / 3.63E-03) in LD city respectively. Those values were below the safe level (HI≤1) suggesting non-adverse health effect derived to the metal exposure.

For dust samples the HI values decreased as Zn>Cr>Cu>Ni>Co>Cd>Pb in HD and LD cities for adults and children and in MD city for children, whereas for adults in MD city the metal distribution was as showed for the soil. Highest risk values in dust samples were found at HD city for both subpopulations although no value indicates adverse effects for human health. The HI values shown by soils and road dust were one order of magnitude higher for adults than children. This behaviour also has been observed on previous researches (Wang et al. 2016; Li et al. 2017b).

Cadmium, Cr, Co and Ni involve a cancer risk because of the exposure to soil and dust by inhalation route. Table 1 showed CR values (10⁻⁸ to 10⁻¹¹) lower than the maximum value accepted, 10⁻⁶ (US-EPA 2002; Li et al. 2013; Lu et al. 2014). Cancer risk (CR) values decreased as Co>Ni>Cr>Cd in soil from HD, MD and LD cities being slightly higher the

risk for Co in HD city and for Cr in MD and LD cities. The CR values for the other metals were similar in all studied cities.

In dust samples cancer risk values decreased as $\text{Co} > \text{Ni} > \text{Cr} > \text{Cd}$ in HD and LD city while in MD city Cr showed higher risk than Ni. Hence, soil or dust cancer risk values never overreach the tolerable values (10^{-4} - 10^{-6}) indicating no adverse health effects.

This model has been proved to be a useful tool to assess the human health risk although exist some uncertainties derived to the exposure to hazard pollutants in urban pathways. Those uncertainties are linked to the missing or incomplete information needed to fully define exposure and dose (scenario uncertainty), regarding some parameter (parameter uncertainty), and gaps in scientific theory required to make predictions on the basis of causal inferences (model uncertainty) (US-EPA 2011b; De Miguel et al. 2007; Li et al. 2013). Regardless, human risk assessment is useful to supply information for public agencies and government about the potential risks associated with trace metals exposure in a given location.

3.3.3. Inhalation of Particulate Matter (PM₁₀)

PM₁₀ is mainly primary in origin, having been emitted as fully formed particles derived from abrasion and crushing processes, soil disturbances, plant and insect fragments, pollens and other microorganisms (US-EPA 2009). The size of particles is directly linked to their potential for causing health problems. Particles smaller than 10 μm pose the greatest problems, because they can get deep into the lungs and some may even get into the bloodstream (US-EPA2016b). According to US-EPA and due to higher concentrations of trace metals that were found in particle size below 10 μm (Fig. 3.3), only the inhalation exposure route was studied for particulate matter in the fine fraction (see Table 3.2).

Inhalation Hazard Quotient (HQ) values for non-cancer trace metals in the soil decreased as follow $\text{Ni} > \text{Cr} > \text{Pb} > \text{Cu} > \text{Co} > \text{Cd} > \text{Zn}$ for both adults and children at the three cities, except for MD where Zn showed a slightly higher value than Cd for adults.

Table 3.2. Hazard quotient and cancer risk for inhalation route in PM10 from urban soil and road dust.

		Pb	Zn	Cu	Cd- non can	Cd-can	Cr- non can	Cr-can	Co- non can	Co-can	Ni- non can	Ni-can
Inhal. RfD		3,50E-03	3,00E-01	4,00E-02	1,00E-03		2,86E-05		2,00E-02		6,00E-06	
Inhal. SF						6,10E+00		4,10E-01		8,40E-01		9,80E+00
High Density City												
C (95% UCL)	Soil	8,93E+01	1,44E+02	2,96E+02	5,34E-01	5,34E-01	4,80E+01	4,80E+01	3,57E+01	3,57E+01	8,55E+01	8,55E+01
	Dust	1,93E+02	5,37E+02	2,90E+02	1,96E+00	1,96E+00	1,14E+02	1,14E+02	5,75E+01	5,75E+01	8,34E+01	8,34E+01
Adults												
HQ	Soil	1,85E-06	3,47E-08	5,36E-07	3,87E-08		1,21E-04		1,29E-07		1,03E-03	
	Dust	3,99E-06	1,29E-07	5,24E-07	1,42E-07		2,88E-04		2,08E-07		1,01E-03	
CR	Soil					1,17E-10		7,04E-10		1,07E-09		3,00E-08
	Dust					4,29E-10		1,67E-09		1,73E-09		2,93E-08
Children												
HQ	Soil	3,27E-06	6,16E-08	9,51E-07	6,86E-08		2,15E-04		2,29E-07		1,83E-03	
	Dust	7,07E-06	2,29E-07	9,29E-07	2,52E-07		5,11E-04		3,69E-07		1,78E-03	
CR	Soil					1,17E-10		7,04E-10		1,07E-09		3,00E-08
	Dust					4,29E-10		1,67E-09		1,73E-09		2,93E-08
Medium Density City												
C (95% UCL)	Soil	1,54E+02	1,90E+02	9,48E+01	5,52E-01	5,52E-01	5,80E+01	5,80E+01	4,11E+01	4,11E+01	6,33E+01	6,33E+01
	Dust	3,05E+02	6,87E+02	1,91E+02	5,66E-01	5,66E-01	8,06E+01	8,06E+01	3,15E+01	3,15E+01	7,06E+01	7,06E+01
Adults												
HQ	Soil	3,19E-06	4,59E-08	1,71E-07	4,00E-08		1,47E-04		1,49E-07		7,64E-04	
	Dust	6,31E-06	1,66E-07	3,45E-07	4,10E-08		2,04E-04		1,14E-07		8,52E-04	
CR	Soil					1,21E-10		8,51E-10		1,24E-09		2,22E-08
	Dust					1,24E-10		1,18E-09		9,46E-10		2,48E-08
Children												
HQ	Soil	5,65E-06	8,13E-08	3,04E-07	7,09E-08		2,60E-04		2,64E-07		1,35E-03	
	Dust	1,12E-05	2,94E-07	6,12E-07	7,26E-08		3,62E-04		2,02E-07		1,51E-03	
CR	Soil					1,21E-10		8,51E-10		1,24E-09		2,22E-08
	Dust					1,24E-10		1,18E-09		9,46E-10		2,48E-08
Low Density City												
C (95% UCL)	Soil	5,63E+01	1,23E+02	8,66E+01	5,43E-01	5,43E-01	6,47E+01	6,47E+01	3,63E+01	3,63E+01	4,86E+01	4,86E+01
	Dust	1,17E+02	3,60E+02	1,73E+02	7,52E-01	7,52E-01	1,05E+02	1,05E+02	3,56E+01	3,56E+01	6,99E+01	6,99E+01

Table 3.2. (Continuation)

		Pb	Zn	Cu	Cd- non can	Cd-can	Cr- non can	Cr-can	Co- non can	Co-can	Ni- non can	Ni-can
Adults												
HQ	Soil	1,16E-06	2,97E-08	1,57E-07	3,93E-08		1,64E-04		1,31E-07		5,86E-04	
	Dust	2,41E-06	8,68E-08	3,14E-07	5,44E-08		2,65E-04		1,29E-07		8,42E-04	
CR	Soil					1,19E-10		9,49E-10		1,09E-09		1,71E-08
	Dust					1,64E-10		1,54E-09		1,07E-09		2,45E-08
Children												
HQ	Soil	2,06E-06	5,27E-08	2,78E-07	6,97E-08		2,90E-04		2,33E-07		1,04E-03	
	Dust	4,27E-06	1,54E-07	5,56E-07	9,65E-08		4,70E-04		2,28E-07		1,49E-03	
CR	Soil					1,19E-10		9,49E-10		1,09E-09		1,71E-08
	Dust					1,64E-10		1,54E-09		1,07E-09		2,45E-08

Although no large differences among cities were found for inhalation HQs, the highest risk values were observed for adults and children respectively at HD city for Cu ($5.36\text{E-}7/5.65\text{E-}6$) and Ni ($1.03\text{E-}3/1.83\text{E-}3$); Pb ($3.19\text{E-}6/5.65\text{E-}6$), Zn ($4.59\text{E-}8/8.13\text{E-}8$), Cd ($4\text{E-}8/7.09\text{E-}8$) and Co ($1.49\text{E-}7/2.6\text{E-}7$) at MD City and only Cr ($1.64\text{E-}4/2.9\text{E-}4$) at LD city.

In road dust samples the HQ inhalation values decreased as $\text{Ni} > \text{Cr} > \text{Pb} > \text{Cu} > \text{Co} > \text{Cd} > \text{Zn}$ for both adults and children at HD city and as $\text{Ni} > \text{Cr} > \text{Pb} > \text{Cu} > \text{Co} > \text{Zn} > \text{Cd}$ in LD city. In MD city a similar order that HD city was observed although the Zn place is inverted with Co. All metals showed highest hazard quotients (HQ) for adults and children at HD city except for Pb and Zn which was higher at MD city.

Comparing results of hazard quotient for inhalation exposure from particle size below $75\mu\text{m}$ and PM10 (Tables 3.1 and 3.2), it can be observed that in adults, the hazard quotient derived to inhalation of trace metals was slightly higher for all the metals in the $10\mu\text{m}$ fraction for the soil samples in HD and LD city and road dust of MD city.

Regarding children, the main difference between $10\mu\text{m}$ and $<75\mu\text{m}$ fractions was observed for the Pb hazard quotient in MD city which presented one order of magnitude higher in PM10. In the same way as adults, Zn, Cu, Cr, Co and Ni showed slight increments in the $10\mu\text{m}$ fraction for soil samples at HD city, road dust samples in LD city and both the soil/dust in MD city.

Cancer risk (CR) values calculated for PM10 decrease in the soil samples as $\text{Ni} > \text{Co} > \text{Cr} > \text{Cd}$ in HD, MD and LD showing Ni in HD city the highest CR value. In road dust samples the CR values decrease as $\text{Ni} > \text{Cr} > \text{Co} > \text{Cd}$ in MD and LD cities whereas in HD city showed similar distribution to the soil. In both type of samples CR values never reach the accepted maximum range values (10^{-4} to 10^{-6}) suggesting non-cancer effects in the exposed population.

Comparing CR results from PM10 and the $<75\mu\text{m}$ fraction was shown that both fractions are in the same order of magnitude, except Cd and Cr in the road dust from the MD city which was one order of magnitude higher than in the fraction $<75\mu\text{m}$. Also, Cd and Cr showed values slightly high in the PM10 fraction for the soil and road dust of HD and LD

cities despite were in the same order of magnitude. Contrary, Ni and Co showed slightly lower values in the PM10 fraction, especially in the HD city.

3.4. Conclusion

Due to the predominance of fine particles sizes ($<75\mu\text{m}$ and PM10) in soil samples and the linkage to a major concentration of metals from this sizes show that the soil represents the higher risk for human health. However, dust samples have been shown as the most hazardous because the dust is more prone to accumulate trace metals than soil (Acosta et al. 2015) and consequently major hazard index (HI) values were reported.

The health risk analysis of the fine particles showed that the most hazardous exposure route was the ingestion via, followed by dermal absorption and the inhalation route for all metals except Ni. Therefore, the inhalation exposure route becomes relevant such as showed by the Hazard Quotient for the inhalation route (HQ_{inh}) in both fractions ($<75\mu\text{m}$ and PM10).

Results from Hazard Quotient (HQ) showed that the risk for children due to the exposure to ingestion and dermal absorption pathways is higher than for adults while the Hazard Index for non-cancer trace metals pointed Zn, Cr and Ni as the most hazardous trace metals at the studied urban sites.

The largest risk index values and the highest concentrations of metals were found in road dust, indicating that road dust is acting as a sink of metals and a source of potential hazard for human health. Fortunately, the Hazard Index and the Cancer Risk Index showed that the exposure to the soil and road dust for children and adults at studied sites is not a cause enough to induce harmful health effects.

Particulate Matter below $10\mu\text{m}$ (PM10) reported slightly higher values of inhalation HQ than the fine fraction ($<75\mu\text{m}$) which suggests that metals in PM10 must be monitoring in urban areas in order to evaluate the metal affection to the human health. However because of some factors such as weather conditions (especially wind) or the feet action of people walking could mobilize respirable particles (bigger than PM10) we suggest that the

monitoring of fractions $<75\mu\text{m}$ can help to evaluate the health risk in urban environments.

Results from hazardous equations should be taken carefully because of the uncertainties that influence them. Despite of this, the human health risk model is a useful tool to supply the government to identify the elements and the pathways more relevant in urban sites and develop the most suitable actions as remedial responses or feasibility studies.

Chapter

4

**EFFECT OF DIFFERENT
INDUSTRIAL ACTIVITIES
ON HEAVY METAL
CONCENTRATIONS
AND CHEMICAL
DISTRIBUTION IN TOPSOIL
AND ROAD DUST**

Chapter 4

EFFECT OF DIFFERENT INDUSTRIAL ACTIVITIES ON HEAVY METAL CONCENTRATIONS AND CHEMICAL DISTRIBUTION IN TOPSOIL AND ROAD DUST

Abstract

The development of industrial activity in recent years has promoted the pollution in this environment causing health problems to workers and the neighbourhood nearby. In order to determine the influence of different industrial activities in metals concentration and behaviour in soil and road dust, samples from three different industrial areas (service industry; refinery, fertilizer and power industry; and tannery industry) and a natural area were collected. Physical–chemical properties, metal content (Pb, Zn, Cu, Cr, Co, Ni) and the chemical distribution of metals were carried out. Results show largest accumulation of metals in road dusts samples for all industrial areas, being Zn, Pb, Cr and Cu the metals with highest concentrations.

Each industrial activity contributes differently to the concentration of metals in soil and dust, and the highest concentrations of Cr were found from tannery industries, while Pb and Zn showed the highest concentration from refinery and fertilizer industry. It has been showed that industrial activity has influence on the physicochemical properties of soil and road dust and on the bioavailability of all metals. Chemical partitioning indicates that Pb, Zn, Cu and Cr distribution in the different solid phases is affected by industrial activity, while Co and Ni distribution is not affected by the industrial activity.

4.1. Introduction

Metals are introduced into soils and environment through both natural and anthropogenic sources. The natural inputs of metals in soils are attributed to geological parent materials (Zhong et al. 2014) but the fast development of industrialization in recent decades had supposed an increase of pollutant emissions becoming serious health problems in many countries. Lands next to industrial sites are vulnerable to metals contamination if used for discharge of poorly treated liquid effluents and disposal of solid wastes as well as deposition of exhaust gas from traffic or industries that release it into the atmosphere and subsequently deposit into the soil nearby (Fakayode and Onianwa 2002; Wu et al. 2011). Most trace metals settle down as surface dust from atmospheric depositions before full incorporation into the soil matrix. Thus, the extent of atmospheric contamination may be better revealed by road dust than soils (Bi et al. 2013; Acosta et al. 2015). Road dust is easily re-suspended or adhered to human skin, being an advantage to assess environmental quality and health risk. However, road dust is often removed by the municipal street cleaning service, hindering appropriately collect road dust samples.

Each industrial activity is usually linked to some specific metals, Cr is usually bound to tannery activity, Pb, Ni, Cu and Co are used as catalyst, modifiers and dryers (Akbar-Jan et al. 2010) or Zn which linked to agrochemical production such as fertilizers. Lead is usually associated to oil refinery activity while Ni is often linked to petrochemical emissions (Duong et al. 2009).

Some authors have developed researches about trace metals pollution in industrial soil (Al-Khashman and Shawabkeh 2006; Krishna and Govil 2008; Akbar-Jan 2010; Gülsen 2011; Wu et al. 2011; Yuan et al. 2014; Peña-Fernandez et al. 2015) and industrial road dust deposition (Duong et al. 2009; Kumar et al. 2013). However, most of the studies are focused on pollution of urban soil or road dust affected by industrial activities instead in pollution inside industrial areas.

The identification of the main binding sites for trace metals and the comparison of differences in metal behavior from different environments could help us understand the geochemical processes governing metal mobilization and potential risks induced (Yuan et al. 2004; Acosta et al. 2014). Sequential extraction procedures are a group of techniques

that provide information about the identification of the main binding sites, the strength of metal binding to particulates and the phase associations of trace elements in soil, road dust or dust (Rauret 1998).

For this reason this study is focused on determine the influence of different industrial activities in heavy metal concentration and behaviour in soil and road dust samples of three different industrial areas. This new information will help environmental scientist and regulators to manage human and environmental risk of harmful metals.

4.2. Materials and methods

4.2.1. Study area

In Murcia there are diverse industrial areas scattered throughout the province. For this study we selected three industrial areas with different industrial activities: (1) Industrial area “P.I. Oeste” where the service industry is the mainly activity, including manufacturing paints, steel products, chemicals, electrical materials, etc., this industrial area is located close to capital of the province with more than 1000 factories operating, from heavy traffic to uncontrolled discharge of waste contribute to the soil pollution by metals (Acosta et al., 2011a), metals associated to this type of industry include Zn, Pb and Cd (Acosta et al. 2010, Fakayode and Onianwa 2002); (2) Industrial area “Escombreras” where refinery, fertilizer and power industry dominated, these industries are a potential source of metals pollution, including a wide range of metals such as Cd, Cu, Pb, Zn, and Ni (Zhang et al., 2015) and finally (3) “Lorca industrial area” where tannery industry is the most important activity, tannery is one of the major sources of Cr pollution in soils and sediments (Dong et al. 2013).

A total of 63 samples were collected, 20 samples from P.I. Oeste, 16 samples from Escombreras, 12 samples from Lorca and 15 samples from natural area as background site (Fig. 4.1).

Fig.4.1. P.I. Oeste (a), Escombreras (b) and Lorca(c), black stars indicate sampling points

Soil was collected from 0-5 cm with a soil spade and packed on plastic bags and road dust by sweeping directly into the plastic bag to avoid the re-suspension (Fig. 4.2) (Acosta et al., 2011a; Zhang et al., 2012; Du et al., 2013). The same natural area was used as background for the three industrial areas because of their similar parental material: alluvial deposits of limestone and marl (Martínez-Martínez 2009).

Fig.4.2. Soil (left column) and road dust samples (right column) from P.I.Oeste (a,b), P.I.Escombreras (c,d), P.I.Lorca (e,f) and natural area (g,h)

4.2.2. Sample analysis

Soil and dust samples were dried for 48 hours at 45°C and passed through a 2 mm sieve. A split of each sample was ground using an agate mortar (RetschRM 100).

The pH was measured in a solution of 1:1 water/soil ratio (Soil Survey Staff, 2004) while the electrical conductivity (EC) was measured in a 1:5 soil/water suspension (Andrades

1996). The equivalent calcium carbonate was determined using the Bernard's calcimeter and Organic carbon by dichromate method (Soil Survey Staff 2004).

For total metal content, samples were digested using HNO_3 and H_3ClO_4 (Risser and Baker 1990). Bioavailable metals were measure using a DTPA extraction (Lindsay and Norvell 1978) and soluble water metals were measured according to Buurman et al. (1996) and Frau (2000). According with the industrial activities develop in each industrial area, Zn, Pb, Cu, Cr, Ni and Co were selected for this study and their concentrations determined by Atomic Absorption Spectrometer (AAnalyst 800, Perkin Elmer).

Chemical speciation of metals was estimated by a sequential digestion procedure adapted from Tessier et al. (1979) and modify by Li et al. (1995) in order to obtain the following fractions: fraction 1: exchangeable; fraction 2: bound to carbonates; fraction 3: reducible phase (bound to Fe-Mn-oxides); fraction 4: oxidizable phase (bound to organic matter and sulphide) and fraction 5: residual phase.

Reference material (BAM-U110) from the Federal Institute for Material Research and Testing (F.I.M.R.T. 2010) and reagent blanks were used as quality control samples during the analyses. We obtained recoveries (the sum of the five fractions to the total element concentration of BAM-U110) of 92-109% for Cd, 164 91-98% for Cu, 94-105% for Pb, 91-99% for Zn, 92-107% for Cr and 96-108% for Ni.

4.2.3. Statistical analysis

Descriptive statistics of total, DTPA and water extractable metals and chemical properties of soil and road dust were performed by Microsoft Excel. The normal distribution of ANOVA residues was studied by Shapiro-Wilk test. Non normal variables were log-transformed and one-way ANOVA test with a Tukey post-hoc were carried for them. For non-normal log-transformed data the Man-Whitney U test was applied instead the ANOVA test. Both were carried out to investigate the differences among industrial sites each other and natural area for soil and road dusts using SPSS 23 for Windows.

4.3. Results and discussion

4.3.1. Effect of different industrial activities on physic-chemical characteristic of soil and road dust

Table 4.1 shows the mean and standard error of physic-chemical properties and metals content, one-way ANOVA and Man –Whitney U test are also included. pH of soil and road dust samples was moderately alkaline due to the presence of high amount of carbonates (>30%). Salinity ranged from 0.09 to 1.87 dS m⁻¹ categorizing as non to slightly saline (Andrades 1996). Moderate levels of organic carbon (OC) were found. Non-statistical differences among industrial sites and the natural area for soil OC content was found, which was due to the similar climatic condition and management (Table 4.1). In contrast, OC in road dust from industry areas was higher than natural road dust probably due to traffic emission of organic compounds (e.g. tires, asphalt debris and oil) associated to the industrial activities (Swietlik et al. 2015). Because of the higher OC content in the road dust, statistical differences were showed with soil in each industrial site.

A statistically significant increment for salinity in soil and road dust among industrial areas and the natural area was found (Table 4.1). Otherwise, statistically higher carbonate contents were reported in soil and dust from Natural area, Lorca and Oeste industrial areas than Escombreras. Thereby, pH in Escombreras road dust was slightly lower than natural road dust. These results indicate that industrial activities are affecting and modified some physic-chemical properties of soil and dust, whose effects on metals behaviour will be shown in the following sections.

4.3.2. Influence of different industrial activities on metal content in soil and road dust

As is shown in Table 4.1, the concentration of metals decreases in the following order: Zn>Pb>Cu>Cr>Ni>Co in soil and Zn>Cu>Cr>Pb>Ni>Co in road dust from P.I. Oeste where only was found significant statistical differences for Zn, Cu and Ni between soil and dust. At Escombreras area metals in soil and dust decrease in the same order: Zn>Pb>Cu>Ni>Cr>Co, with only statistically significant differences for

Table 4.1. Mean and (standard error) of physicochemical properties of soil and road dust samples

	Oeste		Escombreras		Lorca		Natural	
	Topsoil	Road dust	Topsoil	Road dust	Topsoil	Road dust	Topsoil	Road dust
pH	8,0(0,44)ab	7,9(0,54)ab	8,0(0,57)ab	7,7(0,57)a	8,0(0,51)ab	8,0(0,48)ab	8,4(0,38)b	8,3(0,15)b
Salinity (ds/m)	0,44(0,11)bc	0,24(0,02)ab	1,7(0,88)c	0,46(0,08)bc	0,82(0,23)c	0,69(0,11)c	0,11(0,00)a	0,13(0,01)a
Carbonates (%)	37(1,8)b	41(1,2)b	24(2,1)a	28(2,7)a	38(1,9)b	42(2,4)b	39(0,88)b	40(2,3)b
Organic carbon (%)	1,7(0,26)b	4,5(0,86)c	1,9(0,42)b	4,2(1,1)c	2,5(1,1)b	2,7(0,38)c	1,3(0,08)b	0,59(0,29)a
Total Pb (mg kg⁻¹)	85(3,5)c	120(19)c	3115(1332)d	373(90)d	61(3,7)b	77(13)c	34(1,9)a	32(5,1)a
Total Zn (mg kg⁻¹)	176(53)b	474(57)c	4958(2217)d	1022(420)cd	142(21)b	201(33)b	67(1,4)a	59(7,0)a
Total Cu (mg kg⁻¹)	81(11)c	252(39)d	200(61)d	120(36)cd	55(2,5)bc	91(18)cd	29(1,1)ab	23(2,2)a
Total Cr (mg kg⁻¹)	70(6,0)c	141(43)c	44(3,4)b	43(4,1)b	167(62)c	203(68)c	30(3,1)a	24(1,3)a
Total Co (mg kg⁻¹)	31(1,2)ab	35(0,66)ab	38(4,3)b	28(1,5)ab	31(1,1)ab	33(0,86)ab	24(0,40)a	22(0,69)a
Total Ni (mg kg⁻¹)	66(15)c	87(14)d	65(6,3)cd	78(13)cd	57(1,7)c	58(2,1)c	47(1,5)b	38(2,2)a
DTPA Pb (mg kg⁻¹)	3,9(0,63)b	6,8(0,50)b	56(11)c	42(15)c	2,9(1,1)b	3,6(1,6)b	2,1(0,10)b	1,5(0,87)a
DTPA Zn (mg kg⁻¹)	30(19)b	73(14)c	203(77)c	118(31)c	36(31)b	27(8,3)b	0,42(0,04)a	1,0(0,29)a
DTPA Cu (mg kg⁻¹)	3,5(1,2)bc	26(11)d	8,2(2,8)c	8,1(1,8)cd	3,5(0,84)bc	7,1(1,0)cd	1,3(0,02)ab	0,71(0,16)a
DTPA Cr (mg kg⁻¹)	0,29(0,03)ab	0,42(0,03)bc	0,53(0,05)cd	0,72(0,07)d	0,48(0,06)cd	0,78(0,07)d	0,19(0,02)a	0,26(0,02)ab
DTPA Co (mg kg⁻¹)	0,44(0,02)bc	0,36(0,05)bc	0,38(0,04)bc	0,45(0,02)bc	0,52(0,07)c	0,42(0,03)bc	0,29(0,02)b	0,18(0,05)a
DTPA Ni (mg kg⁻¹)	0,78(0,05)b	0,84(0,14)b	0,73(0,05)b	0,78(0,08)b	0,90(0,08)b	0,66(0,06)b	0,52(0,02)a	0,36(0,09)a
Soluble Pb (mg kg⁻¹)	<BDL	<BDL	0,93(0,86)	0,19(0,18)	<BDL	<BDL	<BDL	<BDL
Soluble Zn (mg kg⁻¹)	0,58(0,20)ab	1,3(0,25)bc	7,7(4,5)c	2,9(0,96)c	0,35(0,03)ab	0,60(0,14)ab	0,13(0,01)a	0,20(0,04)a
Soluble Cu (mg kg⁻¹)	0,16(0,03)a	0,76(0,39)b	0,41(0,12)ab	0,41(0,08)ab	0,19(0,03)ab	0,32(0,05)ab	0,33(0,04)ab	0,37(0,01)b
Soluble Cr (mg kg⁻¹)	0,18(0,03)abc	0,33(0,04)d	0,24(0,02)bcd	0,30(0,02)cd	0,20(0,04)bcd	0,38(0,06)d	0,10(0,01)a	0,14(0,01)ab
Soluble Co (mg kg⁻¹)	0,08(0,02)bc	0,13(0,02)bc	0,28(0,02)d	0,33(0,02)d	0,24(0,06)cd	0,18(0,02)bcd	0,09(0,01)b	0,04(0,01)a
Soluble Ni (mg kg⁻¹)	0,44(0,04)b	0,54(0,05)b	0,57(0,05)b	0,57(0,05)b	0,51(0,08)b	0,48(0,04)b	0,38(0,03)b	0,15(0,04)a

a,b,c,d are significant differences (p<0.05). BDL: below detection limit

Pb and Zn. In Lorca industrial area, metals decrease as Cr>Zn>Pb>Ni>Cu>Co for soil and Cr>Zn>Cu>Pb>Ni>Co for road dust where non statistical differences were reported for any studied metals. Non-significant differences in metals contents were found for soil and road dust at natural area that decrease as Zn>Ni>Pb>Cr>Cu>Co, suggesting that natural dust come from natural soil without effect of human activities.

Comparing with the natural area, statistically significant increments were observed in soil and road dust from P.I. Oeste and road dust in Escombreras and Lorca for Pb, Zn, Cu, Cr and Ni. Also higher concentration of Zn Cr and Ni was reported in Lorca soil than natural soils. Finally, higher concentrations for all metals were found in Escombreras soils than natural soils. These results showed an important enrichment in both soils and dust come from industrial activities.

However, the main metals found in each industrial area are the results of the main polluting industrial activity develop in each area. For example, Cr content in topsoil and road dust of Lorca was due to development of leather manufacturing industry and the bad managing of tannery wastes (Rawat et al. 2009). In contrast, the high concentrations of Pb and Zn reported in Escombreras come from refinery, power and fertilizers industries (Gülten 2011).

These results were similar to those obtained by Wu et al. (2011), Gülten (2011) and Han et al. (2009) for soil samples, and by Rawat et al. (2009) and Duong et al. (2009) for road dust. Total Cu content in soil from P.I. Oeste and Lorca was lower than reported by Srinivasa et al. (2010) and Pen-Mouratov et al. (2008) whereas road dust from P.I. Oeste was in the same order of data obtained by Duong et al. (2009), while in Escombreras and Lorca road dusts metals concentrations were below them. Finally, Cr concentrations in dust and soil from Lorca were lower than obtained by Rawat et al. (2009) but higher than Yuan et al. (2014). According with background concentrations from Table 4.2, all studied metals showed concentrations higher than background levels in non-polluted soils for the three industrial areas, except Zn in Lorca compared to Castellón (Peris 2006) and Cr in Escombreras compared with Almería (Sierra et al. 2007), which suggests an enrichment of metals in soil and dust come from industrial activities.

Table 4.2. Background mean concentration of metal (mg kg^{-1}) from world soils, earth crust and Spain

Total metal concentration (mg kg^{-1})	Location	Lead	Zinc	Copper	Chromium	Nickel	Cobalt
Kabata Pendias and Pendias (1992)	World soils	28.6	64	25	54	22	7.9
Alloway (1999)	Earth crust	29	nd	26	84	34	12
Pérez-Sirvent et al. (2009)	Murcia (Spain)	6.8	33.9	13.7	32.4	34	12
Navas and Machín (2002)	Aragón (Spain)	8.3	55.6	10.3	21	19.3	7
Micó et al. (2007)	Alicante (Spain)	28	83	28	36	31	nd
Sierra et al. (2007)	Almeria (Spain)	31.6	69.6	21.2	61.52	28.8	13
Peris (2006)	Castellón (Spain)	51.3	154.9	50.4	42.9	29.2	nd
Hernandez-Crespo and Martín (2015)	Valencia (Spain)	25.5	88.6	28.8	nd	25.9	nd

4.3.3. Effect of industrial activity on chemical partitioning

Single extraction process

Only, statistical differences were observed for DTPA extractable Zn and Cu between soil and road dust in P. I. Oeste (Table 4.1), due to the higher concentration observed in road dust, which suggests that the absorption risk by plants associated to these metals is higher for road dust than soil. However, comparing the DTPA metals concentrations in soil and dust for each industrial area, no significant differences were found, which suggests that physico-chemical properties of soil and dust are not a decisive factor on the bioavailability of these metals.

In contrast, compared to natural site significant differences of DTPA extractable Zn and Ni for soil and road dust, and DTPA extractable Cu and Co for road dust from all industrial areas were found. Also, differences were found for DTPA extractable Pb in road dust and DTPA extractable Cu in soil from Escombreras, and DTPA Cr in soil and dust from Escombreras and Lorca. The concentration of DTPA extractable metals at industrial sites was higher than natural area, indicating that the industrial activity is a relevant factor to the bioavailability of metals.

Concentration of water soluble Cu and Cr were statistically higher in road dust than soil in P.I. Oeste. Significant differences were found for water soluble Zn in Escombreras because of the highest concentrations at this area compared with the rest of the industrial areas. Comparing with the natural area, enrichment of Zn in soil and dust of Escombreras and in Cr, Co and Ni in soil and road dust of the three industrial areas was observed.

Sequential extraction procedure

The distribution of Pb in soil and road dust from the three industrial areas was dominated by the residual fraction, however a high concentration of Pb bound to carbonate and reducible phases in Escombreras soil was reported (Table 4.3). This observation suggests that Pb bound to carbonates could be released to the environment after decrease in pH in Escombreras soil. In addition, highlight that the percentage of Pb bound to carbonate and reducible phases in natural soil is around 55%, which was higher than observed on industrial areas (30-40%), indicating that industrial activities affects the behaviour of Pb

in soils. Oppositely, industrial activities do not affect the distribution patter of Pb in road dust, since this is similar between natural area and industrial dust (Fig. 4.3).

Table 4.3. Concentration of metal (mg kg^{-1}) from sequential extraction procedure

		Oeste		Escombreras		Lorca		Natural	
		Topsoil	Rd Dust	Topsoil	Rd Dust	Topsoil	Rd Dust	Topsoil	Rd Dust
Lead	Exchangeable	0,82	0,83	1,12	1,30	1,47	1,20	0,73	0,44
	Carbonates	9,31	16,91	247,95	63,87	7,07	7,20	6,07	5,98
	Reducible	19,07	40,18	805,71	132,64	19,57	27,99	12,87	7,03
	Oxidizable	2,64	4,74	126,87	9,87	3,09	3,85	0,54	0,53
	Residual	38,01	60,69	1992,63	223,81	37,25	48,14	14,34	14,81
	Recovery %	82	103	102	116	112	114	100	104
Zinc	Exchangeable	0,82	1,12	9,85	3,68	1,04	1,01	0,24	0,80
	Carbonates	6,36	67,67	937,50	196,59	6,91	26,62	1,35	1,80
	Reducible	42,56	155,47	1322,54	336,83	34,63	65,19	5,44	10,76
	Oxidizable	7,64	20,54	356,59	168,90	5,48	9,81	0,85	1,40
	Residual	115,65	149,04	2352,35	393,46	109,70	108,79	57,53	36,51
	Recovery %	98	83	100	108	111	105	98	102
Copper	Exchangeable	0,46	0,91	0,46	0,79	0,75	0,95	0,78	0,93
	Carbonates	2,11	14,46	2,98	3,55	2,20	4,24	2,00	1,33
	Reducible	2,31	12,66	4,20	1,90	2,29	2,88	3,30	3,01
	Oxidizable	9,54	70,77	34,04	33,62	7,63	20,74	1,02	1,64
	Residual	62,76	166,55	158,80	81,94	42,80	55,13	21,94	14,61
	Recovery %	95	105	100	101	102	92	101	110
Chromium	Exchangeable	0,18	0,33	0,77	0,67	1,02	1,48	1,40	0,77
	Carbonates	4,13	3,86	2,80	3,23	4,33	5,48	2,72	1,89
	Reducible	5,92	9,40	6,08	6,90	76,75	123,45	8,97	7,74
	Oxidizable	1,71	2,41	1,28	2,11	12,80	35,59	2,90	1,05
	Residual	55,33	138,48	37,06	38,10	100,30	80,15	16,27	9,51
	Recovery %	96	109	109	118	117	122	108	103
Cobalt	Exchangeable	1,18	1,45	1,63	0,53	0,31	0,37	0,64	1,04
	Carbonates	3,51	3,74	3,82	3,03	3,54	3,46	3,69	3,33
	Reducible	4,45	4,11	4,54	3,82	4,27	4,52	6,31	5,99
	Oxidizable	1,23	1,39	1,57	1,41	1,31	1,63	1,15	0,90
	Residual	13,58	20,36	21,28	13,71	16,73	16,67	12,34	9,84
	Recovery %	78	89	87	81	85	82	99	111
Nickel	Exchangeable	1,01	1,21	1,47	1,68	2,53	1,72	1,37	1,79
	Carbonates	5,18	5,52	4,76	4,64	5,04	5,08	5,55	4,19
	Reducible	7,71	9,21	9,78	7,03	4,93	7,20	9,79	8,54
	Oxidizable	3,28	2,75	2,15	2,58	2,25	1,93	4,53	2,46
	Residual	50,32	70,95	47,81	66,31	41,18	36,08	26,23	16,97
	Recovery %	102	102	101	106	98	90	102	103

Zinc was strongly associated with the residual fraction in soil at P.I. Oeste and Lorca industrial areas while in Escombreras dominated the carbonate and reducible phases, reaching a similar percentage than residual phase. For road dust samples, Zn bound to the residual phase only represented the 40% while more mobile phases such as carbonate and reducible phases grouped the 50% of metal content. The Zn distribution in the natural area was primarily dominated by the residual fraction in soil (80%) and dust (70%), followed to reducible phase in road dust, suggesting a geological origin of Zn in the natural area.

The dominant fraction for Cu was the residual phase, which showed similar percentages of Cu-bound in soils and dusts from the three industrial areas. Also, in road dust samples, the oxidizable fraction of Cu was relevant with a 26% of Cu-bound. This observation suggests that Cu can be mobilized after organic matter mineralization (Acosta et al. 2015). In addition, Cu distribution in the organic phase of natural soil/dust was lower than reported to the industrial sites because an increase of the reducible fraction.

Residual phase dominated the distribution of Cr in both soil and road dust in P.I. Oeste and Escombreras while in Lorca this fraction was notably reduced towards an increase of the reducible phase, overall in dust samples (50%), suggesting that the industrial activity developed in Lorca can be affecting the mobility of Cr, especially in road dust (Rosales et al. 2016).

Cobalt and Ni shown similar distribution in soil/dust of the different industrial areas where dominated the residual phase, indicating that these distributions were not affected by industrial activity. These metals are mainly associated with a geological origin and therefore they are mainly bound to the most stables minerals of soil (Rodriguez et al. 2006). In addition, the distribution of these metals in the natural soil showed an increase of Co and Ni associated to the reducible phase.

Fig.4.3. Chemical partitioning of metals in soil and road dust samples from three industrial areas and natural area

4.3.4. Behaviour of metals in soil and road dust

Lead

In soil, positive correlations were found among total concentration of Pb and carbonate, reducible, oxidizable and residual phases, grouped in factor 1 (Tables 4.4 and 4.5) that explains the 48% of the total variance. This suggests that Pb trends to bind to oxides and

Table 4.4. Principal Component Analysis (PCA) of each metal for soil and road dust samples

	Lead								Zinc								Copper							
	Soil Factor				Road Dust Factor				Soil Factor				Road Dust Factor				Soil Factor				Road Dust Factor			
	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4
pH	-,033	-,262	,802	,235	-,193	-,464	-,364	,714	-,050	-,088	,974	-,120	-,248	-,720	-,371	-,328	-,120	,235	-,827	-,159	-,099	-,217	,745	-,433
Salinity	,009	,798	,202	,395	,179	-,096	,869	-,184	-,094	,894	,139	-,163	-,080	,196	,067	,964	,056	-,135	,100	-,799	-,044	-,060	-,138	,954
Carbonates	-,336	-,702	,227	,028	-,188	-,775	-,167	,077	-,373	-,665	,108	-,077	-,295	-,192	-,738	-,099	-,704	,091	-,218	,447	,146	,142	,898	,094
Organic Carbon	,039	-,319	-,749	,340	-,142	,455	,441	-,469	,028	-,042	-,116	,984	,068	,948	,077	,094	,209	-,100	,324	,646	,515	,247	-,629	,277
Total metal	,944	,246	-,109	,074	,866	,447	-,012	-,017	,985	,154	-,053	,022	,978	,144	,101	-,034	,964	-,105	,119	,028	,325	,935	-,022	-,002
DTPA metal	,588	,730	-,011	,206	,950	,114	,102	,160	,785	,288	-,289	,334	,708	,512	,343	-,102	,809	,169	,461	,088	,905	,377	-,104	-,006
Soluble metal	,906	-,108	,067	-,073	,118	,078	,118	,899	,976	,092	-,034	,036	,933	,139	,128	-,047	,827	,424	-,069	,145	,949	,202	-,094	-,010
Exchangeable	,083	,248	-,011	,869	,141	,393	,754	,245	,317	,774	-,319	,094	-,028	,108	,931	,002	-,148	,776	-,170	,245	,899	,078	,024	,144
Carbonate	,954	,252	,020	,077	,964	-,001	,088	,060	,983	,139	-,055	,026	,937	,114	,267	,002	,368	,401	,667	-,251	,841	,455	,028	-,134
Reducible	,903	,292	-,085	,119	,967	,154	,120	-,037	,969	,061	,042	-,007	,955	,211	,099	,006	,070	,800	,065	-,095	,731	,506	,092	-,236
Oxidizable	,986	,142	-,021	,033	,940	,203	,189	-,041	,968	,176	-,099	,024	,981	-,021	-,029	-,028	,854	-,004	,359	,029	,571	,762	-,140	,059
Residual	,966	,206	-,103	,039	,519	,677	-,108	-,015	,981	,167	-,063	,007	,980	,053	,044	,036	,943	-,173	,030	,027	,183	,948	-,038	-,021

Table 4.4. (continuation)

	Chromium								Cobalt								Nickel							
	Soil Factor				Road Dust Factor				Soil Factor				Road Dust Factor				Soil Factor				Road Dust Factor			
	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4
pH	-,204	-,084	,748	,483	-,052	-,053	-,908	-,056	-,060	-,124	-,197	-,647	-,079	-,295	-,860	-,010	-,006	,710	,161	,022	-,454	-,698	,008	,165
Salinity	-,126	,734	,071	,077	,660	-,097	,484	,283	-,180	,595	,541	-,195	,088	,796	,239	-,032	-,083	,184	-,821	,155	-,077	,754	-,049	-,224
Carbonates	,066	-,718	,186	,227	,306	,363	-,556	-,370	-,451	-,742	-,198	-,054	,521	-,187	-,560	,386	-,257	,214	,710	-,198	-,665	-,213	,421	,382
Organic Carbon	,120	,032	-,001	-,636	-,102	,246	,849	,032	,198	-,061	-,205	,790	,189	,006	,853	-,175	-,031	-,748	,202	,085	,646	,558	,048	,258
Total metal	,957	-,008	-,215	,014	,338	,895	,038	,093	,893	,217	,114	,214	,956	,063	,005	-,150	,953	-,061	-,045	,147	,830	,164	,246	,252
DTPA metal	,232	,813	-,083	-,170	,357	-,021	,096	,883	-,076	-,045	,851	,273	,248	,489	,391	-,448	,261	-,510	,130	,690	,381	,496	,510	,129
Soluble metal	,080	,736	,019	,326	,266	,510	,253	,620	,260	,402	,700	-,032	-,172	,655	,387	-,365	,130	-,029	-,233	,789	,158	,829	,152	,283
Exchangeable	-,031	-,057	,916	-,277	,868	-,227	-,138	,155	,135	,838	-,018	,066	,279	-,752	,428	,265	-,217	,240	-,139	,433	-,251	,037	-,046	-,907
Carbonate	,511	,061	-,110	,704	,546	,505	-,018	,459	,742	-,295	,018	-,329	,489	-,138	,052	,715	,162	,628	,567	,054	,088	,229	,788	,231
Reducible	,950	-,019	-,021	-,050	,806	,441	-,102	,194	-,034	,068	-,403	-,577	-,130	-,079	-,186	,909	,652	,377	-,399	-,346	,185	-,118	,894	-,153
Oxidizable	,939	,036	,289	,010	,817	,425	-,086	,217	,767	,243	-,200	,324	,555	,652	,163	,150	,754	,229	,232	-,397	,633	-,082	,455	,127
Residual	,912	,063	-,328	,014	-,174	,878	,137	-,015	,873	,263	,058	,173	,899	,007	,233	,126	,888	-,132	-,083	,288	,854	,154	,230	,172

Table 4.5. Spearman correlation coefficients

		TOPSOIL							ROAD DUST						
		pH	Salinity	Carbonates (%)	Organic Carbon	Total Metal	DTPA Metal	Soluble Metal	pH	Salinity	Carbonates (%)	Organic Carbon	Total Metal	DTPA Metal	Soluble Metal
Lead	Exchangeable	-,155	,610**	-,118	-,084	,133	,031	-,085	-,349	,709**	-,289	,207	,484**	,466*	,240
	Carbonate	-,235	,564**	-,638**	,224	,938**	,791**	,358*	-,399*	,190	-,447*	,357	,883**	,885**	,313
	Reducible	-,257	,541**	-,566**	,327	,832**	,826**	,358*	-,447*	,380*	-,409*	,393*	,948**	,922**	,294
	Oxidizable	-,410*	,683**	-,676**	,234	,847**	,691**	,383*	-,405*	,425*	-,326	,324	,882**	,805**	,307
	Residual	-,417*	,646**	-,576**	,266	,942**	,737**	,396*	-,533**	,381*	-,308	,475**	,939**	,831**	,371*
Zinc	Exchangeable	-,453**	,720**	-,454**	,147	,758**	,784**	,637**	-,382*	,337	-,394*	,220	,362	,439*	,269
	Carbonate	-,484**	,591**	-,466**	,295	,858**	,884**	,755**	-,685**	,288	-,412*	,530**	,854**	,883**	,707**
	Reducible	-,456**	,521**	-,528**	,440**	,939**	,952**	,871**	-,661**	,252	-,421*	,552**	,958**	,878**	,665**
	Oxidizable	-,447**	,544**	-,629**	,429*	,922**	,930**	,907**	-,692**	,335	-,428*	,595**	,933**	,913**	,779**
	Residual	-,449**	,607**	-,549**	,347*	,952**	,886**	,834**	-,551**	,320	-,379*	,522**	,876**	,740**	,635**
Copper	Exchangeable	,175	-,386*	,315	,013	-,578**	-,321	,275	,041	,127	,205	-,178	-,121	-,060	,321
	Carbonate	-,116	-,017	-,281	,063	,021	,294	,563**	,077	,011	,190	,314	,753**	,748**	,267
	Reducible	,226	-,504**	-,033	,013	-,252	-,083	,358*	,165	-,397*	,416*	,150	,571**	,598**	,133
	Oxidizable	-,533**	,559**	-,581**	,387*	,818**	,892**	,183	-,446*	,279	-,011	,545**	,918**	,840**	,216
	Residual	-,458**	,645**	-,414*	,192	,937**	,624**	-,055	-,321	,128	,084	,518**	,976**	,910**	,135
Chromium	Exchangeable	,482**	-,352*	,153	-,040	-,565**	-,152	-,184	,148	,329	,061	-,292	-,201	,338	-,116
	Carbonate	-,140	,381*	,143	-,047	,631**	,244	,373*	-,070	,627**	,327	,237	,636**	,585**	,606**
	Reducible	,219	-,242	,490**	,000	,086	-,161	-,334	,171	,205	,573**	-,102	,525**	,107	,279
	Oxidizable	,157	-,337	,417*	,055	,053	-,260	-,377*	-,323	,708**	,157	,391*	,687**	,606**	,573**
	Residual	-,577**	,493**	-,065	,316	,954**	,410*	,422*	-,334	,318	,257	,563**	,909**	,221	,552**

Table 4.5. (Continuation)

		TOPSOIL						ROAD DUST							
		pH	Salinity	Carbonates (%)	Organic Carbon	Total Metal	DTPA Metal	Soluble Metal	pH	Salinity	Carbonates (%)	Organic Carbon	Total Metal	DTPA Metal	Soluble Metal
Cobalt	Exchangeable	-,124	,291	-,530**	-,014	,399*	,072	,264	-,170	-,364	,108	,309	,344	-,227	-,386*
	Carbonate	,071	-,172	,105	-,084	,108	-,249	,045	,238	-,343	,607**	-,017	,356	-,304	-,417*
	Reducible	,503**	-,391*	,096	-,363*	-,357*	-,430*	-,154	,261	-,323	,503**	-,326	,153	-,332	-,418*
	Oxidizable	-,218	,114	-,301	,431*	,562**	-,063	,184	-,306	,496**	,167	,296	,386*	,240	,271
	Residual	-,226	,437**	-,335	,357*	,714**	,136	,334	-,185	,163	,247	,297	,883**	,078	-,048
Nickel	Exchangeable	-,153	,413*	-,133	-,069	,230	,123	,255	-,021	,180	-,136	-,384*	-,451*	-,102	-,130
	Carbonate	,504**	-,473**	,294	-,383*	-,064	-,306	-,210	,044	,038	,393*	,216	,322	,266	,394*
	Reducible	,408*	-,272	-,192	-,363*	-,125	-,472**	-,151	,183	-,305	,282	-,183	,172	,001	-,155
	Oxidizable	,443**	-,629**	,307	-,048	-,086	-,338	-,084	-,199	-,124	-,154	,306	,391*	,362	-,016
	Residual	-,342*	,486**	-,251	,144	,769**	,738**	,453**	-,456*	,246	-,238	,676**	,893**	,312	,321

*p-value <0,05

** p-value<0,01

hydroxides and to the organic matter as well as its solubility depends on the carbonate phase-binding of Pb. Factor 2 (18% of the total variance) grouped DTPA extractable Pb, salinity and carbonates content, indicating that bioavailability of Pb is associated to variations on soil salinity and carbonates. For road dust, Pb distribution in the different soil phases was mainly affected by its total concentration; and its bioavailability is linked to the correlation among DTPA, and carbonates, reducible and oxidizable phases (factor 1, representing 40% of variance). Factor 3, which explains the 14.7% of the total variance, grouped salinity and exchangeable phase suggesting that an increment of dust salinity promotes higher mobility of Pb, making it more available for the trophic chain (Abollino et al. 2002). This component model accounts for the 87% and 85% of the soil and road dust variance respectively.

Zinc

Positive correlations were found among total, DTPA and water extractable Zn, carbonate, reducible, oxidizable and residual phases for soil (Table 4.5), grouped in factor 1 (55% of the explained variance) (Table 4.4), indicating that Zn distribution on soil phases is dominated by total Zn concentration, while the bioavailability of Zn is affected by the Zn concentration on carbonate, reducible and oxidizable phases. Factor 2, which explain the 17% of the total variance, grouped salinity and the exchangeable phase, suggesting that an increase on soil salinity will promotes Zn mobility (Acosta et al. 2011b). In road dust, similarly to soil, factor 1 (51.6% of the variance) grouped the total concentration of Zn, DTPA and water extractable Zn, and carbonate, reducible, oxidizable and residual phases indicating that Zn distribution and behaviour on soil/dust phases are similar in both material. This model explains the 91% of the variance for soil and road dust.

Copper

In soil samples, positive correlation was found among total Cu content and DTPA extractable Cu and oxidizable and residual phases (factor 1, 38% of explained variance) (Tables 4.4 and 4.5), suggesting that an increase on total Cu concentration in soils promotes an increment of Cu bound to soil oxidizable phase, which explains the ability of

Cu to form stable complex with the organic matter and sulphurs (Kabata-Pendias and Pendias, 1992). In addition, factor 2 (27% of explained variance) only groups reducible and exchangeable phases, indicating that Cu concentration bound to these phases are independent to any soil physic-chemical properties (Tables 4.4 and 4.5). For road dust samples, factor 1 (37.7% of the variance) shows positives correlations among DTPA extractable Cu and phases bound to carbonates and Fe/Mn oxides (reducible). Contrary, factor 2 which represent the 26% of the total variance, associates the total Cu content to the oxidizable and residual phases, suggesting that an increment on total Cu concentration in dust is mainly distributed in Cu bound to organic matter and stable minerals, respectively. This results suggested that, in the same way than Pb and Zn, Cu is not mainly affected by soil or road dust physic-chemical properties. The PCA analysis for Cu represented 79% and 90% of the soil and road dust variance respectively.

Chromium

The distribution of Cr in soil was dominated by its total concentration (factor 1- 32.7% of explained variance) (Table 4.4), the positive correlation among total Cr concentration and the most stable phase (residual) ($r = 0.954$ $p < 0.01$) suggests the precipitation and immobilization of Cr in soils (Rosales et al. 2016). Factor 2 (19% of the explained variance) grouped salinity, carbonates (negatively correlated), DTPA extractable and water soluble Cr, indicating that an increase of salinity or/and decrease on carbonates content will increase Cr mobility in soils. In addition, positive correlation was found for pH and the exchangeable phase ($r = 0.482$ $p < 0.01$) grouped in factor 3 indicating that Cr is adsorbed to pH-dependent exchangeable sites. In road dust samples, positive correlations were found among salinity, and exchangeable, carbonates, reducible and oxidizable phases (factor 1, 27% of explained variance) while factor 2 (22.6% of explained variance) related the total Cr content with carbonate and residual phases. Therefore, Cr distribution and behaviour in dust is mainly depended to dust salinity, while concentration of Cr in stable minerals (residual phase) depends of total Cr concentration. This model explains the 77.6% and the 82.3% of the variance for all soil and road dust samples respectively.

Cobalt

Distribution of Co in industrial soils is mainly dominated by the total Co content, as showed in Table 4, where the relation among total Co concentration and carbonate, oxidizable and residual phases is grouped in factor 1, which explains the 25.6% of the total variance. Factor 2 (17% of explained variance) showed a negative correlation among carbonates, salinity and the exchangeable phase, indicating that an increase in salinity and/or a reduction on carbonates could increase Co concentration in the most labile phase, and promotes Co mobility. Factor 4 (15% of explained variance) grouped pH, organic carbon and the reducible phase, showed the influence of pH and redox potential in the affinity of Co to Fe/Mn oxides (Kabata-Pendias and Pendias 1992). In road dust samples, factor 1 (23% of the total explained variance) grouped the total Co content and the residual phase suggesting that the higher amount of Co come from most stable dust minerals. Factor 2, which explain the 20% of the total variance, grouped salinity, water and DTPA extractable Co, and exchangeable and oxidizable phases, indicating that salinity is the principal dust property affecting Co mobility. The PCA explains the 73% of the variance for soil and 80% for road dust.

Nickel

In soil, Ni distribution was mainly dominated by its total concentration (factor 1, 24% of explained variance), where positive correlations with residual, reducible and oxidizable phase were observed (Table 4). In contrast, factor 2 (17% of explained variance) established a correlation between pH and carbonate phase, suggesting that a decrease of pH could dissolve carbonates which the consequent release of Ni from Ni-carbonates minerals. In road dust, factor 1, which explains the 26% of the total variance, grouped carbonates, organic carbon content, total Ni concentration and the oxidizable and residual phases, indicating that variations on organic matter content affects the concentration on oxidizable phase while total concentration is the main factor controlling the concentration on mineral soil matrix. Factor 3 (18.4% of explained variance) grouped DTPA extractable Ni and carbonate and reducible phases, indicating that Ni bioavailability is mainly controlled by Ni bound to carbonate and Fe/Mn oxides (Kabata-Pendias and Pendias 1992). This model explains 72% and 77% of the soil and road dust variance, respectively.

4.4. Conclusion

The industrial activities are increasing both organic carbon content in road dust due to traffic emissions, and salinity in soils and road dust. In addition, pH has been lightly reduced by the effect of petrochemical industry in road dust, likely due to atmospheric deposition of acidic compounds.

Zinc, Pb, and Cu showed the highest concentrations in soil for the services industrial area (P.I. Oeste) and the petrochemical activity (Escombreras), while in Lorca (tannery activity) the highest concentrations were for Cr, Zn and Pb. For road dust, Zn, Pb and Cu shown the highest concentrations in Escombreras while in P.I. Oeste and Lorca dominates Zn, Cu and Cr. The results showed that both the type of industrial activity and the type metal determine the place where the metals are accumulated (soil or dust).

Results showed that bioavailability of studied metals is affected by the industrial activity, however, no differences statistically significates were found between bioavailable concentration of metals in dust and soil from the same industrial area.

All metals distributions were dominated by the residual phase in industrial soils, however remarkable differences between industrial areas were observed (e.g. high concentration of Pb and Zn bound to carbonate and reducible phases in Escombreras soils, or high Cr concentrations bound to reducible phase from Lorca). Oppositely, only Cu, Co and Ni were dominated by residual phase in industrial road dust, while Pb and Zn were dominated by residual and reducible phases, and Cr by the reducible phase from Lorca. Therefore, results suggest that Pb, Zn, Cu and Cr distribution in the different solid phases is affected by industrial activity while Co and Ni distribution is not affected by the industrial activity.

The distribution of Pb, Zn, Cu, Ni, Co and Cr in the different solid phases in industrial soils and the distribution of Pb, Zn, Cu and Co in road dust are mainly dominated by the total metal concentration. In contrast, the bioavailability and mobility of Pb, Cr and Co in soils are mainly affected by salinity and carbonates content, while the mobility of Zn and Ni is mainly affected by salinity and pH-carbonates content respectively. Finally, the mobility of Pb and Co in dust is mainly dominated by salinity, while for Zn, its total concentration determine its mobility.

Chapter 5

**ASSESSMENT OF METALS
BEHAVIOUR IN INDUSTRIAL
SOIL USING SEQUENTIAL
EXTRACTION,
MULTIVARIABLE ANALYSIS
AND A GEOSTATISTICAL
APPROACH**

Chapter 5

ASSESSMENT OF METALS BEHAVIOUR IN INDUSTRIAL SOIL USING SEQUENTIAL EXTRACTION, MULTIVARIABLE ANALYSIS AND A GEOSTATISTICAL APPROACH

Abstract

The main objectives of this study were to evaluate the degree of Pb, Cu, Zn, Cd, Cr and Ni pollution using pollution indexes and geostatistical approach, and to assess metals dynamic using sequential extraction procedure and multivariable statistical analysis in surface soils and soil profiles from an industrial complex as a base for a correct management in order to avoid health and environmental problems. Results showed that the industrial activity increases both Pb (103 mg kg⁻¹), Zn (526 mg kg⁻¹) and Cu (39 mg kg⁻¹) concentrations and salinity in soil. Pollution indexes showed that industrial soils were moderately contaminated by Zn, Pb, Cu, Cr and Ni as well as a moderate ecological risk was reported. Two main areas were identified: southeast area with the highest metal concentrations, and northwest area with the lowest levels. Chemical speciation of metals showed that the residual phase was the dominant phase for all metals. However, Pb and Zn were highly associated to the reducible phase (25-30% and 35-40% respectively) and a significant concentration was associated to carbonates (5% for both metals). In contrast, Cu, Cr and Ni were mainly bound to the residual phase (>80% for all metals) with low concentrations retained to reducible phase, and very low concentrations bound to the most labile phases. Cd was the most mobile metal with high concentration associated to exchangeable (5%) and carbonates (15-20%) phases. Therefore, Pb, Zn and Cd represent the greatest risk for human health and the environment.

5.1. Introduction

The development of industrialization has caused an increase of soil pollution by metals in the last decades, whose effects are not only limited to industrial soils but also affect to the adjacent lands, which is especially intense when soils are used for discharge poorly treated liquid effluents and disposal of solid waste as well as deposition of exhaust gas from the industries (Fakayode and Onianwa 2002; Wu et al. 2011). However the persistence and distribution of metals in industrial areas is mainly affected by factors such as the nature of parental material, properties of soil or climatic condition (Krishna and Govil 2008). Metals in soil can remain for a long period of time acting as source and sink of contamination (Acosta et al. 2015) and therefore they are potentially hazard to ecosystems and human health (Yaylali-Abanuz 2011). Human exposure to metal pollutants may cause nervous, renal, cardiovascular and reproductive systems diseases (Christoforidis and Stamatis 2009). Therefore, in order to develop policies on pollution control and environmental management, as well as, to make decisions on soil remediation procedures, it is necessary to carefully evaluate the behaviour and distribution of metals in soils.

The contribution of metals to environmental pollution from industrial emissions has been the main subject of many studies in the recent years (Ordoñez et al. 2003; Al-Khashman and Shawabkeh 2006; Sekhar et al. 2006; Govil et al. 2008; Krishna and Govil 2008; Wu et al. 2011), where different indexes, such as contamination factor, enrichment factor or ecological risk index, have been used for determining the degree of soil pollution (Loska et al. 2004; Yaylali-abanuz, 2011; Yuan et al. 2014). However, although the total metal content in soil is useful to estimate the degree of soil pollution, the mobility of metal does not necessarily depend directly on its total metal content (Kumar et al. 2013). Chemical speciation is usually used to understand the geochemical processes governing metal mobilization (Yuan et al. 2004) because provide knowledge about the identification and quantification of different species, forms or phases of metals present in a material such as soil, sediment or waste (Naji et al. 2010), and its availability on the environment.

In addition, the identification of pollution sources, the risk areas, and the evaluation of metals behaviour in soil have been identified as key points to reach effective soil reclamations (Chen et al. 2009, Acosta et al. 2011). The use of multivariate statistical

analysis combined with geostatistical techniques have been successfully applied in the identification of sources, evaluation of metal behaviour in soil and mapping of metal spatial distribution (Rodríguez-Martín et al. 2006; Saby et al. 2009; Maas et al. 2010; Lu et al. 2012; Li et al. 2013b; Shao et al. 2014), being useful tools for developing future reclamation plans in industrial areas and its surrounding. However, the use of advanced analytical and statistical methods combined with spatial distribution analysis for evaluating the risk posed at the specific site has been little studied.

The main objective of this study was to demonstrate that the combination of different techniques and methods (sequential extraction procedure, multivariable statistical analysis and geostatistical approach) is a powerful tool for an integral evaluation of the environmental risk in areas affected by metals. To reach this objective, the degree of metals pollution (Pb, Cu, Zn, Cd, Cr and Ni) and the delimitation of risk areas using pollution indexes and a geostatistical approach were carried out. Otherwise, the identification of sources of metals and their behaviour were evaluated using a sequential extraction procedure and a multivariable statistical analysis.

5.2. Materials and methods

5.2.1. Study area and sampling

In order to evaluate the combination of analytical, statistical and geostatistical techniques for assessing contaminated sites, the most important industrial complex of Murcia city was selected (southeast of Spain), which is located in the southwest of the city. About 841 companies are situated in this industrial area, such as manufacturing paints, steel product, chemicals, electrical materials, etc. The climate of the area is semiarid Mediterranean with an annual average temperature of 18°C and annual precipitation of 350 mm. The geology of the area is dominated by Quaternary alluvial deposits from the Segura and Guadalentín rivers (I.G.M.E. 1976). In the last decades, the soils where the industrial area is currently located were subjected to intense agricultural cultivation of lemon, oranges, cereals and vegetables. Currently, the industrial soil is classified as Calcaric Regosol (W.R.B., 2014), characterized by low differentiation among horizons, a low organic matter content and high carbonates content. The study area also includes a natural area,

without any influence of the industrial activities and with the same geological material. According to W.R.B. (2014) the natural soil is classified as Haplic Calcisol, characterized by the presence of calcic horizon, with low organic matter content. This area was used as control site to determine the pollution degree of the industrial soils.

The industrial area has a surface of 3 km² where 10 surface soil samples (0-5 cm) were collected (Fig.5.1). In addition, another 10 soil samples from the natural area were also sampled. At each sampling point, three sub-samples were collected 1 meter apart from the vertices of a triangle to form a composite sample. Soil samples were taken using a soil spade. Two soil profiles were identified in the north-west and south-east of the industrial area corresponding to low and high pollution respectively (Fig.5.1); four samples were collected from different depths (0-5 cm, 5-10 cm, 10-15 cm and 15-30 cm). All samples were taken to the laboratory, and then they were air dried at room temperature during 72 hours and sieved to less than 2 mm prior to physicochemical analyses.

Fig.5.1. Sampling location

5.2.2. Analytical methods

The following properties were analysed: soil organic carbon (OC) contents by the dichromate method (Soil Survey Staff 2004); soil pH in H₂O using a glass electrode in a 1:1 soil/water suspension (Soil Survey Staff 2004); electrical conductivity (EC) in a 1:5 soil/water suspension (Andrades 1996); equivalent calcium carbonate by the volumetric method using Bernard's calcimeter, and cation exchange capacity (CEC) using sodium chloride and ammonium acetate (Soil Survey Staff 2004).

For total metal content, 1 g of ground sample was digested in 10 mL nitric acid and 10 mL perchloric acid at 210 °C during 90 minutes. After cooling, 0.1 N HCl was added to fill a 100 mL volumetric flask (Risser and Baker 1990). For soil extractable metals, DTPA (diethylene triamine pentaacetic) was used (Linsay and Norvell 1978). Water soluble metals were determined according to Ernst (1996). Total DTPA extractable and water soluble metals (Pb, Cu, Zn, Cd, Cr, Co and Ni) were measured by atomic absorption spectrometry (AAS).

Sequential extraction procedure by Tessier et al. (1979), modified by Li et al. (1995), was used for the identification of the main binding sites, the strength of metal binding to particulates and the phase associations of metals in soils (Rauret 1998). This provides information of mobility, bioavailability and toxicity of metals bound to different soil phases. The extraction was carried out in order to obtain the following fractions: 1: exchangeable; 2: carbonate bound and specifically adsorbed; 3: bound to Fe–Mn-oxides; 4: bound to organic matter and sulfide and 5: residual.

Certified reference material (BAM-U110) from the Federal Institute for Materials Research and Testing (F.I.M.R.T. 2010) and reagent blanks were used as quality control samples during the analyses. We obtained recoveries (the sum of the five fractions from sequential extraction analysis to the total element concentration of BAM-U110) of 92-109% for Cd, 91-98% for Cu, 94-105% for Pb, 91-99% for Zn, 92-107% for Cr and 96-108% for Ni.

5.2.3. Enrichment factor

Enrichment factor (EF) was calculated using the modified formula (1) from Loska (2004). The EF is based on the standardization of a tested element against a reference one. In this study cobalt was used as reference element due to its low occurrence. The reference environment adopted was the average concentration of elements in the natural area.

$$EF = (C_n(\text{sample})/C_{ref}(\text{sample})) / (B_n(\text{background})/B_{ref}(\text{background})) \quad (1)$$

where $C_n(\text{sample})$ is the content of the examined element in the industrial soils, $C_{ref}(\text{sample})$ is the content of the reference element in the industrial soils, $B_n(\text{background})$ is the content of examined element in the natural soils and $B_{ref}(\text{background})$ is the content of the reference element in the natural soils. According with Saedi (2012), EF was divided into five groups: $EF < 2$: deficiency to minimal enrichment; $2 \leq EF < 5$: moderate enrichment; $5 \leq EF < 20$: significant enrichment; $20 \leq EF < 40$: very high enrichment; $EF \geq 40$: extremely high enrichment.

5.2.4. Concentration factor

Concentration factors (CF) were calculated as the ratio of the content of a given metal (C_{metal}) to the background value ($C_{\text{background}}$):

$$CF = C_{\text{metal}} / C_{\text{background}} \quad (2)$$

The background concentration adopted was the average concentration of elements in the natural area. According to Buhiyan (2010) and Varol (2011), CF was divided into six groups: $CF \leq 0$: non contaminated, $0 < CF \leq 1$: slightly contaminated; $1 < CF \leq 3$: moderately contaminated; $3 < CF \leq 5$: considerably contaminated; $5 < CF \leq 6$: strongly contaminated; $CF > 6$: very strongly contaminated.

5.2.5. Ecological risk

This index comprises a single contamination coefficient, a comprehensive contamination measure, the toxic response factor for each metal. and a potential ecological risk index. The specific formulas are:

$$\text{The single contamination coefficient: } C_{fi} = C_i / C_b$$

where C_{fi} is the contamination coefficient of a particular metal. C is the measured data of soil metals, and C_b is the background value.

The comprehensive contamination measure: $E_i = C_{fi} \times T_i$

where T_i is the toxic response factor. According to Hakanson (1980) the toxicity values (T_i) are: Pb, Ni and Cu (5), Cd (30), Cr (2), Zn (1) and Ni (5).

The potential ecological risk index is: $RI = \sum E_i$

According to Sun et al. (2010), RI was divided into four groups: $RI \leq 50$ low risk; $50 < RI < 100$ moderate risk; $100 \leq RI \leq 200$ considerable risk y $RI > 200$ very strong risk.

5.2.6. Statistical treatment and spatial distribution of metals

The fitting of the data to a normal distribution for all properties and metal concentrations was checked with the Kolmogorov–Smirnov test at $P < 0.05$. We carried out a one-way ANOVA to investigate the differences among industrial and natural soils. Principal Component Analysis (PCA) was used to study the relationships among metals fractions and physicochemical properties and their grouping into a few factors. Varimax rotation was applied because it minimizes the number of variables with a high loading on each component and facilitates the interpretation of results (Micó et al. 2006). These analyses were carried out using SPSS 19.0 for Windows (Norusis 1993)

The total concentrations of metals were used as the input data to produce distribution maps using Arcview 3.1. An Inverse Distanced Weighted (IDW) method was adopted to generate the distribution maps (Burrough and McDonnell 1998; Lee et al. 2006).

5.3. Results and discussion

5.3.1. Geochemical characterization of soil

Geochemical characterization is essential to evaluate the environmental risk by metals in soil, since the processes and mechanisms involved on metals behaviour are affected by soil constituents and its properties (Acosta et al. 2011; Xiao et al. 2015). In this study, soils were slightly alkaline, with high amount of carbonates and moderate levels of OC, with no significant differences for pH, OC and carbonate contents between industrial and

natural areas (Table 5.1), therefore it is expected a low metals mobility. Similar OC content in both areas is due to the former land use of the industrial soils where the application of organic fertilizers took place for crop production. In contrast, electrical conductivity was higher in the industrial soils than natural areas, which indicated that industrial activities increase soil salinity through spill or dump of industrial waste.

In addition, the comparison of the metals concentrations between affected areas by human activities and natural areas can be used to identify potential sources. Concentrations of total and DTPA extractable metals, except for Cd, were higher in industrial soils than in natural soils, showing the influence of industrial activities on metals accumulation in soils. This trend for Pb suggests the influence of traffic as main source of this metal, where Pb can be released from brake, tyres and exhaust fumes. Our results are consistent with other studies where the highest Pb concentrations occurred in areas near to industrial activities and main highways and roads (Han et al. 2009; Aelion et al. 2009).

Table 5.1. Geochemical characterization of soil surface samples

	Industrial area				Natural area			
	Mean	Stand. Dev.*	Min	Max	Mean	Stand. Dev.*	Min	Max
pH	8.0	0.2	7.8	8.3	8.4	0.3	8.2	9.2
E.C. (dS m⁻¹)*	0.4a**	0.3	0.1	1.3	0.1b	0.0	0.1	0.1
Carbonates (%)	37	5.7	28	45	39	2.8	36	46
Organic carbon (%)	1.7	0.8	0.6	3.0	1.3	0.3	1.1	1.8
Total Pb (mg kg⁻¹)	85a	11	71	103	67b	4.4	57	71
Total Zn (mg kg⁻¹)	176a	167	53	526	34b	6.2	25	43
Total Cu (mg kg⁻¹)	39a	39	19	149	29b	3.6	22	35
Total Cd (mg kg⁻¹)	1.2b	0.4	0.3	1.7	1.8a	0.6	0.6	2.5
Total Cr (mg kg⁻¹)	43a	20	25	96	30b	9.7	18	47
Total Ni (mg kg⁻¹)	66a	46	46	196	24b	1.3	22	27
DTPA extr.* Pb (mg kg⁻¹)	3.9a	2.0	1.25	6.8	0.42b	0.12	0.28	0.67
DTPA extr. Zn (mg kg⁻¹)	30a	60	0.76	187	2.11b	0.30	1.50	2.59
DTPA extr. Cu (mg kg⁻¹)	3.5a	3.7	0.77	13	1.33b	0.06	1.22	1.40
DTPA extr. Cd (mg kg⁻¹)	0.05b	0.03	0.00	0.09	0.08a	0.04	0.01	0.12
DTPA extr. Cr (mg kg⁻¹)	0.29a	0.10	0.08	0.45	0.19b	0.05	0.13	0.29
DTPA extr. Ni (mg kg⁻¹)	0.78a	0.16	0.63	1.16	0.29b	0.07	0.20	0.45
Water sol.* Pb (mg kg⁻¹)	BDL†	-	-	-	0.13	0.03	0.09	0.19
Water sol. Zn (mg kg⁻¹)	0.58a	0.62	0.00	1.89	0.10b	0.03	0.05	0.15
Water sol. Cu (mg kg⁻¹)	0.17b	0.11	0.08	0.42	0.33a	0.12	0.11	0.46
Water sol. Cd (mg kg⁻¹)	0.01b	0.01	0.00	0.02	0.06a	0.03	0.01	0.09
Water sol. Cr (mg kg⁻¹)	0.20a	0.10	0.08	0.37	0.10b	0.03	0.06	0.15
Water sol. Ni (mg kg⁻¹)	0.44a	0.13	0.26	0.65	0.09b	0.04	0.04	0.17

*E.C.: electrical conductivity; extr.: extractable; sol.: soluble; stand. dev.: standard deviation.

**Means followed by different letters are significantly different ($p < 0.05$).

† BDL: below detection limit.

The high variability of Zn concentrations (53-526 mg kg⁻¹) in the industrial soils indicated that this metal came from a variability of industrial activities, due to the presence of many types of factories in this area (e.g., metals recycling, steel products, plastic plants, electrical materials, etc.). Although the highest concentration of Zn reached was 526 mg kg⁻¹, the mean value (176 mg kg⁻¹) was lower than those reported by Fakayode and Onianwa (2002) and Abollino et al. (2002), in industrial areas where the main activities were the production of plastic materials, paints and pharmaceutical products, 282 and 361 mg kg⁻¹, respectively.

Mean concentration of Cu in the industrial area was low (39 mg kg⁻¹), although higher than the concentration found in the natural area. This value was lower than those reported in other industrial sites (Ravera et al. 2006; Pen-Mouratov et al. 2008), which suggests a low industrial influences on soil Cu concentrations.

Mean Ni and Cr concentrations in industrial soils were higher than in natural soils, but lower than those reported in other industrial areas (Jean et al. 2007; McNear et al. 2007). So, the concentrations of these metals are likely associated to the geological material and came from the materials used in the construction of this industrial complex, and not from the industrial activities themselves.

The DTPA extractable concentrations of Pb, Zn, Cu, Cr and Ni were higher in industrial soils (Table 5.1). Therefore, high concentrations of these metals can be absorbed by plants causing a potential risk for the food chain (Pastor et al. 2007). Among all metals, Zn showed the highest water soluble fraction. With regard to Pb, despite the high total and DTPA extractable concentration, the soluble fraction was below the detection limit. This highlights the low solubility of this metal also reported by other authors (Burgos et al. 2006), and indicates that Pb is not highly mobilized in the environment.

5.3.2. Soil pollution and spatial distribution of metals

In order to determine the degree of pollution in contaminated soils, concentration factors (CF), enrichment factors (EF) and ecological risk indices (ERI) has been widely used (Zhang et al. 2009, Guillen et al. 2012; Saeedi et al. 2012; Lu et al. 2014; Yuan et al. 2014; Lin et al. 2016) and they were calculated in this study (Table 5.2). Results showed

that industrial soils had high concentrations of Pb and Zn, followed by Cr, Ni and Cu exceeding the limits proposed by Varol (2011) for considering a moderately contaminated soil ($1 < CF < 3$). Some samples of the industrial soil was classified as very strongly contaminated by Zn ($CF = 7.8$). Mean values obtained from the enrichment factors showed that industrial soils were moderately enriched by Zn ($2 < EF < 5$) (Saedi 2012). However, some samples exceeded this value for Pb, Cu, Cr and Ni. The highest EF value for industrial soil was classified as significantly enriched by Zn ($EF = 5.98$). Results obtained from ERI showed that industrial soils exceeded the values proposed by Sun et al. (2010) to consider a moderate risk ($50 \leq RI < 100$), with the highest values near to 90.

Table 5.2. Concentration, enrichment and ecological risk indexes from industrial soils

	Concentration factor			Enrichment factor			Ecological risk		
	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max
Lead	2.47	2.05	2.98	1.98	1.52	2.63	52	29	88
Zinc	2.63	0.79	7.85	2.10	0.61	5.98			
Copper	1.35	0.68	5.17	1.07	0.52	3.94			
Cadmium	0.69	0.16	0.96	0.54	0.14	0.73			
Chromium	1.44	0.82	3.21	1.12	0.63	2.07			
Nickel	1.42	0.99	4.21	1.08	0.78	2.72			

According to these results some remediation actions should be carried out in order to reduce the risk for human health and the environment. However, the selection of the best available technology for soil remediation must be based on an exhaustive knowledge on metals behaviour. In addition, the only use of these indices is not enough to develop the remediation plans or monitoring strategies since it is necessary to identify the main impacted areas to focus the major and more intense actions. In this way, spatial distribution maps are useful to visualize the spatial pattern of metals in soils (Li et al. 2013a). These maps must be used to identify metal-enriched areas for applying the remediation strategies or the placement of stations for monitoring metals concentrations. Based on the spatial distribution of Zn and Cd concentrations (Fig. 5.2a and 5.2c), the study area can be divided into two zones: i) southeast, with the highest Zn and Cd concentrations, located in the main entrance to the industrial complex with high traffic density take place; and ii) northwest, with moderate levels of Zn and Cd. Some authors

have reported that high levels of Cd come from atmospheric deposition from highways or main roads in urban and industrial areas (Manta et al. 2002; Imperato et al. 2003).

Fig. 5.2. Spatial distribution of total metals in the industrial area

The spatial distribution map of Pb (Fig 5.2b) showed that the higher concentrations were located in the southern section of the study area with a narrower range than the previous metals; therefore, the differences between north and south are not so evident with regard

to Pb concentration. Lead is mainly released from smelting, motor-vehicle exhaust fumes and from corrosion of lead pipe work (Gowd et al. 2010); in this study the main source of Pb was likely the heavy traffic.

Figure 5.2d shows the spatial distribution of Cu. The highest Cu concentration occurred in an isolated spot, likely associated to a discharge point of industrial waste. In general, as observed in the previous metals, the southeast area showed higher Cu concentrations than the northwest area.

The distribution of Ni and Cr concentrations (Fig. 5.2e and 5.2f) showed that there was a discordant area with a very high concentration in the southeast, corresponding to the main road and the main entrance of the industrial complex. However, since Ni and Cr concentrations in the rest of the area were not high, being only slightly higher than those found natural soils, the origin of Ni and Cr can be associated with the materials used during the construction of the industrial complex (building, roads etc.).

It was found from the concentration pattern of seven metals that the importance of identify the more impacted areas is crucial to develop remediation or monitoring strategies, since some metals, such as Cu, Ni and Cr, affected mainly small areas easily delimited where specific action can be carried out, e.g. waste discharge control. In contrast, the impact of other metals such as Pb, Zn and Cd is distributed in a wider area and therefore other strategies must be carried out, such as the implementation of phytotechnologies.

5.3.3. Behaviour of metals in industrial soils

For an appropriate assessment of contaminated areas it is necessary to know the behaviour of metals which helps to design sustainable actions for reducing the environmental and human health risks. In addition, it has been demonstrated that metals behaviour in soils depends of many factors, such as soil properties and characteristics, source of metals, metal distribution in soil constituents, anthropogenic activities, etc. (Abollino et al. 2002; Micó et al. 2006; Wu et al. 2011). Because of the complex mechanisms and processes occurring in the soil and in order to reach a thorough knowledge on metal behaviour is necessary to use advanced analytical and statistical

extraction and multivariable analysis (Nogueirol et al. 2010; Acosta et al. 2014; Hossain et al. 2015; Gasparatos et al. 2015; Schneider et al. 2016).

Table 5.3 shows the geochemical characterization of samples collected from soil profiles. Physicochemical properties such as pH, EC and carbonates were similar between both profiles and among depths, being alkaline, saline and with high percentage of carbonates. In contrast, organic carbon contents and CEC showed differences among profiles and depths being higher in surface soil. In addition, the profile located in the northwest area had higher organic carbon content and CEC than the profile located in the southwest. Total concentrations of Pb, Zn, Cu, Cr and Ni were higher in the southwest profile, while total Cd was similar in both profiles. The DTPA concentrations of Pb and Zn were higher in the southwest profile, while Cu, Cd, Cr and Ni concentrations were similar between both profiles. However, the DTPA concentrations for all metals were similar between depths.

Table 5.3. Geochemical characterization of soil profiles

	North-West (Industrial area)				South-West (Industrial area)			
	0-1 cm	1-5 cm	5-15 cm	15-30 cm	0-1cm	1-5 cm	5-15 cm	15-30 cm
pH	7.6	8.0	7.7	7.8	7.9	7.6	7.7	7.8
E.C.* (dS m⁻¹)	2.4	1.6	1.8	2.0	2.5	2.1	3.0	3.5
Carbonates (%)	47	49	46	48	44	43	41	35
Organic carbon (%)	1.9	1.1	0.7	0.6	0.9	0.8	0.6	0.5
C.E.C.* (cmol kg⁻¹)	20	13	9.7	7.6	9.7	9.8	8.3	7.8
Total Pb (mg kg⁻¹)	22	24	21	20	214	183	107	79
Total Zn (mg kg⁻¹)	68	61	56	56	173	114	111	90
Total Cu (mg kg⁻¹)	24	23	21	27	34	47	48	47
Total Cd (mg kg⁻¹)	1.7	1.3	1.2	1.1	1.5	1.3	1.8	1.4
Total Cr (mg kg⁻¹)	45	49	50	48	63	65	54	61
Total Ni (mg kg⁻¹)	28	23	23	24	48	46	32	29
DTPA Pb (mg kg⁻¹)	0.4	0.6	0.5	0.5	1.0	1.3	1.4	1.3
DTPA Zn (mg kg⁻¹)	1.1	0.8	0.6	0.6	2.1	2.3	1.6	1.7
DTPA Cu (mg kg⁻¹)	0.4	0.6	0.4	0.4	0.4	0.4	0.5	0.5
DTPA Cd (mg kg⁻¹)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
DTPA Cr (mg kg⁻¹)	0.3	0.3	0.2	0.2	0.4	0.3	0.2	0.2
DTPA Ni (mg kg⁻¹)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

*E.C.: electrical conductivity; C.E.C: cation exchange capacity.

Concentration of each metal in each fraction from chemical speciation is reported in Table 5.4, while the percentage of contribution of each fraction to the total concentration for a specific metal is shown in Fig. 5.3. The results from principal component analysis are showed in Table 5.5. The highest concentration of Pb in the industrial soils was

observed in the residual phase for both profiles and for the different depths. However, when the total Pb concentration increased (northwest profile), Pb was more associated to labile phases, mainly bound to Fe-Mn oxides and carbonate.

Fig.5.3. Chemical partitioning of metals in soil profiles

This is supported by the results from PCA (Table 5.5) where Pb total concentration and all phases, except for exchangeable Pb, were associated to Factor 1. These results suggest that an increase in the anthropogenic Pb is proportional to Pb associated to the reducible and carbonates phases, especially observed in the northwest profile, and therefore a higher risk of mobility occurs in this area.

Zinc concentration was mainly associated to the residual phase in all samples, although the fraction bound to the reducible phase was high (Table 5.4, Fig. 5.3), even higher than the value reported for Pb which had higher total concentration. In addition, and similarly to Pb, the profile collected from the southwest area, with higher Zn concentrations, showed an important fraction of Zn bound to carbonates. PCA showed that all phases of Zn, except for Zn bound to Fe and Mn oxides, were associated to its total concentration in Factor 1 (Table 5.5). This indicates that Zn total concentration controls the behaviour of this element in soils, and it can be more easily mobilized from soils affected by anthropogenic pollution, since an increase of total concentration will likely promote higher concentrations of exchangeable Zn and Zn bound to carbonate.

Chemical partitioning of Cd was dominated by the residual and reducible phases, although a significant percentage of Cd was bound to the carbonate and exchangeable phases (Fig. 5.3). PCA showed that the concentration of Cd from the most labile fractions (exchangeable and bound to carbonates) were mainly affected by EC and carbonates content (Factor 2), while the other fractions were affected by pH, OC, CEC and its total concentration (Factor 3) (Table 5.5). These results suggest that Cd can become easily mobilised under pH and salinity variations, and therefore a higher environmental risk is expected for this metal than for the previous ones (Osakwe 2013).

Cu was mainly associated to the residual phase, although a low but significant content was bound to the reducible and oxidizable phases (Table 5.4 and Fig. 5.3). The behaviour of Cu is mainly dominated by the carbonate content, EC and its total concentration, as reported in Factor 2 (Table 5.5) where all phases, except for soluble Cu, were included. However, soluble Cu was correlated to OC and pH in Factor 3. These observations indicate that Cu can be mobilized after organic matter mineralization, as reported by Ma and Rao (1997). However, a high environmental risk is not expected due to the low organic matter content and the low concentration of this metal in the studied soils.

Table 5.4. Concentration of metal (mg kg^{-1}) from sequential extraction procedure

Metal	Fraction	North-West of the industrial area				South-West of the industrial area			
		0-1 cm	1-5 cm	5-15 cm	15-30 cm	0-1cm	1-5 cm	5-15 cm	15-30 cm
Pb	Exchangeable	0.2	0.2	0.2	0.2	0.1	0.1	0.1	0.1
	Carbonate	0.3	0.2	0.3	0.2	9.5	7.8	7.4	5.3
	Reducible	8.2	7.1	7.1	6.4	102	104	50	31
	Oxidizable	0.1	0.1	0.1	0.1	0.9	0.8	0.7	0.2
	Residual	14	13	15	12	100	74	70	40
	Sum	23	20	23	19	213	187	129	76
	% recovery	105	84	108	98	100	102	120	97
	Exchangeable	0.1	0.1	0.1	0.1	2.0	1.6	0.2	0.2
Zn	Carbonate	1.0	1.6	0.9	0.6	13	10	5.6	2.7
	Reducible	18	13	14	15	29	37	27	34
	Oxidizable	0.3	0.2	0.2	0.6	1.9	1.6	1.5	1.5
	Residual	51	54	50	45	138	81	74	56
	Sum	70	69	65	61	184	132	108	94
	% recovery	102	113	115	109	106	116	96	104
	Exchangeable	0.3	0.2	0.2	0.1	0.2	0.3	0.2	0.2
	Carbonate	0.1	0.2	0.1	0.1	0.2	0.3	0.5	0.6
Cu	Reducible	1.0	1.3	1.8	1.7	3.0	3.5	4.5	6.5
	Oxidizable	0.5	0.3	0.3	0.3	0.6	0.7	1.1	1.4
	Residual	23	23	27	23	31	37	39	38
	Sum	25	25	29	25	36	41	45	46
	% recovery	106	106	136	91	104	89	95	99
	Exchangeable	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
	Carbonate	0.2	0.2	0.2	0.2	0.2	0.2	0.3	0.2
	Reducible	0.4	0.4	0.3	0.4	0.4	0.4	0.4	0.3
Cd	Oxidizable	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
	Residual	0.8	0.5	0.5	0.4	0.6	0.5	0.6	0.6
	Sum	1.6	1.2	1.2	1.1	1.3	1.3	1.5	1.3
	% recovery	89	92	96	102	88	97	84	94
	Exchangeable	0.1	0.2	0.2	0.2	0.1	0.1	0.2	0.2
	Carbonate	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
	Reducible	1.4	1.6	1.9	1.6	2.1	2.9	2.7	4.7
	Oxidizable	0.6	0.7	0.7	0.4	0.9	0.8	0.7	0.5
Cr	Residual	44	47	54	47	59	64	52	58
	Sum	47	49	57	50	62	68	56	63
	% recovery	104	102	114	102	98	105	104	104
	Exchangeable	0.2	0.1	0.1	0.1	0.2	0.2	0.1	0.1
	Carbonate	0.1	0.2	0.3	0.4	0.4	0.4	0.4	0.4
	Reducible	3.5	4.1	4.4	4.3	6.8	6.6	4.5	4.4
	Oxidizable	0.3	0.3	0.4	0.4	0.3	0.2	0.2	0.2
	Residual	23	23	19	23	41	46	28	32
Ni	Sum	27	27	25	29	49	53	33	37
	% recovery	98	120	107	120	103	114	103	125

Cr and Ni were mainly bound to the residual phase in all samples, with very low concentration in the rest of the chemical phases (Table 5.4 and Fig.5.3). These results suggest that Cr and Ni came from other sources different to current industrial activities, such as lithological materials (Shi et al. 2008, Li et al. 2013a) or other materials used for constructing the industrial complex as they are incorporated in the lattice of minerals. PCA showed that the concentration of Cr from exchangeable bound to carbonates and bound to Fe and Mn oxides were mainly affected by EC and carbonates content (Factor 2), while the other fractions were associated in Factor 1 (Table 5.5). In contrast, most labile fractions of Ni (exchangeable and bound to carbonates) were mainly affected by variation of pH, OC and CEC (Factor 3), while Ni bound to Fe and Mn oxides and residual fraction are associated to its total concentration.

These results suggest that the sources of metals and the soil properties (pH, CEC and EC) are important in the speciation of the studied metals in contaminated soils. Additionally, the soil composition (organic carbon and carbonates content) will determine the form of metals that dominates in the soil fractions.

5.4. Conclusion

The industrial soils were moderately contaminated by Zn, Pb, Cr, Cu and Ni, with a moderate ecological risk, and therefore some remediation actions should be carried out in order to reduce the risk for human health and the environment, techniques as phytoremediation or physical-chemical metal extraction could be used to reduce total metal content in soils, although further studies are necessities for an adequate selection. Spatial distribution maps showed two different areas, the southeast area with the highest concentration of metals and the northwest area where moderate levels of metals were found. Metals associated to industrial activity, such as Pb and Zn, showed a more disperse distribution into the industrial complex.

Results suggested that when Pb and Zn come from anthropogenic sources, they are mainly associated to the most labile phases; in contrast, when these metals come from geological sources, they are mainly bound to the most immobile phases. Cu, Cr and Ni were mainly associated to the residual phase, with very low concentrations bound to Fe-Mn oxides, and with insignificant levels bound to the most labile phases. Cd was the most

mobile metal since a high percentage of its concentration was associated to the exchangeable and carbonates phases. Therefore, Pb, Zn and Cd pose higher health and environmental risk because of their mobilization capacity, and should be monitored.

The optimal remediation techniques for dealing with metals contaminated soil will depend on the metal speciation, since this will influence the efficiency of these techniques. Therefore, a comprehensive and detailed understanding of the metals behavior is critical for developing and evaluating remediation strategies at a site, which can be carried out through advances analytical, statistical and geostatistical methods such as sequential extraction, multivariable analysis and mapping.

Chapter 6

**USE OF MULTIVARIABLE
AND REDUNDANCY
ANALYSIS TO ASSESS
ENVIRONMENTAL RISK IN
URBAN SOIL AND ROAD
DUST AFFECTED BY
METALLIC MINING**

Chapter 6

USE OF MULTIVARIABLE AND REDUNDANCY ANALYSIS TO ASSESS ENVIRONMENTAL RISK IN URBAN SOIL AND ROAD DUST AFFECTED BY METALLIC MINING

Abstract

The vicinity of abandoned mining ponds to populated areas may suppose a high environmental and health risk being necessary evaluate unreclaimend ponds as source of metal(loid)s. In order to evaluate the environmental and health risk from tailing ponds and their effects in urban areas, 10 mine wastes samples, 10 urban soil and 10 urban road dust samples were collected from two mining districts (La Unión and Mazarrón, SE Spain). Physicochemical properties and total, available and water-soluble concentration of metals (Cd, Co, Cr, Cu, Fe, Ni, Mn, Pb, Zn) and As were analyzed. Results suggest enrichment in Fe, Mn, Pb and Zn of urban soil and road dust in both studied towns. Multivariable analysis indicated that Cd, Mn, Pb and Zn in La Unión urban soil, and As, Cd, Cu, Pb and Zn in soil and Fe in road dust of Mazarrón come from mining districts. In addition, redundancy analysis showed that mobility of metal(loid)s related to mining sources were more influenced by their total concentration, while metals with a lithogeny origin were more affected by physicochemical properties.

6.1. Introduction

The extractive activity in the southwest of Spain has been an important source of economical incomes from the romans period to the latest nineties as evidence the 85 tailing ponds scattered in La Unión and Mazarrón mining districts. Mainly mined ores were Sphalerite, Pyrite and Galena (Manteca and Ovejero, 1992). Therefore, the tailing ponds are composed by high amounts of Fe-oxyhydroxides, sulphates, and potentially leachable metal(loid)s due to extreme acidic conditions.

It is known that even after mine closure, unrestored tailings ponds are a potential environmental and health risk causing negative impacts in the surrounding areas (Zornoza et al., 2012, Alcolea et al., 2015), particularly in populated areas. Mine wastes containing high sulphide concentrations are one of the most serious sources of environmental pollution (Candeias et al., 2015), which is due to the potential production of acid drainage of mine (ADM) formed by the oxidation of sulphide mineral, commonly Pyrite (Galan et al., 2003; García-Lorenzo et al., 2016). Also, under semiarid conditions metal(loid)s can be suspended in the air bound to particulate matter and redistributed into the environment (Castillo et al., 2013; Yun et al., 2016). The inherent toxicity of the dust depends upon the proximity of environmental receptors and type of ore being mined. High levels of As or Pb in windblown dust usually pose the greatest risk (Candeias et al., 2015).

Wastes from mining activity generally contain metal-rich particles that can be easily mobilized and may reach residential areas posing an increase of the risk derived to the exposure to metals via inhalation, ingestion and absorption (Carkovic et al., 2016; Lee et al., 2016), causing the accumulation of metals in the human body and diseases (Varrica et al., 2014; Nkosi et al., 2015). The abandonment of tailing ponds and transfer of metals from mines to populated areas has been reported by different researches around the world (Martínez et al., 2008; Park et al., 2014; Candeias et al., 2015; Lee et al., 2016; Castillo et al. 2013; Kribek et al., 2016). Liao et al. (2005) and Song et al. (2013) reported urban soils affected by mine wastes from 7 to 24 km far away from mine ponds, while La Unión and Mazarrón mining districts are less than 1 km to La Unión and Mazarrón towns respectively. Therefore and enrichment of metal(loid)s in these urban areas from mine wastes is expected.

In order to known the potential risk derived to the proximity of the unreclaimed ponds, the objectives of this study were evaluate the influence of the mine area as source of

metals and arsenic in urban soils and road dust in both studied towns, and identify the physicochemical properties involved on the potential mobility of metal(loid)s in each type of sampled material (mine wastes, urban soil and urban road dust).

6.2. Materials and methods

6.2.1. Study area and sampling collection

Sampling areas were located in two different mining districts: La Unión (37°37'05.7''N, 0°54'17.2''W) and Mazarrón (37°36'1''N, 1°19'52.2''W) (SE, Spain). The climate is semiarid Mediterranean characterized by an annual average temperature of 18°C and an annual precipitation of 290 mm (AEMET, 2016). Two tailing ponds from the extractive activity of Pb, Zn and Fe sulphides were selected. This selection was carried out according to their proximity to the towns (<1 km), surface area (>5000 m²), acidic conditions and high concentration of metals. La Unión pond has an extension approximately of 15500 m² and Mazarrón pond of 6100 m².

Ten waste samples from the mine ponds (5 samples from each pond) were collected, each sample were composed by 5 sub-samples from 0-15 cm depth. In addition, 10 urban soil (5 from each town) were taken in the topsoil from urban parks with a soil spade and 10 road dust samples (5 samples for each town) were collected by sweeping an area of 1 m² using a polyethylene brush (Acosta et al. 2015) (Fig. 6.1).

Fig.6.1. La Union (on the top) and Mazarrón (bottom) sampling. Red cross are soils samples and yellow dots road dust samples

6.2.2. Analytical methods

Soil and waste samples were dried at 40°C for 48 h and passed through a 2 mm sieve. A subsample of each sample was ground using an agate mortar (RetschRM 100). The pH was measured in a 1:1 water/soil suspension (Soil Survey Staff, 2004) while the electrical conductivity (EC) was measured in a 1:5 soil/water suspension (Andrades, 1996). The

equivalent calcium carbonate was determined using the Bernard's calcimeter and the organic carbon content by dichromate oxidation method (Soil Survey Staff, 2004).

The total metal(loid)s concentration (As, Cd, Co, Cr, Cu, Fe, Ni, Mn, Pb, and Zn) in soil, dust and mine waste were determined by acid digestion using a nitric-perchloric solution (Risser and Baker, 1990). Bioavailable metals and arsenic were extracted using diethylenetriaminepentaacetic acid (DTPA) for neutral soils/dust and ethylenediaminetetraacetic acid (EDTA) for acid wastes (Lindsay and Norvell, 1978).

Water soluble metals and arsenic were measured according to Buurman et al. (1996) and Frau (2000) method. The concentrations of metal(loid)s were determined by ICP-OES/MS (Agilent 7500CE).

Certified reference material (BAM-U110) from the Federal Institute for Materials Research and Testing, and reagent blanks were used as quality control samples during the analyses.

Mineral and chemical compositions of samples were determined by X-ray diffraction (XRD) and scanning electron microscopy (SEM). X-ray diffraction analysis was conducted on randomly oriented ground samples using Bruker D8 X-ray diffractometer. The morphology and in situ chemical composition of selected particles were observed and determined using a Philips XLS-30 SEM equipped with energy dispersive system (EDS). Sample for SEM analysis was mounted on an aluminum stub and coated with gold for 90 s using a Denton™ vacuum system prior to submicroscopic observations. The SEM was operated between 15 kV and 1.94 A filament current. In situ chemical composition of particles were recorded in EDAX spectrum collected either in spot (~1 µm) or full field of view mode for 400 s. Semi-quantitative (±5%) elemental composition of particles were corrected for Z (atomic number), A (absorption), and F (fluorescence) factors.

6.2.3. Statistical analysis

To ensure the fitting of the data to a normal distribution the Kolmogorov-Smirnov test was applied and data that did not follow a normal distribution were log transformed. A One-way ANOVA test was used to identify differences among groups of variables using a Tukey's post hoc with a significance <0.05. Data that failed on normality, even log-transforming, were submitted to non-parametric test such as Kruskal-Wallis test and Mann-Whitney U test at $p < 0.05$ to assess the differences between variables.

A principal component analysis (PCA) was done aiming to identify association among metal(loid)s sources, grouping variables into a few factors or principal components (PCs) that explain the data variance (Acosta et al. 2010). The PCs were determined by the correlation matrix applying a Varimax rotation with Kaiser Normalization and only components with eigenvalues above 1 were considered. Cluster analysis (CA) was used to elucidate the relationships between metal(loid)s and was undertaken according to the average linkage method. Results are shown in a dendrogram where steps in the hierarchical clustering solution and values of the distances between clusters (Pearson correlation distance) are represented (Acosta et al. 2010).

In order to know the relationship between the mobility of metal(loid)s (response variable) in wastes, soils and road dust and their total concentration and physicochemical properties a redundancy analysis (RDA), which has been successfully used in environmental studies (Van den Brink et al. 2003; Zhao et al. 2014; Lv et al. 2015; Shangguan et al. 2016; Song et al. 2016), were performed using CANOCO 4.5 (Microcomputer Power, Inc.). The resulting ordination diagrams shows the bioavailable and water-soluble metal(loid)s and environmental factors as vectors whose magnitude and angle indicate statistical significance and magnitude of the correlations with an ordination axis or another vector (Song et al. 2016).

6.3. Results and discussion

6.3.1. Soil, dust and waste characterization

Urban soil and road dust from La Unión and Mazarrón towns showed neutral pH due to the presence of high carbonate content ($>200 \text{ g kg}^{-1}$) (Table 6.1). Organic carbon content was high, 20 g kg^{-1} in soil and over 50 g kg^{-1} in road dust. Urban soil and road dust from La Unión and road dust from Mazarrón were categorized as non-saline, while urban soil from Mazarrón was slightly saline (Andrades, 1996).

Wastes from both studied ponds were extremely acid, slightly saline, and with a low organic carbon and carbonates content. Statistical significant differences on Fe, Pb and Zn and As concentrations were found between La Unión mine wastes and urban soil and road dust, but only Co was similar to La Unión road dust. For Mazarrón district the statistical

Table 6.1. Mean and (standard error) of physicochemical properties of mine wastes and urban soil and road dust samples

	LU mine	LU urban soil	LU road dust	MA mine	MA urban soil	MA road dust
pH	3,4(0,07)b ¹	7,4(0,10)c	7,0(0,14)c	2,4(0,05)a	7,5(0,12)c	7,1(0,13)c
CE *(dS/m)	4,1(0,88)bc	0,68(0,12)a	0,63(0,04)a	6,0(0,56)c	2,3(0,65)ab	0,88(0,13)a
C.O.* (%)	0,37(0,08)b	2,2(0,71)c	5,4(1,1)c	0,06(0,03)a	2,1(0,53)c	5,8(0,60)d
CaCO₃ (%)	0,62(0,08)a	17(3,8)b	30(3,2)c	0,08(0,05)a	26(2,8)bc	30(1,6)c
Total Pb	4199(846)b	1035(270)a	902(125)a	1257(148)a	803(362)a	914(267)a
Total Zn	2473(441)b	800(202)a	802(105)a	5436(565)c	331(61)a	829(163)a
Total Cu	95(14)b	101(47)b	77(5,3)b	61(5,7)b	34(4,9)a	92(7,3)b
Total Cd	5,8(1,4)ab	2,6(0,73)ab	3,2(0,44)ab	8,1(2,1)b	1,3(0,30)a	5,3(1,7)ab
Total Cr	31(2,3)b	27(0,86)ab	35(2,0)b	19(1,6)a	31(4,7)b	36(1,6)b
Total Co	4,5(0,31)a	7,5(0,66)b	5,9(0,16)ab	5,8(0,27)ab	11(0,87)c	10(0,22)c
Total Ni	17(1,2)ab	20(1,6)b	18(0,84)b	13(0,77)a	21(1,3)b	21(0,52)b
Total Fe	102762(2523)b	46365(4307)a	42751(2036)a	142919(15591)c	36481(2205)a	35890(4311)a
Total Mn	1052(123)ab	1341(223)b	868(65)ab	882(95)ab	803(188)ab	543(18)a
Total As	1908(14)c	73(23)a	68(10)a	436(51)b	31(3,9)a	63(22)a
Bioav.*Pb	77(60)b	119(50)b	99(10)b	2,0(1,4)a	53(17)b	62(16)b
Bioav. Zn	868(276)c	70(38)ab	120(20)b	2525(687)c	21(4,2)a	134(21)b
Bioav. Cu	4,2(0,91)a	13(8,8)a	14(2,4)b	17(4,0)b	3,4(0,34)a	21(2,9)b
Bioav. Cd	3,8(1,2)ab	0,54(0,24)a	0,74(0,15)a	6,7(1,6)b	0,27(0,06)a	1,5(0,59)a
Bioav. Cr	0,23(0,04)a	0,18(0,00)a	0,18(0,00)a	0,78(0,10)b	0,18(0,01)a	0,16(0,03)a
Bioav. Co	0,92(0,29)b	0,40(0,07)a	0,62(0,09)a	1,4(0,27)b	0,37(0,09)a	0,67(0,26)a
Bioav. Ni	1,8(0,63)bc	0,69(0,25)a	0,79(0,15)a	3,5(0,65)c	0,51(0,11)a	0,90(0,09)ab

Table 6.1. (Continuation)

	LU mine	LU urban soil	LU road dust	MA mine	MA urban soil	MA road dust
Bioav. Fe	267(85)c	24(10)ab	46(12)b	870(133)d	13(3,9)a	52(4,9)b
Bioav. Mn	365(124)bc	79(21)ab	100(20)ab	499(109)c	62(19)a	81(11)ab
Bioav. As	0,04(0,00)a	0,17(0,05)ab	0,17(0,02)b	0,07(0,01)a	0,14(0,04)b	0,15(0,04)b
Sol.* Pb	2,2(1,9)a	0,27(0,13)a	0,38(0,08)a	0,08(0,03)a	0,12(0,04)a	0,23(0,10)a
Sol. Zn	777(285)b	0,71(0,27)a	1,0(0,17)a	2377(662)c	0,44(0,03)a	0,89(0,10)a
Sol. Cu	2,3(0,73)c	0,69(0,26)ab	0,57(0,05)ab	12(2,4)d	0,36(0,01)a	1,4(0,28)bc
Sol. Cd	3,5(1,3)b	0,01(0,00)a	0,01(0,00)a	6,5(1,6)b	0,00(0,00)a	0,01(0,00)a
Sol. Cr	0,14(0,05)a	0,01(0,00)a	0,03(0,00)a	0,62(0,10)b	0,02(0,01)a	0,07(0,03)a
Sol. Co	0,86(0,30)b	0,02(0,00)a	0,02(0,00)a	1,3(0,27)b	0,02(0,01)a	0,03(0,01)a
Sol. Ni	1,7(0,61)b	0,09(0,01)a	0,09(0,01)a	3,2(0,65)b	0,07(0,01)a	0,14(0,02)a
Sol. Fe	8,5(4,6)b	3,0(0,81)a	4,1(0,84)a	227(103)b	2,0(0,51)a	4,1(0,83)a
Sol. Mn	334(119)b	0,63(0,13)a	1,9(0,41)a	470(105)b	2,4(1,9)a	1,7(0,44)a
Sol. As	0,02(0,00)a	0,13(0,05)a	0,09(0,02)a	0,05(0,01)a	0,09(0,03)a	0,10(0,03)a

*CE: electrical conductivity; O.C.: organic carbon; Bioav.: bioavailable metals; Sol.: soluble metals. All metals are expressed in mg Kg⁻¹.

¹Different letters indicate significant differences (p<0.05) between means after an ANOVA test.

analysis showed significant differences for Co, Cr, Fe, Ni, Zn and As among mine wastes and urban soil and road dust, while Cd and Cu showed only differences with urban soil.

Metal(loid)s in urban soil decrease as follow $\text{Fe} > \text{Mn} > \text{Pb} > \text{Zn} > \text{Cu} > \text{As} > \text{Cr} > \text{Ni} > \text{Co} > \text{Cd}$ in both studied towns and as $\text{Fe} > \text{Pb} > \text{Zn} > \text{Mn} > \text{Cu} > \text{As} > \text{Cr} > \text{Ni} > \text{Co} > \text{Cd}$ in road dust. No significant statistical differences were found for metals and arsenic among soil and road dust samples in both towns, except for Zn and Cu in Mazarrón, which showed higher concentration in the dust. Concentrations of Pb and Zn in soil and road dust and Mn in soil were higher than reported by Acosta et al. (2009; 2015) from different cities in the same Province, indicating a potential enrichment of these elements from mine area. In contrast, the Mn concentration observed in road dust was similar to values reported by Lu et al. (2009). Iron concentration was also higher in urban soil and road dust than values reported by Madrid et al. (2002) and Zhang et al. (2012) respectively, suggesting a possible enrichment from mine area.

Metals in mining ponds were in a more mobile fraction than in urban soils and road dust due to the low pH and low carbonate and organic matter content (Gupta et al. 1996; Martínez-Pagán et al. 2011). Zinc is the most mobile metal in both mine ponds followed by Mn in La Unión and Fe in Mazarrón, and continue decreasing as $\text{Cd} > \text{Ni} > \text{Co}$ in both ponds. No statistical differences were found among available metals and arsenic in La Unión soil and road dust, while in Mazarrón road dust significant differences were found with soil for Zn, Fe and Cu, being more mobile in road dust.

The concentrations of water soluble Fe, Mn and Zn in mine ponds were high, constituting a potential source of pollution by metals water runoff and leaching to populated areas and subsoils, respectively. Also, statistical differences for all water soluble metals concentration were found among mine wastes and urban soils and road dust, except for Pb in both ponds, due to the low solubility of this metal (Sun et al. 2001; Burgos et al. 2006) and Cr in La Unión which had statistically similar concentrations.

According to XRD and SEM-EDX observations the soil and dust matrix of La Unión is mainly composed of quartz (SiO_2) (Fig. 6.2a) and carbonates such as calcite (CaCO_3) and dolomite ($\text{CaMg}(\text{CO}_3)_2$) (Fig. 6.2b) with lower amounts of micas such as muscovite ($\text{KAl}_2(\text{Si,Al})_4\text{O}_{10}(\text{OH})_2$) or biotite ($\text{K}_2\text{Mg}_6\text{Al}_2\text{Si}_6\text{O}_{24}\text{H}_4$). In contrast, mine waste is

composed mainly by jarosite ($\text{K}(\text{Fe}_{0.92}\text{Al}_{0.08})_3(\text{SO}_4)_2(\text{OH})_6$), gypsum (CaSO_4), quartz (SiO_2) and clinocllore ($(\text{Mg}, \text{Fe}^{++})_5\text{Al}(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_8$), some of these minerals are grouped forming aggregates (Fig. 6.2c).

Fig. 6.2. Summary of the SEM-EDX observations of particles in dust, soil and mine samples of La Unión and Mazarrón (a. quartz, b. dolomite, c. aggregate of minerals, d. mica, e. jarosite f. gypsum).

Mineralogical composition of soil and dust matrix from Mazarrón are very similar to la union, where the main minerals are quartz (SiO_2) and carbonates such as calcite (CaCO_3) and dolomite ($\text{CaMg}(\text{CO}_3)_2$) with lower amounts of micas (Fig. 6.2d) such as muscovite ($\text{KAl}_2(\text{Si,Al})_4\text{O}_{10}(\text{OH})_2$) or biotite ($\text{K}_2\text{Mg}_6\text{Al}_2\text{Si}_6\text{O}_{24}\text{H}_4$), however in dust samples we found jarosite ($\text{K}(\text{Fe}_{0.92}\text{Al}_{0.08})_3(\text{SO}_4)_2(\text{OH})_6$) (Fig. 6.2e) likely from the mine area, where the main minerals are jarosite ($\text{K}(\text{Fe}_{0.92}\text{Al}_{0.08})_3(\text{SO}_4)_2(\text{OH})_6$), gypsum (CaSO_4) (Fig. 6.2f) and quartz (SiO_2) with lower amounts of hematite (FeO_2) and feldspars such as sanidine ($\text{K}_{0.831}\text{Na}_{0.169}(\text{AlSi}_3\text{O}_8)$).

6.3.2. Source identification of metals and arsenic

Principal component analysis and cluster analysis were used to identify sources of metal(loid)s (Facchinelli et al. 2001; Yun et al. 2016). According to results of the eigenvalues from the PCA analysis (Tables 6.2 and 6.3), three principal components were considered for all studied areas, which account for over 90% of the total variance.

Table 6.2. Varimax-rotated factor matrix for La Unión (LU) soil road dust

	Mine- LU				Soil- LU				Road dust-LU			
	PC1	PC2	PC3	Com	PC1	PC2	PC3	Com	PC1	PC2	PC3	Com
Pb	,254	,944	,181	,989	,991	-,012	,056	,986	,004	,960	,157	,946
Zn	,692	,713	,016	,987	,978	,040	,184	,993	,241	,938	-,102	,948
Cu	,352	,735	,558	,975	,077	-,913	,177	,871	-,498	-,151	-,712	,778
Cd	,990	-,027	,043	,983	,933	-,184	,303	,996	,908	,188	,175	,890
Cr	-,083	,363	,922	,989	,089	-,102	,988	,994	-,852	-,074	-,238	,788
Co	,981	-,091	,170	1,000	,087	,724	,450	,734	,943	,138	-,244	,968
Ni	,158	,125	,979	1,000	-,067	,829	,465	,908	-,837	,489	,245	1,000
Fe	-,175	,727	,406	,724	,254	,343	,720	,699	-,161	,102	,948	,936
Mn	,989	,096	-,057	,991	-,789	,148	,550	,947	,905	-,413	,016	,990
As	-,291	,923	,128	,954	,618	-,761	,183	,995	-,310	,898	,296	,990

Table 6.3. Varimax-rotated factor matrix for Mazarrón (MZ) soil road dust

	Mine-MA				Soil-MA				Road dust-MA			
	PC1	PC2	PC3	Com	PC1	PC2	PC3	Com	PC1	PC2	PC3	Com
Pb	,018	,995	-,078	,997	,857	-,288	,426	1,000	,986	,119	-,052	,988
Zn	,995	,042	,086	,999	,967	,037	-,055	,939	,989	,136	-,017	,996
Cu	,745	-,459	-,093	,775	,850	-,007	,508	,980	,009	,955	,296	1,000
Cd	,918	-,364	,044	,978	,944	-,216	,117	,951	,400	,737	-,545	1,000
Cr	,188	-,793	-,568	,987	-,226	,892	,347	,967	-,200	,979	,029	1,000
Co	,899	,328	,265	,985	-,041	,350	-,877	,893	-,882	-,192	,420	,991
Ni	,982	,183	,021	,999	-,093	,833	-,506	,959	-,156	,274	,945	,993
Fe	,217	,787	,492	,908	,251	,154	,881	,863	,952	-,068	-,221	,959
Mn	,884	,050	,435	,973	,208	,960	-,189	1,000	,633	,719	,285	,999
As	,219	,153	,960	,993	,814	,275	-,011	,738	,978	-,182	-,069	,995

Sources in mine ponds

For La Unión mine wastes, PCA grouped total Cd, Co, Mn and partially Zn concentrations in the PC1, which explains the 37% of the variance. PC2 explains the 35% of the variance of As and Pb, Cu, Fe and partially Zn, while PC3 grouped Cr and Ni (Table 6.2). Principal component analysis results were supported by results from cluster analysis (Fig 6.3a). Metals from PC1 are typically associated to zinc sulphurs in mine environments (Kabata-Pendias and Pendias, 1992), highlighting the high concentration of Mn on this area. Metals included in PC2 were associated to mineable ores as galena (PbS), sphalerite (ZnS) and pyrite (FeS₂), being the presence of Cu and As due to metal impurities associated to primary minerals or even the presence of arsenopyrite (Manteca and Ovejero, 1992). PC3 included metals which have not undergone an extractive procedure as Cr and Ni, being in lower concentrations on mine area (Table 6.1).

Fig.6.3. Hierarchical dendrogram for metals of La Unión mine wastes (a), urban soil (b), and road dust (c) and Mazarrón mine wastes (d), urban soils (e) and road dust (f)

For Mazarrón mine wastes, PCA grouped in the PC1 Cd, Co, Cu, Mn, Ni and Zn, which explains the 51% of the variance, while in PC2 were included Pb, Fe and Cr. The PC3 explains the 18% of the variance and includes only As. The Zn found in Mazarrón mine

comes from the extraction process of Sphalerite as well as its associated metals (Cu, Cd, Co, Ni, and Mn) (Table 6.3). PC2 consisted on metals Fe and Pb that comes to the alteration process of Pyrite and Galena minerals. Finally, PC3 included As which showed an independent behaviour. However, the cluster analysis (Fig 6.3b) indicated that As could be associated with Pb and Fe minerals building minerals as arsenopyrite, always in a lower concentration than others iron sulphurs.

Sources in urban areas

In La Unión urban soil, Cd, Mn, Pb and Zn were grouped in the PC1, explaining the 39% of the variance, while PC2 consisted on Co, Cu, Ni and As with a 28% of the variance explained. The PC3 grouped Cr, Mn and Fe, explaining the 24% of the variance.

For road dust samples of La Unión town, PCA grouped Cd, Co and Mn in PC1, explaining the 44% of the total variance. PC2 grouped Pb, Zn and As, representing the 31% of the variance. Finally, PC3 included Cu and Fe, explaining the 17% of the variance (Table 6.2).

For urban soil samples, the results indicated a similar behaviour of Cd, Mn, Pb and Zn, the high concentrations of these metals (Table 6.1) and the similar association found in mine pond suggest the unrestored mine ponds as the source of these metals in urban soils. A similar behaviour of Co and Ni and inverse for As and Cu was reported, indicating an geogenical origin. The association of Fe with Cr, Co and Ni, elements with a geogenical origin in the study area (Fig 6.3c), indicates that Fe, although in high concentrations (Table 6.1), comes from the geological background of the urban soils.

For road dust, PC1 was composed by Cd, Co and Mn being similar to the PC1 from the mining area, which suggests the mine wastes as source of these metals. In addition, the behaviour of metals grouped in PC2 of road dust from La Unión was similar to the metals associated to PC1 in urban soil and PC2 of mine wastes of La Unión. This relation indicated that probably the main source of Pb, Zn and As in road dust was also unrestored mine wastes. Iron in road dust of La Unión was included in PC3 showing a similar behaviour that PC3 of urban soils, suggesting the geochemical background of eroded

urban soils as source of Fe. However, cluster analysis (Fig 6.3d) linked Fe with anthropic metals indicating a partial influence of the mining activity as a secondary source.

In Mazarrón urban soils, PC1 grouped As, Cd, Cu, Pb and Zn, explaining the 41% of the variance. PC2 includes Cr, Mn and Ni that explains the 28% of the variance, while in PC3 are grouped Fe and Co with a 24% of the variance (Table 6.3). These results suggest that As, Cd, Cu, Pb and Zn have a mining origin while Cr, Ni, and Mn have a geogenical origin. Due to Fe was grouped in PC3, showing an independent behaviour from the other metal(lod)s, cluster analysis (Fig 6.3e) showed that Fe is associated to Co, Ni, Cr and Mn indicated a geological origin for this metal.

In road dust of Mazarrón PC1 associated As, Fe, Pb and Zn, that explains the 52% of the total variance, while PC2 grouped Cd, Cr, Cu and Mn, explaining the 31% of the variance. Finally, Co and Ni were included in the PC3, explaining the 16% of the variance.

Similar behaviour of As, Fe, Pb and Zn (PC1) and their high concentrations suggest a mine origin for these metal(lod)s, being the sulphured minerals of the mine wastes the main source. However, Cd, Cr, Cu and Mn (PC2) showed a different behaviour, indicating a mixed origin. Concentrations of Cu and Cr (Table 6.1) were higher in road dust than urban soils and mine wastes therefore although urban soils and mine waste contributed to increase Cu and Cr in road dust the main source comes from the urban activity. Contrary, as the concentration of Cd was higher in road dust than urban soil but lower than mine wastes the main source of Cd seems to be the mine area. Finally, PC3 (Table 6.3) and cluster (Fig 6.3f) grouped Co and Ni, which are usually associated to geological sources.

6.3.3. Effect of physicochemical properties and total metal concentration in metal mobilization

The RDA model examines the relationship between species and environmental gradients on the same diagram (McKinley et al. 2005). All environmental factor included in the RDA model has been results as significant predictors ($p < 0.05$) for the bioavailable and water-soluble metals (Lv et al. 2016).

In mine wastes of La Unión, environmental factors explained 99.2% of the variance of the metal(loid)s mobility. Axis 1 explained 96.9% of the total variance while Axis 2 explained 2.3%. The mobility of metal(loid)s (blue arrows) and the environmental variables (red arrows) are shown in Fig 6.4a. Bioavailable and water-soluble Cd, Co, Cr, Ni, Fe, Pb and water-soluble Cu were grouped in the lower right quadrant as same as properties electrical conductivity (E.C.), carbonates and total Cd and Co. Close to the Axis 1 were located total Mn and bioavailable and water-soluble Mn and Zn. In the upper right quadrant were located organic carbon (O.C.) and total Cu, Ni, Fe, Pb and Zn as well bioavailable Cu and As, while pH, total Cr and total As was located in the left upper quadrant. These results suggest that the mobility of Cd and Co in mine wastes is strongly correlated with their total concentrations and affected by E.C. and carbonate content. In addition to the previous metals, mobility of Cr, Cu, Fe and Pb was strongly associated to carbonates content, so variation of this constituent will affect the mobility of these metals (Izquierdo et al. 2015). Finally, we reported that mobility and bioavailability of Mn and Zn were strongly conditioned by their total concentrations in the mine waste (Gabarrón et al. 2017). Lin et al. (2017) reported that the behaviour of metals come from natural sources were more affected to physicochemical properties than metals from anthropogenic sources.

Urban soil of La Unión showed 96.5% of the total variance, where Axis 1 explained 86.4% of the variance and Axis 2 explained 10.1%. The RDA model showed (Fig 6.4b) that bioavailable and water soluble Cd, Co, Fe, Mn, Ni, Pb and Zn, carbonates and total As, Cd, Pb and Zn were located in the lower right quadrant. The upper quadrants include bioavailable and water-soluble Cr and Cu, pH, carbonates, EC and total Cu. These results indicate that mobility and bioavailability of Cd, Pb and Zn was strength correlated with their total concentrations in soil. As well the amount of Fe, Ni and Co in soil was also related, although negatively, with their total concentration. The bioavailability of Mn and Cr seems to be related with O.C. content for Mn, and pH and carbonate content for Cr (Shangguan et al, 2016; Gabarrón et al, 2017).

In La Unión road dust samples, environmental factors explained 96.1% of the variance of the metal(loid)s mobility. Axis 1 explained 86.5% of the total variance while Axis 2

explained 9.6%. The upper right quadrant grouped bioavailable and water-soluble As and water-soluble Cd, while within the down and right quadrant included bioavailable and

Fig. 6.4. Biplot of bioavailable (B) and water –soluble (W) metals and arsenic concentrations with physicochemical properties and total metal concentration from redundancy analysis (RDA) for La Unión mine wastes samples (a), urban soil (b) and road dust (c)

soluble Cu, Ni, Mn and Zn and soluble Fe and Pb, associated to O.C, E.C and total Cr and Ni. Finally, in the upper left quadrant were grouped bioavailable Pb, soluble Cr and pH and total Cu, Fe and Mn (Fig 6.4c). These results suggest that the bioavailability of Cd, Co, Mn and Zn was strength correlated with OC and total Cd and Zn concentrations. However, the solubility and bioavailability of As is mainly affected by its total concentration. The behaviour of water soluble Cr and bioavailable Pb were different to the other metals because of their negative correlation with pH. In addition, mobility of Cu was associated to the carbonate content.

In Mazarrón mining pond, environmental factors explained 99.9% of the total variance of metal(loid)s mobility. Axis 1 explained 99.6% of the variance and Axis 2 explained 2.3%. As is shown in Fig 6.5a, all metals except Pb were grouped to the positive part of the Axis 1, suggesting a similar behaviour on the availability and solubility of metal(loid)s. Cadmium, Cu, Ni, Mn and Zn seem to be mainly influenced by their total concentrations and EC, while Pb, which is located within the upper left square, was affected by the OC and carbonate content.

For Mazarrón soil samples, RDA analysis explained 96.6% of the total variance of metal(loid)s mobility. Axis 1 explained 63% while Axis 2 explained 33.6% of the variance. The solubility and bioavailability of metals in urban soil from Mazarrón showed similar behaviour than metals from La Unión urban soils. The solubility of Co, Mn and Ni and the bioavailability of Cd, Pb and Zn was correlated with the total metal concentration and O.C. content although their solubility is more affected by soil pH (Fig 6.5b).

In road dust samples of Mazarrón, RDA analysis explained 99.5% of the total variance, where Axis 1 explained 86.5% of the variance and Axis 2 explained 4.6%. The distribution into the RDA biplot of bioavailable and water-soluble metals of Mazarrón road dust was different to La Unión road dust. On this case, metal(loid)s were located near to the both axis in a short angle, indicating a large level of significance in the correlations (Shangguan et al. 2017) (Fig 6.5c). The bioavailability and water solubility of Pb, Zn and As was strength correlated with their total concentrations while the Cd and Cu concentrations were mainly correlated with their total concentrations and carbonate

content. The bioavailability and solubility of Mn and Co were mainly correlated with the organic carbon but also with their total concentrations.

Fig. 6.5. Biplot of bioavailable (B) and water-soluble (W) metals and arsenic concentrations with physicochemical properties and total metal concentration from redundancy analysis (RDA) for Mazarrón mine wastes samples (a), urban soil (b) and road dust (c)

6.4. Conclusions

Multivariate analysis methods can be used to classify the relationship among metal(loid)s and to identify the sources of metal(loid)s pollution in urban areas. The lack of significant statistical differences in metals and arsenic content among urban soil and road samples in both studied towns suggest a similar source of metal(loid)s. In addition, it was observed that concentrations of Cd, Fe, Mn, Pb and Zn in urban soil and road dust from La Unión and Mazarrón were anomaly higher compared to values from urban areas not influenced by mine activity, indicating a enrichment from the unrestored mine ponds.

This hypothesis were supported by PCA results, which showed that Cd, Mn, Pb and Zn in La Unión urban soil and As, Cd, Cu, Pb and Zn in soil from Mazarrón town mainly comes from the mining district. Otherwise, CA results showed that soils from Mazarrón were partially enriched on Fe from the mine, although mainly comes from the soil background as well as happens with Fe in road dust of La Unión. The behaviour observed in road dust from Mazarrón was more complex because Cd, Cr, Cu and Mn had urban and mining origin, while the Fe, Pb and Zn source was unreclaimed ponds.

The RDA analysis was performed to know if the studied physicochemical properties and the total concentration of metal(loid)s were a key factor on the mobility of metal(loid)s in mine wastes and urban soils and road dust. Thus, it was observed that metals with mining origin in soil and road dust were mainly affected by their total concentration followed by the organic carbon and carbonates content. Therefore, if abandoned tailing ponds were reclaimed the spread and the mobile fraction of metals will be lower.

Chapter 7

**DYNAMIC OF METALS AND
ARSENIC IN SOIL-PLANT
SYSTEM OF *BALLOTA*
HIRSUTA AND *HORDEUM*
VULGARE FROM TWO
ABANDONED MINING
AREAS**

Chapter 7

DYNAMIC OF METALS AND ARSENIC IN SOIL-PLANT SYSTEM OF *BALLOTA HIRSUTA* AND *HORDEUM VULGARE* FROM TWO ABANDONED MINING AREAS

Abstract

The objectives of this study were to determine the influence of mine ponds in agriculture and forest soils, and identify the dynamic of metals in the soil-plant system for native plant species (*Ballota hirsuta*) and crop species (*Hordeum vulgare*) in two ancient mining districts: La Unión and Mazarrón. Soil and plants from mine ponds and natural and agriculture areas were sampled and analysed for soil properties, and chemical partitioning of Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Zn and As. Mine, natural and agricultural soils were contaminated by As, Cd, Cu, Pb, and Zn. Chemical partitioning revealed higher mobility of metals in mine ponds than natural and agriculture soils while Fe and As were mostly bound to soil matrix due to the mineralogical compositions of soils. The accumulation of metals in *Ballota hirsuta* in La Union decrease as Fe>As>Cr>Ni>Cu>Zn>Cd>Mn>Co>Pb while in Mazarrón did as As>Fe>Cr>Pb>Cu>Ni>Co>Mn>Zn>Cd. *Ballota hirsuta* showed high ability to bio-accumulate Cu, Cr, Fe, Ni, and As, transferring a large amount to edible parts without exceeding the toxicity limits for animals. Therefore, *B. hirsuta* could be useful in phytoextraction in mine areas, especially for toxic metals such as Cr, Ni, Pb and As. Results for barley plants (*Hordeum vulgare*) showed the ability to absorb and accumulate in aerial and root systems Cr, As and Fe, and only in roots Pb, Cd, Ni and Zn, although the transfer ability was lower for all metals, except Mn. Therefore, the behaviour of metals reflects a root barrier effect although the amount of Pb, As and Cr in grain overreach the permissible limit in aliments.

7.1. Introduction

Mine activities have a negative impact on the environment, changes in landscapes, destruction of habitats, contamination of soil and water, and degradation of land resources (European Environmental Bureau 2000). Even after mine closure, huge unrestored tailings ponds remain in the mining areas with the consequent environmental risks.

In semiarid regions, lack of vegetation and scarce but torrential precipitation favour erosion of abandoned and unreclaimed mining tailing ponds, promoting dust spread and acid mining drainage generation, which affects adjacent natural and agricultural lands (Li et al. 2006; Liao et al. 2016). Once the metal(loid)s reach these areas, native and crop plants can uptake metal(loid)s and accumulate them on their tissues (Chopra and Pathak, 2012; Gitet et al. 2016; Moreno-Jimenez et al. 2016) causing a high environmental, ecological and human health risk. The accumulation of metal(loid)s by consumables plants can result toxic for wild fauna, cattle and human. In order to reduce this risk, various agencies have established metals allowed limits in food and feed (McGrath and Zhao, 2015). The metal exposure for wild fauna by ingestion becomes mainly to the accumulation of metals in edible parts of plants used as feed. A similar dietary exposure occurs for humans mainly through directly plants consumption as cereals and vegetables that can accumulate metals in grains and leaves, being the soil-to-plant transfer one of the main pathway of human and animal exposure to soil contamination (Li et al. 2006).

La Unión and Mazarrón municipalities (Murcia Region, southeast Spain) have been highly exposed to the negative effect of mining and ore operation during decades. Although the mine activity was abandoned twenty years ago, more than eighty tailings ponds remain in the area, most of them unrestored. These mine ponds are composed by high amounts of Fe-oxyhydroxides, sulphates, and potentially leachable metal(loid)s due to extreme acidic conditions. For a long time, these mine residues have been transported downstream during periods of high rainfall and atmospherically dispersed, negatively affecting natural, agricultural and populated areas (Zornoza et al., 2012, Alcolea et al., 2015). However, the dynamic of metal(loid)s in soil-plant systems from natural and crop lands have not been yet investigated, therefore, the objectives of this study were focus: (1) to determine the influence of mine ponds in near agriculture and natural soils; (2) to evaluate the dynamic of metals and arsenic in the soil-plant system for a predominant

endemic natural species (*Ballota hirsuta*) and a crop species (*Hordeum vulgare*, barley); and (3) to investigate the ability of metal(loid)s accumulation and transfer of both plant species in order to evaluate the potential use of *Ballota hirsuta* as phytoremediation plant, and to determine the human health risk of *H. vulgare* used for feed and food.

7.2. Materials and methods

7.2.1. Study area and sampling collection

Sampling areas were located in two different mining districts: Cartagena- La Unión (37°37'05.7''N, 0°54'17.2''W) and Mazarrón (37°36'1''N, 1°19'52.2''W) (southeast of Spain) (Fig 7.1). The climate of the area is semiarid Mediterranean characterized by an annual average temperature of 18°C and an annual precipitation of 290 mm (AEMET, 2016). Wastes from both ponds comes from the extractive activity of Pb, Zn and Fe sulphides that started in romans times until 1991 in La Unión and 1960 in Mazarrón. La Union pond has an extension approximately of 15500 m² and Mazarrón pond of 6100 m², both are surrounded of croplands and natural areas.

Fig.7.1. Mazarrón (left) and La Unión (right) mining districts

In order to achieve the objectives, 10 waste samples from the mine ponds (5 samples from each pond), 12 soil samples from natural soils (6 from rhizosphere soil of *Ballota hirsuta* and 6 non-rhizosphere soils) and 10 soil samples from cropland adjacent to the ponds (5 samples in each area) were collected in La Union and Mazarrón mining districts. Each sample was composed by 5 sub-samples from 0-15 cm of depth (Figures 7.2, 7.3, 7.4).

Fig.7.2. Sampling points in La Union (left) and Mazarron (right). Cross marks are mine waste samples, point marks are cropland soil and triangles are natural soil samples

Three plants of *Ballota hirsuta* from natural area and 3 plants of *Hordeum vulgare* from croplands were collected in Mazarron district. In addition, 3 plants of *Ballota hirsuta* were collected in La Unión. In contrast, orange trees have been planted recently in croplands affected by mining pond in La Unión, because of metals accumulation in orange trees is not expected, no plant samples was collected in this mining district.

Fig.7.3. Wastes samples from mining pond (a, b), agriculture soil (c,d), natural soil (e,f) from La Unión

Fig.7.4. Wastes samples from mining pond (a, b), agriculture soil (c,d), natural soil (e) from Mazarrón and *Ballota hirsuta* sp.(f)

7.2.2. Analytical methods

Soil and waste samples were dried at 40°C for 48 h, and passed through a 2 mm sieve. A subsample of each sample was ground using an agate mortar (RetschRM 100). The pH was measured in a 1:1 water/soil solution (Soil Survey Staff, 2004) while the electrical conductivity (EC) was measured in a 1:5 soil/water suspension (Andrades, 1996). The equivalent calcium carbonate was determined using the Bernard's calcimeter and the organic carbon by dichromate oxidation method (Soil Survey Staff, 2004).

The total metal(loid)s content (As, Cd, Co, Cr, Cu, Fe, Ni, Mn, Pb, and Zn,) in soil and waste were determined by acid digestion using a nitric-perchloric solution (Risser and Baker, 1990). Bioavailable metals and arsenic were extracted using DTPA for neutral soils (Lindsay and Norvell, 1978) and EDTA for acid waste. Soluble water metals and arsenic were measured according to Buurman et al. (1996) and Frau (2000) method. The concentrations of metal(loid)s were determined by ICP-MS (Agilent 7500CE)..

Chemical speciation of metals in soil and waste was determined by a sequential digestion procedure adapted from Tessier et al. (1979) and modify by Li et al., (1995). The following fractions were obtained: F1- exchangeable; F2-bound to carbonates; F3-reducible phase (bound to Fe/Mn-oxides); F4-oxidizable phase (bound to organic matter and sulphide) and F5-residual phase.

For plants analyses, each plant was separated in roots, stems and leaves, carefully washed with deionized water and dried at 50° for 72h. The dried material was grounded using a mill and 0.7 g of each sample was calcined at 450°C prior to metal redilution in 0.6N nitric acid. Metals and arsenic concentration in each plant tissue were measured by ICP-MS (Agilent 7500CE).

The reliability of the method for metals analysis in soil and waste was evaluated using a reference material (BAM-U110) from the Federal Institute for Material Research and Testing (F.I.M.R.T. 2010), reagent blanks were used as quality control samples during the analyses.

7.2.3. Data treatment

7.2.3.1. Statistical analysis

To ensure the fitting of the data to a normal distribution the Kolmogorov-Smirnov test were applied. Some data do not followed normal distribution and log transformation was

done. ANOVA test was used to identify differences among groups of variables using a Tukey's post hoc with a significance <0.05 . Data that failed on normality, even log-transforming, were submitted to non-parametric test such as Kruskal-Wallis test and Mann-Whitney U test at $p < 0.05$ to assess the differences between variables.

The relationship among metal content in soil and metal uptake by plants were study by Spearman correlations. All statistical analysis was performed using the statistics software SPSS 23 (IBM).

7.2.3.2. Bioaccumulation and translocation factors

The plant ability to accumulate metals from soils can be measured with the Bioaccumulation Factor (BAF), that is defined as the ratio of the metal concentration in the roots and the metal concentration in soil (Yoon et al. 2006; Mendez and Maier, 2008; Zornoza et al. 2016). The computation of soil to plant transfer was based on the available metal concentration on soil because it is taking account the interaction among metals and soil properties which modifies the availability of metal (Li et al., 2006).

The Translocation Factor (TF) describes the ability of plants to transfer metals from the roots to other tissues as stems, leaves, grains, and fruits. It is calculated as the ratio of the metal concentration in stem, leaf, grain and fruit tissue and the metal concentration in the root tissue (Yoon et al. 2006; Mendez and Maier, 2008; Liao et al. 2016).

7.3. Results and discussion

7.3.1. Effect of mine pond in soil properties and metal(loid)s content from natural and agricultural soils

Soil properties and metals concentrations of both studied mining districts are shown in Table 7.1.

La Union mine pond showed an extreme acidity, due to the metal extraction process, while the agriculture and natural soils have a neutral pH associated to higher carbonate content, indicating that atmospheric deposition of waste particles or runoff of acid waste material are neutralized by carbonates.

Table 7.1. Soil properties and metal/arsenic concentration, mean (standard deviation), in mine wastes, agriculture soils and natural soils

LA UNIÓN					MAZARRÓN			
	Mine	Agricultural	Natural	Natural Rhizosphere	Mine	Agricultural	Natural	Natural Rhizosphere
pH	3.4(0.07)b ¹	7.4(0.06)d	7.2(0.17)d	6.4(0.09)c	2.4(0.05)a	7.7(0.03)d	5.9(0.92)c	6.9(0.20)c
CE								
*(dS/m)	4.1(0.88)cd	1.5(0.53)b	0.6(0.15)a	1.0(0.22)ab	5.9(0.56)d	0.35(0.03)a	1.5(0.64)b	1.0(0.13)ab
C.O.* (%)	0.37(0.08)b	0.4(0.01)b	2.3(0.32)c	6.8(0.23)d	0.1(0.03)a	1.5(0.13)c	1.6(0.53)c	6.3(1.4)d
CaCO₃								
(%)	0.62(0.08)b	15(1.52)d	1.4(0.15)c	1.3(0.17)c	0.1(0.05)a	10(1.8)d	0.39(0.06)b	0.57(0.03)b
Total Pb	4199(846)c	860(180)a	2582(100)b	2857(224)b	1257(148)ab	1785(317)ab	6208(1473)c	4576(1428)c
Total Zn	2473(440)b	1660(362)ab	1893(101)ab	1969(147)ab	5436(565)c	1005(140)a	1668(194)ab	1754(38)ab
Total Cu	95(14)c	50(6.9)ab	51(11)ab	59(5.4)ab	61(5.7)ab	32(2.4)a	60(3.8)ab	58(5.8)ab
Total Cd	5.8(1.4)a	6.0(1.3)a	6.8(0.46)a	8.5(0.9)a	8.1(2.1)a	4.9(1.1)a	7.3(0.74)a	9.1(0.53)a
Total Cr	31(2.3)ab	26(3.3)ab	37.2(8.5)ab	26(5.7)ab	19(1.6)a	58(2.2)c	45(5.2)bc	47(11)bc
Total Co	4.5(0.31)a	8.0(0.13)b	13(0.95)c	11(0.51)c	5.8(0.27)ab	6.8(0.16)ab	4.6(0.19)a	5.1(0.60)a
Total Ni	17(1.2)a	19(0.31)a	80(55)c	25(1.7)c	13(0.77)b	17(0.34)a	13(0.69)bc	13(0.87)bc
Total Fe	102762(2523)b	49809(4423)a	57092(2060)a	53093(625)a	142919(15591)bc	55077(4179)a	169048(36891)bc	136265(26732)bc
Total Mn	1052(123)c	1130(77)c	1861(176)d	1743(121)d	882(94)bc	316(17)a	319(54)a	377(105)a
Total As	190(14)b	98(19)a	79(14)a	65(8.1)a	436(51)c	149(12)ab	706(155)cd	513(112)cd
Bioav.*Pb	77(59)ab	37(2.6)a	457(29)c	391(137)bc	20(1.4)a	165(50)b	791(519)c	31(21)a
Bioav. Zn	868(276)c	113(41)ab	144(27)ab	208(87)ab	2525(687)c	45(12)a	165(89)ab	308(96)bc
Bioav. Cu	4.2(0.91)ab	1.4(0.05)a	4.0(0.37)ab	3.5(0.7)a	16.8(3.9)c	2.6(0.34)a	2.9(0.77)a	3.0(0.29)a
Bioav. Cd	3.8(1.2)a	1.1(0.25)a	2.4(0.21)a	2.7(1.2)a	6.7(1.6)a	0.82(0.27)a	2.1(0.29)a	4.1(0.30)a
Bioav. Cr	0.23(0.04)a	0.2(0.01)a	0.17(0.01)a	0.19(0.01)a	0.78(0.1)b	0.19(0.01)a	0.2(0)a	0.19(0.01)a
Bioav. Co	0.92(0.29)ab	0.20(0.01)a	0.41(0.07)ab	0.42(0.09)ab	1.39(0.27)b	0.30(0.02)ab	0.36(0.18)ab	0.30(0.09)ab

Table 7.1. (Continuation)

	LA UNIÓN				MAZARRÓN			
	Mine	Agricultural	Natural	Natural Rhizosphere	Mine	Agricultural	Natural	Natural Rhizosphere
Bioav. Ni	1.8(0.63)bc	0.19(0.01)a	0.37(0.08)a	0.82(0.36)ab	3.5(0.65)c	0.31(0.04)a	0.58(0.2)ab	0.78(0.31)ab
Bioav. Fe	267(85)c	13(1.2)b	19(3.5)b	28(11)b	870(133)d	8.2(1.1)a	57(51)b	17(0.92)b
Bioav. Mn	365(124)b	32(0.95)a	75(7.1)a	93(41)ab	499(109)b	26(1.7)a	59(35)ab	76(6.8)b
Bioav. As	0.04(0)a	0.02(0)a	0.11(0.02)ab	0.14(0.04)ab	0.07(0.01)a	0.17(0.02)ab	0.10(0.04)ab	0.25(0.07)b
Sol.* Pb	2.2 (1.9)b	0.06(0.01)a	2.1(0.93)b	2.9(0.72)b	0.1(0.03)a	0.90(0.24)b	4.74(3.3)bc	0.67(0.29)b
Sol. Zn	777(285)b	1.7(1.3)a	1.6(0.65)a	7.9(2.2)a	2377(662)c	0.57(0.13)a	48.7(46)a	4.7(1.5)a
Sol. Cu	2.3(0.73)b	0.32(0.01)a	0.46(0.04)a	0.71(0.17)a	11(2.4)c	0.39(0.02)a	0.34(0.03)a	0.60(0.06)a
Sol. Cd	3.5(1.3)b	0.01(0.0)ab	0.01(0.0)a	0.04(0.01)a	6.5(1.6)b	0.01(0.0)a	0.33(0.24)ab	0.03(0.0)a
Sol. Cr	0.14(0.05)b	0.01(0.0)a	0.01(0.0)a	0.02(0.01)a	0.62(0.1)c	0.01(0.0)a	0.06(0.04)ab	0.02(0.0)a
Sol. Co	0.86(0.3)b	0.01(0.0)a	0.04(0.01)a	0.05(0.02)a	1.3(0.27)b	0.01(0.0)a	0.15(0.12)a	0.03(0.0)a
Sol. Ni	1.7(0.61)b	0.08(0.02)a	0.18(0.08)a	0.19(0.05)a	3.2(0.65)b	0.06(0.0)a	0.23(0.16)a	0.13(0.02)a
Sol. Fe	8.5(4.5)a	1.3(0.1)a	7.1(3.58)a	6.4(1.0)a	227.4(103)b	2.7(0.45)a	2.1(0.93)a	8.1(4.3)a
Sol. Mn	334(119)c	0.27(0.08)a	2.6(0.85)ab	10(2.7)b	469(105)c	0.29(0.02)a	36.4(29)b	4.6(2.2)b
Sol. As	0.02(0.0)a	0.01(0.0)a	0.08(0.03)ab	0.11(0.03)b	0.05(0.01)ab	0.13(0.01)b	0.06(0.04)ab	0.16(0.05)b

*CE: electrical conductivity; O.C.: organic carbon; Bioav.: bioavailable metals; Sol.: soluble metals. All metals are expressed in mg Kg⁻¹.

¹Different letters indicate significant differences (p<0.05) between means after an ANOVA test.

Agricultural and natural soils were classified as non-saline in both studied areas, while mine ponds were categorized as slightly saline. The organic carbon (OC) content is very low and statistically similar in agricultural soils and mine waste. Contrary the natural area showed high OC, especially in rhizosphere soil (Table 7.1).

In Mazarrón district, mine pond showed an extremely acid pH, while natural soil was categorized as moderately acid and agricultural soils were slightly alkaline, which is in accordance to the carbonates content found for each type of sampled material (Table 7.1). In contrast, salinity and OC content in natural and agricultural soil, classified as non-saline with low organic carbon content, did not shown statistically significant differences among them. However, OC content was statistically higher in rhizosphere soil than natural and agricultural soils. Kabas et al. (2014) reported an increment of organic carbon from 6.6 to 19.5 g kg⁻¹ in rhizosphere soil of *Zygophyllum fabago L.* growing in a tailing pond. McGrath and Zhao (2015) indicated that different soil physical-chemical properties affect the bioavailability and transfer of metals through plants and food chain and therefore it should be consider in metals mobility studies.

Highest concentrations in mining, agricultural and natural soils in both mining district were found for Fe, Pb, Zn, Mn and As (Table 7.1), which is in accordance with results obtained in other studies in the same mining districts (Martínez-Pagán et al. 2011; Acosta et al. 2011; Conesa and Faz, 2011). Concentrations of As, Cd, Cu, Pb, and Zn exceed the limits to consider a soil as contaminated (Table 7.2) while for Fe and Mn does not exist threshold values or background levels in European legislations. High levels of Fe, Zn and Pb were linked to the nature of the original materials enriched on pyrite, sphalerite and galena, respectively.

Table 7.2. Guidelines maximum allowed concentration and local background of metals and arsenic in soil (mgkg⁻¹).

	Pb	Zn	Cu	Cd	Cr	Co	Ni	As
Spain ^a	300	450	210	3	150	-	112	-
Netherland ^b	400	1000	500	5	-	190	100	76
Finland ^c	60	200	100	1	100	20	50	5
Background zone 3a ^d	57	90	30	0,5	114	21	57	16
Background zone 4 ^d	27	103	43	0,5	101	22	51	19

^aReal Decreto 1310/1990; ^bSRC (2009); ^cMEF (2007); ^dMartinez and Perez (2007). Zone 3a corresponds to La Union and zone 4 to Mazarrón.

The worldwide mean concentration of Cd in surface soils is 0.53 mg kg^{-1} but it has been reported that its concentration is much higher in the vicinities of Pb and Zn mines, reaching values from 3.2 to 1781 mg kg^{-1} of Cd (Kabata-Pendias and Pendias, 1992). In the study areas the concentrations of Cd were twice higher than values from European legislations and ten-fold higher than background values (Table 7.2). High Cd concentrations are associated to the exploitation of some sulphured and zinc minerals such as Sphalerite (Alvarez-Ayuso et al. 2013).

The As content in uncontaminated soils ranges from $1\text{-}40 \text{ mg kg}^{-1}$ (Li et al. 2006), and the background level for the studied areas ranges from $16\text{-}19 \text{ mg kg}^{-1}$ (Martinez and Perez, 2007), being the concentration of As six-fold higher in La Union agriculture soil and nine-fold higher in Mazarrón agriculture soil. However, it has been demonstrated that soils becoming from metal processing can reach concentrations up to $300\text{-}2000 \text{ mg As kg}^{-1}$ (Kabata Pendias and Pendias, 1992); although, the less restrictive regulation allows 76 mg kg^{-1} (SRC, 2009). The presence of high concentrations of As can be associated to ferrous minerals as arsenopyrite (Esteve et al. 2003), common on the studied area.

No statistical significant differences on the total concentration of Cd and Zn in the agricultural and natural soils and mine wastes from La Union were found, indicating that Cd and Zn in agricultural and natural lands clearly come from mine activities. Contrarily, higher concentrations of Pb, Cu, Fe and As were reported in mine waste than natural and agricultural soils (Table 7.1), which indicates that a less transfer from mine to agricultural/natural soils of these metal(loid)s is taking place, however the high concentration of Pb, Fe and As in agricultural soils suggests an enrichment of these metal(loid)s from mine waste. Statistical differences on concentration of Mn were found between mine wastes (lower) and natural soil (higher) while concentration in agricultural soil was statistical similar to mine pond. Finally, cobalt showed statistical differences among agricultural and natural soils and the mine wastes, with the highest concentration on natural soil. On the same way, Ni concentrations in mining and agricultural soils were lower than concentrations in natural soils, indicating the geological origin of both metals.

No statistical significant differences in the total concentrations of Pb and Cd were found between agricultural soils and mine wastes from Mazarrón (Table 7.1), indicating an important transfer of these metals from mine pond to croplands. In contrast, statistically

higher total concentrations of Zn, Cu, Fe, Mn and As were reported in mine waste than agricultural soils, suggesting a less transfer of these metal(loid)s from mine area to croplands compared with Pb and Cd. However the high concentration of Zn, Fe and As in agricultural soils indicates a enrichment of these metal(loid)s from mine waste. Concentrations of Cr were statistically higher in natural/agricultural soils than mine waste, suggesting a geological origin of this metal. Similarity, concentrations of Ni and Co was low and statistically similar between uses, indicating a geological origin of these metals.

7.3.2. Chemical partitioning of metals and arsenic in soil/waste

Residual phase was the predominant for all metals in mine wastes from La Unión, except for Cd where the exchangeable phase was the dominant (Fig. 7.5). In contrast, in agriculture and natural soils, Cd was mainly bound to carbonates and Fe and Mn oxides. Carbonates has been identified as a sink of metals (e.g. Pb, Zn, Cd) (Acosta et al., 2014), where metals reach with CO_3^{2-} to form metals-carbonates complex/minerals o the surface of calcitic or dolomitic crystals (Acosta et al., 2009).

In natural and agriculture soils of La Unión, a large percentage of Co, Ni, Pb and Zn bound to Mn/Fe oxides (reducible phase) was reported, revealing a redox process on the oxidized forms of metals that is not occurring in the mine pond. Results showed a higher percentage of metals bound to organic matter (oxidizable fraction) in the natural area than in agricultural soils due to the higher amount of organic matter, allowing the organometallic complexation (Table 7.1).

The behaviour of metals in Mazarrón mine pond was similar to La Union, even being higher the percentage of Cd bound to the exchangeable phase. The exchangeable fraction of all metal(loid)s was higher for mine wastes than natural and agricultural soils, which is due to the higher pH and larger concentration of carbonates in natural and agricultural soils (Table 7.1). Additionally, water-soluble concentrations of Cd, Co, Cr, Cu, Fe, Mn, Ni and Zn in the mining ponds were higher than agriculture and natural soils, which is due to the low pH and the presence of a large amounts of sulphurs in mining ponds entail a potential risk of pollution by acid mine drainage (AMD) by the accelerated dissolution of sulphide-minerals (Cruz-Hernandez et al. 2016).

Fig.7.5. Chemical partitioning of metals and arsenic

The percentages of Pb and Zn bound to residual phase in the mine wastes, agricultural soils and natural soils from Mazarrón were higher than La Unión, indicating a higher risk of Pb and Zn mobility in la Unión mining district, oppositely, higher percentage of Cd was associated to exchangeable phase in mine pond from Mazarrón than in la Unión. Finally, in both studied mine districts As was mainly bound to the soil matrix (residual phase).

7.3.3. Metals and arsenic in plants

7.3.3.1. Metals and arsenic dynamic in soil-plant system for *Ballota hirsuta*

Plants are readily to uptake the fractions of metal(loid)s that are dissolved in soil solutions in either organic or chelated forms. The ability to absorb trace elements by roots varies

greatly depending on the metal and the specie. For example, Cd is easily up taken while Zn and Fe are often slightly available to plants (Kabata-Pendias and Pendias, 1992).

Table 7.3 shows the metal concentrations obtained in different tissues for *Ballota hirsuta* from the natural area of both mining districts, and *Hordeum vulgare* (barley) from agricultural area of Mazarrón.

The behaviour of metal(loid)s is similar for *B. hirsuta* in both natural areas, despite the variation on metal(loid)s concentration, such was confirmed by non-significant differences found among metal(loid)s in plant tissues from both locations (Table 7.3). Iron, Zn, Pb and Mn showed the highest concentrations followed by As, Cu and Cr. Only statistical significant differences were observed for Mn among roots and stems in La Unión and steam and leaves in Mazarrón; and for Fe in steam and leaves in Mazarrón (Table 3), which indicates a low accumulation of these metals in stems of *Ballota hirsuta*.

A key factor in the human and ecological exposure risk is the accumulation of metal(loid)s in plants (Li et al., 2006; Clemens, 2006, McGrath and Zhao, 2015) that can be quantified using bioaccumulation factors (BAF). Figure 7.6 shows the BAF values for *B. hirsuta*. In general, the bioaccumulation of metals in La Unión decreases as Fe>As>Cr>Ni>Cu>Zn>Cd>Mn>Co>Pb while in Mazarrón did as As>Fe>Cr>Pb>Cu>Ni>Co>Mn>Zn>Cd, where any metal(loid) in the soil-plant complex exceed the soil-plant toxicity level (Table 7.4), ensuring the metal tolerance for plants (Mendez and Maier, 2008).

BAF values in root for Cd (1.11-0.39), Co (0.88-0.90) and Mn (1.01-0.57) of La Unión and Mazarrón, Pb (0.19) of La Union and Zn (0.54) of Mazarrón were close or lower than

Table 7.3. Metals and arsenic concentrations (mg kg⁻¹) in plants of natural and agriculture areas, mean (standard deviation)

La Union <i>Ballota Hirsuta</i>				Mazarrón <i>Ballota Hirsuta</i>			Mazarron <i>Hordeum vulgare</i>			
Root	Stem	Leaf		Root	Stem	Leaf	Root	Stem	Leaf	Grain
Pb	66(14)c*	35(3.4)bc	38(7.4)bc	178(70)cd	55(14)c	96(23)c	501(12)d	2.6(0.46)a	7.1(1.3)ab	3.6(2.4)a
Zn	184(44)ab	84(11)ab	95(17)ab	161(42)ab	78(29)a	137(40)ab	231(25)b	112(24)ab	83(20)ab	64(5.9)a
Cu	12(1.1)d	9.8(0.58)cd	15(1.6)d	8.6(0.61)bcd	11(2.0)d	10(0.28)cd	5.7(0.23)abc	3.9(0.35)ab	3.2(0.80)a	3.5(0.42)a
Cd	1.3(0.46)cd	1.1(0.28)cd	0.84(0.16)cd	1.5(0.36)cd	0.49(0.08)bc	0.46(0.06)bc	3.3(1.5)d	0.16(0.07)ab	0.12(0.04)ab	0.08(0.03)a
Cr	3.3(0.49)ab	2.2(0.20)ab	4.4(1.1)b	4.9(0.26)bc	2.2(0.14)ab	3.6(0.39)ab	14(3.2)c	1.5(0.32)a	3.7(0.82)ab	3.3(0.95)ab
Co	0.33(0.04)a	0.20(0.02)a	0.24(0.03)a	0.22(0.01)a	0.10(0.02)a	0.21(0.03)a	0.77(0.13)a	0.03(0.00)a	0.13(0.02)a	0.04(0.01)a
Ni	1.7(0.34)c	1.2(0.09)abc	1.8(0.37)c	1.2(0.08)abc	1.0(0.01)abc	1.6(0.18)bc	1.7(0.14)c	0.36(0.08)a	0.68(0.07)ab	0.62(0.07)a
Fe	328(62)abcd	387(52)bcd	645(91)d	512(60)cd	239(33)abc	653(116)d	893(121)d	27(3.1)a	179(19)abc	87(40)ab
Mn	64(8.4)d	28(2.7)abc	55(12)bcd	43(3.7)abcd	23(3.3)ab	59(14)cd	33(2.3)abcd	19(2.3)a	47(4.2)abcd	19(3.4)a
As	2.3(0.53)bcd	1.3(0.22)abc	2.1(0.30)bcd	12(3.0)d	2.4(0.45)cd	6.6(1.2)d	23(2.9)d	0.53(0.15)ab	2.3(0.50)cd	0.76(0.52)a

*Different letters indicate significant differences (p<0.05) between means after an ANOVA test.

Table 7.4. Toxicity levels of metals and arsenic in plants (mg kg⁻¹)

	Pb	Zn	Cu	Cd	Cr	Co	Ni	Mn	As
Soil-plant toxicity level ¹	100-500	400	200	3	1-10	-	90	3000	15
Leaf tissue toxicity limit ¹	30-100	100-400	20-100	5-30	-	-	10-300	400-1000	5-20
Domestic animal toxicity limit ²	100	500	40	10	-	-	100	2000	30
Permissible limit in aliments ³	0.3	99.4	73	0.2	2.3	50	67.9	500	-

¹Kabata-Pendias and Pendias, (1992); Mendez and Maier (2008).

²NRC (2005).

³FAO/WHO (2001)

one, indicating that *Ballota hirsuta* does not accumulate these metals of its tissues. However, a high bioaccumulation of As, Cr and Fe was reported in both mine districts and for Pb in Mazarrón (Fig. 7.6). Especially important is the bioaccumulation of As and Pb due to the high toxicity of these elements (OSHA, 2016), reaching values higher than 10.

Fig.7.6. Bioaccumulation factor of *Ballota hirsuta* in La Union (LU) and Mazarrón (MA) mining district (plant parts differentiation)

Differences in the absorption of Pb for the same plant species in natural soil with similar properties (Table 7.1) suggest that the bioavailable and water soluble Pb concentrations are the main responsible of the differential absorption of Pb by *Ballota hirsuta* (Table 7.1 and 7.3).

Translocation factors (TF) from roots to leaves in *Ballota hirsuta* were higher than the translocation factors from roots to stems, indicating that metals preferably are accumulated in leaves (Fig. 7.7a and 7.7b). For Cr, Ni, Fe, Mn and As, values of TF higher than one was reported (Fig. 7.7a and 7.7b), implying that this species accumulate

these metals in its aerial parts, specifically in leaves. Also, in any case leaf tissue toxicity levels and domestic animals toxicity limits had been exceeded (Table 7.4).

Fig.7.7. Translocation Factor of *Ballota hirsuta* in La Union (a) and Mazarrón (b) mining district

Bioaccumulation factor of Cu had a positive correlation with both the most mobile fractions of Cu in soils (F1 $r=0.81$ $p<0.01$; F2 $r=0.87$ $p<0.01$ and F3 $r=0.941$ $p<0.05$) and the transfer factor of Cu from roots to leaves ($r=0.94$, $p<0.05$), indicating that the absorption of this metal is mainly affected by its labile concentration in soils and immediately is translocated to areal tissues of *B. hirsuta*.

Behaviour of Cr in *B. hirsuta* from either natural area was similar, with highest contents of Cr in roots and leaves, as showed by the translocation factor (TF) which indicates that the Cr transfer to stem is just an intermediate step in the transfer from roots to leaves as shows the positive correlation among Cr concentration in stems and leaves ($r = 0.87$, $p < 0.01$).

Nickel concentration in *B. hirsuta* is correlated with its bioavailable concentration in soil ($r = 0.94$, $p < 0.05$), indicating that an increment in soil levels of Ni will cause an increase in plant tissues of *B. hirsuta*. Although Ni is mobile and used to be accumulated in leaves as is showed by the accumulation and translocation factors (Fig.7.4 and 7.5), however its transfer and accumulation depends on plants metabolism (Kabata-Pendias and Pendias, 1992).

Although huge concentrations of Fe have been reported for the mining natural soils (Table 7.1), its bioavailability concentrations were low. However, a positive correlation among Fe in root and the residual fraction has been found ($r = 0.83$, $p < 0.01$). Highest values of TF were found for leaves of *B. hirsuta*, reaching the highest value of all transfer factors calculated. Manganese is associated to Fe-enriched soils in arid and semiarid zones (Kabata-Pendias and Pendias, 1992) showing a similar behaviour to Fe. Hence, Mn was positive correlated ($r = 0.83$, $p < 0.01$) with the residual fraction (mineral matrix of soil) explaining its low accumulation ability in *B. hirsuta*. The Mn concentration in plants is preferentially transported to meristematic tissues, thus its concentration is mostly observed in young tissues, although it can fluctuates greatly within the plant parts and the vegetative period (Kabata-Pendias and Pendias, 1992).

Arsenic was likely bound to Fe-minerals, and therefore presented in more insoluble and less labile forms (Signes-Pastor et al. 2016), however As bound to Fe-minerals can be liberated by hydrolysis processes (Obeidy et al. 2016). In this study, a positive correlation among root As concentration and As bound to residual fraction of soil was reported ($r = 0.88$, $p < 0.01$), indicating that As can be mobilized and absorbed by roots of *B. hirsuta*. The major part of As mobilized from mineral fraction was likely re-distributed on the less available fractions on the soil solid-phase (Obeidy et al. 2016).

Cadmium in plant is very mobile and is easily adsorbed by roots and quickly transferred and accumulated in leaves (Sghayar et al. 2015) such is showed by the positive

correlation of stem with leaf ($r = 0.88$, $p < 0.01$) and the bioavailable fraction of soil ($r = 0.83$, $p < 0.01$). The bioaccumulation factor of Cd for *B. hirsuta* showed a low level of accumulation but the little amount accumulated is transferred to edible parts (Fig. 7.6 and 7.7).

7.3.3.2. Metals and arsenic dynamic in soil-plant system for *Hordeum vulgare*

For the agricultural area close to Mazarrón mining pond statistical differences in the mean concentrations of Cd, Cr, Fe, Ni, and Pb among roots and edible parts (stem, leaf and grain) of barley (*Hordeum vulgare*) were observed (Table 7.3). For Zn were only found differences among root and grain, while for As roots showed significant differences with stem and grain but not with leaves. It was related to the bioaccumulation factor (Fig. 7.8) that shows values higher than one in roots for Pb (2.28), Zn (3.88), Cu (1.66), Cd (3.06), Cr (54.91), Co (1.93), Ni (4.01), Fe (81.24) and As (99.28) indicating that barley adsorbs and accumulates these metal(loid)s on their tissues. The highest concentrations were reported for Fe, Zn, Pb, Mn and As, although Cd, Cr and As exceed the soil-plant toxicity levels (Table 7.4).

Fig.7.8. Bioaccumulation Factor of *Hordeum vulgare* (barley) in Mazarron agriculture area

The transfer of metals from roots to the edible part of the plant was measured by the translocation factor (Fig. 7.9). Metal(loid)s with less translocation to leaves and grain were some of the most toxic elements as Pb, Cd or As that were mainly retained in root as

is supported by BAF results (Fig.7.8). Results obtained for Cd are in accordance to describe by Zhao et al. (2004) in cereal growing areas of United Kingdom. The root barrier effect was also described in Basta et al. (2005) and Soriano-Disla et al (2014).

Fig.7.9. Translocation Factor of *Hordeum vulgare*

The Spearman's correlation showed that the Pb in barley roots is positively correlated with the exchangeable ($r = 1$, $p < 0.005$), oxidizable ($r = 1$, $p < 0.005$) and residual ($r = 1$, $p < 0.005$) fractions in soils. Additionally, Pb in edible parts is correlated to the most soluble Pb species ($r = 1$, $p < 0.005$). In spite of low accumulation trend, the amount of Pb in grain overreach the permissible limit in aliments suggested by FAO/WHO (2001), while the concentration of Pb in grain, stem and leaf was within the limits for domestic animals (Table 7.4).

The BAF for Cr was one of the highest values reported and a positive correlation with the reducible fraction was found ($r = 1$, $p < 0.05$) while a negative correlation was found among Cr concentrations in roots and grains ($r = -1$, $p < 0.05$), indicating that Cr is immobilized in roots and it cannot be transferred to grain. According to Singh et al. (2013) the maximum amount of Cr is usually accumulated in roots followed by leaves and fruits, probably due to the poor translocation of this element because of the formation of insoluble Cr compounds in the roots system. However, some plants from hyper-Fe ambient are more effective translocating Cr to aerial parts (Singh et al. 2013), as consequence barley grains exceeded the permissible limit in aliments (Table 7.4).

The accumulation of Fe and As was 10 and 30 times higher respectively in root tissues than in grain, which can be explained by the poor ability of barley to translocate them to the edible parts. However, the amount of As in grain exceed the permissible limit in aliments being a risk for the human health (Table 7.4).

7.4. Conclusions

The highest concentration of metal(loid)s in mining, agriculture and natural soils in both mining districts were found for Fe, Mn, Pb, Zn and As. However, the concentration of Cd, Cu, Pb, Zn, and As exceed the limit to consider contaminated soil, which is likely due to the enrichment of the agriculture soils by As, Cd, Fe, Pb and Zn from the mine wastes. The chemical partitioning revealed higher mobility of metals in mine ponds than natural and agriculture soils where metals are mainly bound to carbonates and Mn/Fe oxides (reducible phase). Only arsenic is mostly bound to the soil matrix due to the mineralogical compositions of soils in both mine districts.

The ability of plants to uptake metals and arsenic from the soil solution and incorporate to their tissues has often been used in soil reclamation, but this ability varies depending on the metal and the specie. In natural areas, *Ballota hirsuta* showed a higher ability to bioaccumulate Fe, As, and Cr transferring a large amount of them to the edible parts, preferably leaves, without exceeding the toxicity limits for animals. Therefore *B. hirsuta* could be useful in phytoremediation of these elements in mining areas under semiarid climate. Differences observed on Cu and As transfer and accumulation in both mine districts can be explained by the different concentration of these metals in the most labile fractions.

The behaviour of metals in barley (*Hordeum vulgare*) reflects a root barrier effect for all metals, even for some potentially toxic elements as Cd, Pb and As. However, although the translocation factor to leaf and grain is low, the accumulation of Cr, Pb and As in grains overreach the permissible limit in aliment suggested by FAO/WHO (2001) but not the limits for domestic animals (NRC, 2005). Therefore, agricultural areas near to mining ponds can contribute to metal(loid)s enrichment of crops with the consequent environmental and human risk.

Chapter 8

**INFLUENCE OF
AGRICULTURE
MANAGEMENT OF
DIFFERENT CROPS IN THE
SPECIATION OF METALS
AND ARSENIC IN SOILS**

Chapter 8

INFLUENCE OF AGRICULTURE MANAGEMENT OF DIFFERENT CROPS IN THE SPECIATION OF METALS AND ARSENIC IN SOILS

Abstract

Soil affected by an intensive agriculture production could result in metal pollution if bad management practices are carried out. The aim of this study is evaluate the influence of crops management on soil metal speciation and identify sources of metals in each crop. To achieve these objectives, 40 soil samples from cereal, fruit, citrus and horticultural crops and 15 samples from non-disturbed areas were collected. Physic-chemical properties such as pH, salinity, texture, organic carbon and carbonate contents were analysed. In addition, total metal, DTPA-extractable and water-soluble Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Zn and As concentration and their chemical speciation were determined. Results showed that citrus and horticultural soils were enriched by Pb and Cd, cereal by Pb, fruit by Zn, while all crops are prone to accumulate Cu in soils, especially citrus crop. According to metal speciation, cereal soils was who pose a higher risk because the high mobility of Cd, while in horticultural crops the highest risk was caused by Pb mobility. Hence the crop management enriched soils in Cd, Cu, Pb and Zn being practices on citrus crops the major contributor to soil pollution.

8.1. Introduction

Soils can act as sink and source of metal(loid)s involving potential harmful effects for human health and the environment (Cai et al., 2015; Acosta et al., 2015). Concretely, agricultural soil may have direct and indirect influences on public health via food production (Huang, 2007) because of the persistent nature of metal(loid)s in soil, making them potentially hazardous due to the absorption and accumulation in edible parts and fruits that later are eaten by human and animals causing a risk for the human and environmental health (Khan et al., 2013). The presence of metal(loid)s in agricultural soils is derived to undisturbed and anthropogenic sources. Undisturbed contents of metal(loid)s depends on the geology of the parent materials (Lu et al., 2012), however long-term agricultural practices cause enrichment of metals, particularly Zn, Cu, and Cd, due to the application of mineral fertilizers, pesticides and organic amendments (Rodriguez et al., 2008; Liu et al., 2015). Many metals are essential micronutrients however an excess of metals in soils can have a negative effect on the quality of agricultural products (Nicholson et al., 2003).

Otherwise, the chemical speciation of metal(loid)s in agriculture soils provide knowledge about its mobility and retention as well as their availability to crops and the potential toxicity in order to avoid environmental and health risks (Sofianska and Michailidis, 2015; Zong et al., 2016).

Murcia Province is characterized by intensive agriculture, representing the cultivated land more than 50% of the total province surface and being one of the major economic drivers of the area. These factors exert a high pressure on the soils, which could result in metal(loid)s pollution. This land use pattern is typical and representative of Mediterranean semiarid areas (Micó et al., 2006b); hence a good management of agriculture soils is essential for a sustainable agriculture development.

Many authors has used the multivariate analysis as method for the identification of sources of metals in agriculture soils (Facchinelli et al., 2001; Micó et al., 2006,2006b; Peris 2007,2008; Rodriguez-Martín et al., 2006, 2013; Deng et al., 2016; Lin et al., 2017) but none have compared different types of crops. The aim of this study was to identify the source of metal(loid)s in each type of crop and elucidate the crop management influence on the metal(loid)s speciation.

8.2. Material and methods

8.2.1. Study area and sampling collection

Four agricultural areas were selected from different municipalities within Murcia Province (southeast Spain) according to the predominant type of farming: cereal (CER), fruit (FRU) (peach production), citrus (CIT) (oranges and lemons) and horticultural (HOR). The climate is Mediterranean semiarid characterized by an annual average of temperature of 18°C and an annual precipitation of 290 mm (AEMET, 2016). This low rainfall requires in many cases the use of water for irrigation using drip irrigation in most of the agricultural lands.

Forty crop soil samples (10 by each type of crop) and 10 undisturbed soil samples close to each crop were collected, (CER-UND, FRU-UND, CIT-UND) (Fig. 8.1). Neither undisturbed soil samples were collected for the horticultural agriculture area because of the highly alteration of soil around. Instead, has been used the non-disturbed soil from citrus sampling area because of the same parental materials, deposited eroded quaternary conglomerates, gravels, sands and silts (Alias and Ortiz, 1975; IGME, 2016). Each sample was composed by 5 sub-samples from 0-30 cm of depth.

Fig.8.1. Soil sampling locations of cereal (a), natural cereal (b), fruit (c), natural fruit (d), citrus (e), natural citrus (f) and horticultural (g) crops

8.2.2. Analytical methodology

Soil samples were dried at 40°C for 48 h and passed through a 2 mm sieve. A split of each sample was ground using an agate mortar (RetschRM 100). The pH was measured in a 1:1 water/soil solution (Soil Survey Staff, 2004) while the electrical conductivity (EC) was measured in a 1:5 soil/water suspension (Andrades, 1996). The equivalent calcium carbonate was determined using the Bernard's calcimeter and the organic carbon by dichromate oxidation method (Soil Survey Staff, 2004). Particle size distribution of soil was determined using a laser diffraction particle sizer (Mastersizer 2000).

To determine the total metal (Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn) and arsenic concentrations, samples were digested using nitric-perchloric solution (Risser and Baker, 1990). Bioavailable metals were determined using a diethylenetriaminepentaacetic acid (DTPA) extraction (Lindsay and Norvell, 1978) and water soluble metals were measured according to Buurman et al. (1996) and Frau (2000) method. Metals and arsenic concentrations were determined by ICP-OES/MS (Agilent 7500CE).

Chemical speciation of metals in soil was determined by a sequential digestion procedure adapted from Tessier et al (1979) and modify by Li et al, (1995). The following fractions were obtained: F1- exchangeable; F2-bound to carbonates; F3-reducible phase (bound to Fe/Mn-oxides); F4-oxidizable phase (bound to organic matter and sulphide) and F5-residual phase.

The reliability of the method for metals analysis in soil was evaluated using a reference material (BAM-U110) from the Federal Institute for Material Research and Testing (F.I.M.R.T. 2010) and reagent blanks were used as quality control samples during the analyses.

8.2.3. Statistical analysis

The fitting of the data to a normal distribution for all properties and metal(loid)s concentrations was checked with the Kolmogorov–Smirnov test ($p\text{-value} < 0.05$). A one-way ANOVA with a Tukey's post hoc ($p\text{-value} < 0.05$) was carried out to elucidate the differences among type of crops. Data that failed on normality, even log-transforming,

were submitted to non-parametric test such as Kruskal-Wallis test and Mann-Whitney U test at $p < 0.05$.

In order to identify the possible sources of metal(loid)s in agriculture soils a Principal Component Analysis (PCA) was performed grouping variable into a few factors or principal components (PCs). The PCs were determined by the correlation matrix applying a Varimax rotation with Kaiser Normalization and only components with eigenvalues above one were considered. Cluster Analysis (CA) was used to elucidate the relationships between metal(loid)s and was undertaken according to the average linkage method. Results are shown in a dendrogram where steps in the hierarchical clustering solution and values of the distances between clusters (Pearson correlation distance) are represented (Acosta et al., 2010). All statistical analyses were carried out using SPSS 23 for Windows.

8.3. Results and discussion

8.3.1. Geochemical characterization of soils

Studied agriculture soils were non-saline and moderately alkaline due to the large amount of carbonates (>35%). Most of studied soils showed low organic carbon content as consequence of the intensive farming and the quick mineralization of the organic matter under semiarid conditions (Micó et al., 2006b), except CER-UND soils, that showed a higher percentage of organic carbon (>2%). The soil texture (USDA, 1987) of CER and CER-UND soils, CIT-UND soils and HOR soils were silt loam whereas FRU and FRU-UND soils had a loam and sandy loam texture respectively. Texture for CIT soils was silt (Table 8.1).

Mean total metals and arsenic concentrations (Table 1) decreased as follow: $\text{Fe} > \text{Mn} > \text{Cu} > \text{Zn} > \text{Cr} > \text{Pb} > \text{Ni} > \text{As} > \text{Co} > \text{Cd}$ in soils from cereal, fruit and citrus crops, in both type agricultural and undisturbed soils. Contrary, accumulation of metals in horticultural crop soil was $\text{Fe} > \text{Mn} > \text{Zn} > \text{Pb} > \text{Cu} > \text{Cr} > \text{Ni} > \text{As} > \text{Co} > \text{Cd}$.

Table 8.1. Soil properties and metal/arsenic concentration, mean (standard deviation), in natural and crop soils

	Cereal	Cereal Undist.	Fruit	Fruit Undist.	Citrus	Citrus Undist.	Horticultural
pH	8.3 (0.02)a**	8.0 (0.04)a	8.1 (0.05)a	8.5 (0.10)b	8.5 (0.03)b	8.21 (0.04)a	8.1 (0.06)a
CE *(dS/m)	0.18 (0.01)a	0.24 (0.01)b	2.1 (0.48)d	0.17 (0.01)a	0.39 (0.04)c	0.44 (0.05)cd	1.2 (0.20)d
CaCO₃ (%)	36 (3.4)a	37 (1.7)a	57 (2.5)b	51 (1.9)b	39 (0.31)a	39 (0.22)a	32 (0.82)a
C.O.* (%)	1.4 (0.09)ab	4.0 (0.24)c	0.97 (0.17)a	1.4 (0.18)ab	1.5 (0.07)ab	1.8 (0.05)b	0.97 (0.07)a
Clay (%)	16 (1.0)c	5.8 (0.51)a	7.2 (0.55)a	4.7 (0.31)a	11 (0.34)b	13 (0.40)bc	15 (0.47)c
Silt (%)	68 (2.2)c	50 (2.8)b	44 (2.8)ab	37 (3.0)a	81 (1.1)d	76 (1.9)cd	69 (1.5)c
Sand (%)	16 (3.0)a	44 (3.3)b	49 (3.3)bc	58 (3.3)c	8.3 (1.1)a	11 (1.6)a	16 (1.4)a
Total Pb	29 (1.2)c	36 (1.6)d	18 (0.72)a	18 (1.0)a	23 (0.84)b	22 (0.87)b	98 (9.6)d
Total Zn	62 (1.3)bc	61 (3.0)bc	54 (2.7)b	40 (2.1)a	83 (5.5)ab	74 (4.5)a	102 (2.6)d
Total Cu	120 (10)bc	106 (7.1)abc	144 (6.5)c	130 (25)c	141 (10)c	83 (0.80)a	86 (2.1)ab
Total Cd	0.49 (0.04)ab	0.46 (0.02)ab	0.36 (0.02)a	0.39 (0.02)ab	0.52 (0.04)b	0.89 (0.08)c	0.84 (0.05)c
Total Cr	37 (2.0)b	30 (4.3)b	28 (1.96)ab	18 (1.4)a	33.7 (1.8)b	33 (1.3)b	28 (2.2)ab
Total Co	8.2 (0.28)d	6.3 (0.21)c	4.0 (0.15)b	2.8 (0.11)a	7.2 (0.16)cd	6.7 (0.09)c	7.7 (0.23)d
Total Ni	24 (2.9)d	16 (0.72)c	12 (0.35)b	9.5 (0.42)a	22 (0.50)d	32 (8.0)d	23 (0.73)d
Total Fe	26005 (1218)b	26018 (2136)b	17774 (362)a	17298 (538)a	27134 (1226)b	26503 (1264)b	28070 (1026)b
Total Mn	412 (20)c	310 (12)b	167 (6.6)a	148 (9.7)a	334 (12)b	308 (2.6)b	369 (16)bc
Total As	12 (0.34)ab	12 (0.30)ab	12 (0.25)ab	11 (0.36)a	14 (0.40)c	13 (0.17)bc	12 (0.38)ab
Bioav.*Pb	1.2 (0.07)a	2.2 (0.15)b	0.97 (0.11)a	1.8 (0.33)ab	2.5 (0.20)b	2.3 (0.03)b	19 (2.1)c
Bioav. Zn	0.30 (0.02)a	0.77 (0.07)b	2.4 (0.44)c	0.45 (0.15)a	3.5 (0.62)c	1.7 (0.09)c	9.9 (0.61)d
Bioav. Cu	0.62 (0.02)b	0.42 (0.02)a	5.3 (0.73)d	0.35 (0.03)a	5.5 (2.7)d	2.2 (0.11)c	3.2 (0.29)c
Bioav. Cd	0.03 (0.00)ab	0.04 (0.00)bc	0.02 (0.0) a	0.02 (0.00)a	0.05 (0.00)cd	0.06 (0.00)cd	0.13 (0.01)d
Bioav. Cr	0.12 (0.00)a	0.13 (0.01)a	0.13 (0.00)a	0.12 (0.00)a	0.12 (0.00)a	0.10 (0.02)a	0.13 (0.00)a
Bioav. Co	0.09 (0.01)ab	0.07 (0.01)ab	0.14 (0.01)c	0.10 (0.01)ab	0.06 (0.00)a	0.15 (0.01)c	0.11 (0.01)bc
Bioav. Ni	0.40 (0.02)b	0.30 (0.02)ab	0.41 (0.04)b	0.24 (0.01)a	0.63 (0.03)cd	0.78 (0.02)d	0.56 (0.05)d
Bioav. Fe	4.1 (0.16)a	6.5 (0.52)c	3.1 (0.54)b	3.1 (0.31)b	15 (2.6)d	12 (0.71)d	4.8 (0.24)a
Bioav. Mn	13 (0.81)cd	11 (1.4)bc	8.4 (0.82)ab	6.9 (0.93)a	7.9 (0.49)ab	11 (0.51)bc	15 (0.70)d

Table 8.1. (Continuation)

	Cereal	Cereal Undist.	Fruit	Fruit Undist.	Citrus	Citrus Undist.	Horticultural
Bioav. As	0.02 (0.00)a	0.03 (0.01)a	0.02 (0.00)a	0.01 (0.00)a	0.06 (0.01)b	0.06 (0.01)b	0.06 (0.00)b
Sol.* Pb	<BLD	0.01 (0.00)	<BLD	0.03 (0.01)	<BLD	<BLD	0.02 (0.01)
Sol. Zn	0.04 (0.01)a	0.08 (0.04)b	0.07 (0.01)b	0.07 (0.02)b	0.06 (0.01)ab	0.05 (0.02)ab	0.07 (0.01)b
Sol. Cu	0.03 (0.00)a	0.06 (0.02)b	0.17 (0.02)c	0.03 (0.00)a	0.11 (0.01)c	0.10 (0.02)c	0.13 (0.01)c
Sol. Cd	<BLD	<BLD	<BLD	<BLD	<BLD	<BLD	<BLD
Sol. Cr	0.01 (0.00)a	0.01 (0.00)a	0.01 (0.00)a	0.02 (0.00)a	0.01 (0.00)a	0.01 (0.00)a	0.01 (0.00)a
Sol. Co	0.01 (0.00)	0.01 (0.00)	0.03 (0.01)	<BLD	<BLD	0.01 (0.00)	0.01 (0.00)
Sol. Ni	0.05 (0.00)a	0.06 (0.01)a	0.17 (0.04)c	0.06 (0.00)a	0.07 (0.00)b	0.08 (0.02)b	0.08 (0.00)b
Sol. Fe	1.63 (0.19)ab	1.9 (0.30)ab	1.3 (0.12)a	1.9 (0.46)ab	3.2 (0.32)b	2.5 (0.89)ab	1.7 (0.46)a
Sol. Mn	0.12 (0.01)ab	0.11(0.03)ab	0.16 (0.03)b	0.13 (0.03)ab	0.04 (0.01)a	0.06 (0.01)ab	0.09 (0.02)ab
Sol. As	0.01 (0.00)a	0.01 (0.00)a	0.02 (0.00)a	0.01 (0.00)a	0.04 (0.00)b	0.04 (0.01)b	0.04 (0.00)b

*CE: electrical conductivity; O.C.: organic carbon; Bioav.: bioavailable metals; Sol.: soluble metals. All metals are expressed in mg Kg⁻¹. Undist.: undisturbed soil.

¹Different letters indicate significant differences (p<0.05) between means after an ANOVA test.

The high concentration of Fe and Mn reported likely derive from the composition of the parent material (Peris et al., 2008), however the concentration of Mn in cereal crop soils was slightly higher than in the other crops and also higher than concentration reported by Micó et al., (2006) and Peris et al., (2008) for Mediterranean agriculture soils, indicating a potential enrichment from other source.

Reference concentrations of trace metals in soils from Murcia Province (Martínez and Perez, 2007) were used to evaluate the soil enrichment in the studied soils. Concentrations of Cu in CER, CER-UND, FRU, FRUT-UND soils overreach twice-fold the reference value for these areas (50 mgkg^{-1}), as same Pb in CER and CER-UND soils (26 mgkg^{-1}). In soils from horticultural crops, Cd, Cu, Pb and Zn were over their reference values (0.6, 23, 43 and 96 mgkg^{-1} , respectively) whereas citrus crop presented large amount of Pb and Cu in both undisturbed and crop soils, and Cd in undisturbed soils, becoming four times higher the amount of Cu in crop soils than the threshold value (33 mgkg^{-1}). Contrary, none studied soil overreach the threshold values set in the European Council Directive 86 / 278 / CEE for soils with $\text{pH} > 7$. Micó et al. (2006), Peris et al. (2008), Zhang et al. (2016) and Ding et al. (2017) also reported enrichment by Cd, Cu, Pb and Zn in agriculture soils.

Results showed significant statistical differences among crop soils and their undisturbed soils for Co and Ni in cereal, fruit and horticultural crops, being higher in crop soils than undisturbed soils. Also, statistical differences were reported for Pb in cereal and horticultural crops, showing higher concentration in cereal undisturbed soils, while horticultural crop soil showed the highest concentrations of Pb.

Soils from fruit and horticultural crops reported enrichment in Zn, showing statistical significant differences with their corresponding undisturbed soils. Same was observed for Cu in citrus crop soils whose concentration was twice-fold higher than its undisturbed soils. Contrary, Cd showed higher amount of Cd in undisturbed soil.

Bioavailability of metals in agriculture soils is related to the ability of plant to uptake metals through the roots (Li et al., 2006). Statistical significant differences were found among cereal crop soils and undisturbed soils for DTPA extractable Cu, Fe, Pb and Zn (Table 8.1) being undisturbed soils more prone to the bioavailability of Fe, Pb and Zn.

However, DTPA-Cu showed higher concentration in labour soils maybe due to the application of organic or inorganic fertilizers (Acosta et al., 2011). A similar behavior was found for Cu and Zn in fruit crops where the bioavailability reached concentrations 5 to 15-fold higher than undisturbed soils.

In the citrus crop, Cu was statistically high than Cu in undisturbed soils, oppositely Co in undisturbed soils was higher than agricultural land. Horticultural soils showed significant higher concentrations of Pb and Zn than those reported in undisturbed soils, while the bioavailability of Fe was lower.

Water-soluble Cu and Zn showed significant differences for cereal farmland with higher concentrations in undisturbed soils, while Cu and Ni reported higher water soluble concentration for fruit farmland (Table 8.1).

8.3.2. Chemical partitioning

Understand the behaviour of metal(loid)s in soils is essential for the environmental risk assessment. The residual phase was predominant for Cr, Cu, Fe and As in all crop and undisturbed soils. Chemical distribution of cadmium and Mn were governed by carbonate, reducible and oxidizable phases (Fig 8.2), being more easily leachable and available for plants uptake.

The mobility of the other metals varied depending of the crop. In cereal crop soils, 10% of Cd concentration was bound to the exchangeable phase despite in alkaline soils Cd trends to precipitate (Kabata-Pendias and Pendias, 1992), which suggests the addition of anthropogenic Cd to the crop soils.

The concentration of Pb and Zn bound to reducible and carbonates phases were higher in citrus and horticultural crop. The undisturbed content of Pb in soils is strongly related to the composition of the bedrock although due to the widespread pollution some soils can be enriched in Pb (Kabata-Pendias and Pendias, 1992). Thus, although Pb is reported as the least mobile among the other metals, the mobility of Pb was higher in undisturbed soils of cereal and fruit crops than theirs crop lands as was supported by DTPA results (Table 8.1). This can be due to the retention of Pb by silt and clays in agriculture soils and instability of Pb compounds from the vehicle exhaust that affect cereal undisturbed soils

(Olson and Skogerboe, 1975). Contrary, Zn was more mobile in agriculture soils, except in cereal crop (Fig 8.2 and Table 8.1) likely due to differences in the Zn sources, lithogeny for undisturbed soils or anthropic for agricultural lands.

Fig. 8.2 Chemical partitioning of metals and arsenic in cereal soil (a), natural cereal soil (b), fruit soil (c), natural fruit soil (d), citrus soil (e), citrus and vegetable natural soil (f) and vegetable soil (g)

The mobility of Co and Ni varied with the type of crop but its behaviour in crop soils seems to be linked to the behaviour in the respective undisturbed soils. Thus, although the concentration of Co bound to the residual phase was higher in fruit soils than the other crops, the bioavailability of Co in fruit crop soils was the highest (Table 8.1). It was due to Co in fruit crops was bound to mobile phases (exchangeable and carbonates) while in cereal, citrus and horticultural crops mostly of Co was bound to the reducible phase whose mobility is associated to redox processes. Compared with undisturbed soils, in cereal crop area Co is less mobile, decreasing the percentage bound to the reducible phase in favour of oxidizable phase, which suggests a lithogenic origin.

For nickel the dominant phase, after residual one, was the reducible phase because Ni is usually adsorbed to Fe-oxides and Mn-oxides in alkaline soils (Gasparatos et al, 2015), although in cereal and fruit crop soils a low percentage of Ni was bound to more soluble phases as exchangeable and carbonates being more mobile than in undisturbed soils.

The availability of As in soil is mainly governed by redox processes (Guo et al, 1997) although in Murcia soils mostly As is usually found in the less labile form (Signes-Pastor, 2016) as was showed by cereal soils. Citrus crop showed among 15% more of As bound to the reducible phase than the others crop soils maybe due to the natural redox processes, because of the similar distribution showed in the undisturbed citrus soil.

Despite the higher total Cu content in both agriculture and undisturbed soils, the mobility of Cu were low due to the presence of organic matter and high carbonate content (Cavani et al, 2016). The percentage of Cu bound to the reducible phase made this element more mobile in crop soils than in undisturbed soils.

8.3.3. Source identification

Multivariable analysis (PCA) results for the cereal agriculture area (Table 8.2) explained 81.87% of the total variance. The first component (PC1) explained 29.55% of the variance and included the following metals, Pb, Co, Ni and Mn as was supported by cluster analysis (Fig 8.3a). The total amount of Co, Mn and Ni was below the reference values for this area while concentrations in cereal crop soils were higher than undisturbed

soil, indicating a partial enrichment of these metals. Therefore, although agricultural practices played an important role on soil enrichment, the undisturbed background was more significant for these metals.

The second component (PC2) grouped Cr, Fe and Zn explaining 18.13% of the variance while PC3 included As and partially Cd and explained 17.63% of the variance. In Mediterranean regions Cr and Fe are mainly lithogenic elements (Peris et al., 2008) as well Zn which can form soluble or insoluble salts according to the pedogenic processes (Micó et al., 2006; Sun et al., 2013; Zhang et al., 2016). Despite PCA grouped Pb into PC1, the Cluster Analysis included together Cd and As (Fig 8.3a). Previous researches (Facchinelli et al., 2001; Sun et al., 2013, Kelepertzis, 2014; Deng et al., 2016) have reported that Pb concentrations in agricultural soils usually come from vehicle exhaust, and lead-arsenate pesticides. On this case, samples from cereal undisturbed areas has reported a higher Pb concentration than crop soils maybe influenced by the main road next to the sampled undisturbed area, relating PC3 with an anthropic source.

The accumulation of Cu in Mediterranean agriculture soils is mainly due to the use of agrochemical products, especially Cu-based pesticides (Toth et al., 2016; Cavani et al., 2016) as well some mineral fertilizers, livestock manure and sewages sludge that in addition provide Cd to agricultural soils. Finally, PC4 explains 16.57% of the total variance, and it can be consider an anthropic source of Cu and Cd.

For the fruit trees area, PCA results explained 87.32% of the total variance. PC1 included Co, Cr, Fe, Mn and Ni and explained 34.39% of the variance. High loading factors of PC1 for Fe, Mn and Ni suggest lithogenic sources as is supported by cluster (CA) results (Fig 8.3b). In European Mediterranean regions, Cr and Co are mainly lithogenic elements (Peris et al., 2008) as was supported by PCA, even were also included into PC2 together Pb and Zn; so CA grouped them together Fe, Mn and Ni. Some agrochemicals as fertilizers and pesticides are anthropic sources of Pb, Zn and Cu that enrich agriculture soils mostly in soluble forms, represented in PC2 and PC3. The isolation of As in PC4 and the connexion with lithogenic metals in the CA suggest the parent material as the main source.

Table 8.2. Varimax-rotated factor matrix for cereal, fruit, citrus and horticultural crops

	CEREAL					FRUIT					CITRUS					HORTICULTURAL			
	PC1	PC2	PC3	PC4	COM*	PC1	PC2	PC3	PC4	COM	PC1	PC2	PC3	PC4	COM	PC1	PC2	PC3	COM
Total Pb	-,872	,081	,337	-,202	,922	-,402	,528	-,504	-,410	,863	,746	,084	-,311	,484	,895	,917	,150	-,006	,863
Total Zn	,127	,814	-,263	,213	,793	,080	,929	-,059	,211	,918	,848	,027	-,094	,356	,855	,863	-,144	,285	,846
Total Cu	,126	,105	-,087	,683	,502	-,123	,050	,964	-,019	,946	,015	,471	-,752	,298	,876	,730	,541	,237	,882
Total Cd	-,080	,099	,644	,577	,764	-,060	,037	-,536	-,545	,590	-,038	-,946	,245	,000	,956	-,216	-,683	,421	,691
Total Cr	,063	,786	,293	-,053	,711	,643	,537	,118	,084	,723	,118	,036	,066	,852	,745	-,630	,124	,112	,425
Total Co	,920	,204	,300	-,013	,979	,644	,715	,167	-,027	,954	,779	,491	,140	-,225	,918	,880	,311	,196	,909
Total Ni	,598	,125	,439	-,535	,852	,821	,290	,312	,284	,936	-,115	,035	,805	,203	,703	-,440	,721	,249	,775
Total Fe	,028	,658	-,172	-,684	,932	,939	-,052	-,099	-,216	,941	,305	,492	,296	,382	,568	,212	,008	,924	,899
Total Mn	,962	,093	,103	,005	,944	,931	,052	-,206	,078	,918	,912	,153	,050	,021	,858	,886	,356	,108	,924
Total As	-,148	,075	-,865	,117	,789	-,035	,190	-,012	,951	,942	,893	-,059	-,105	,087	,819	,228	,758	,003	,627

* COM: communalities

Fig.8.3. Dendrogram for metal(loid)s from cereal (a), fruit (b), citrus (c) and horticultural (d) crops

Otherwise, similar loading values were found for Cd in PC3 and PC4 indicating a mixed origin although CA grouped it with Pb, Zn and Cu, giving more weight to the anthropic origin.

PCA for citrus agriculture soils explained 81.92% of the total variance. Arsenic, Co, Mn, Pb and Zn were included within PC1 and close in the same cluster (Fig 8.3c). Also, soils from both citrus undisturbed and agriculture areas reported enrichment in Pb and Cu. Usually Mn and As has been associated to geogenic sources but Kelepretzis (2014) reported that Mn may become from pesticide applications and As from phosphate fertilizers and vehicle exhaust. These results suggest the PC1 as anthropic source of metal(loid)s. The highest loading for Cd was located in PC2 (16.36% of the variance), and for Cu and Ni in PC3 (15.03% of variance) considering both components

anthropogenic sources. Finally, although PCA analysis located Fe in PC2, the cluster analysis (Fig 8.3c) grouped it with Cr, which was in accordance with the undisturbed origin reported by Peris et al. (2008) for Mediterranean regions.

In horticultural soils Co, Cu, Mn, Pb, and Zn were grouped in PC1, explaining 44.11% of the total variance. The continuous application of livestock manures, fertilizers, agrochemicals and other soil amendments may lead to the concentration of metals in agriculture topsoil (Zhang et al., 2016; Lin et al., 2017). Thus, the high loading of Co, Cu, Mn, Pb, and Zn within the PC1 indicates an anthropic source of these metals. Contrary, Fe was isolated into the PC3 (12.93% of the variance) suggesting an independent behaviour from other metals. However, cluster results (Fig 8.3d) grouped Fe with Cd, Ni and As included into the PC2 (21.36% of the variance). According to Toth et al. (2016), metals from PC2 seems have a lithogenic origin, therefore Fe mainly becomes from the parent materials. Similarly behaviour was found for Cr which reported the highest loading for the PC1 but cluster analysis associated this metal to lithogenic origin together As, Cd, Fe and Ni.

8.4. Conclusions

Multivariate analysis is a useful tool to elucidate potential sources of metal(loid)s in agriculture soils. The comparison of metal(loid)s concentration among crop and undisturbed soils has allowed establish the trend of each type of crop to accumulate certain metals that overreach the reference values at the same time that chemical partitioning provide information about the mobility of these metals, which determines the availability and potential risk for human and environmental health.

Generally, studied soils has presented an enrichment in Cu, being the management of citrus crops who supply the higher amount of Cu to soil. Cereal, citrus and horticultural soils tend to accumulate Pb as same citrus and horticultural crops accumulate Cd. Horticultural crop soil was the most prone to accumulate Pb that was in a huge percentage in a mobile form, bound to reducible and carbonate phase constituting a potential risk for the environment and human risk. Despite the higher amount of Cd was found for citrus and horticultural crops, cereal soils pose a higher risk since near 30% of Cd was in the

exchangeable phase. Fruit crops revealed the highest enrichment on Zn that was also very bioavailable in the labour soil.

Results from the multivariable analysis suggests two main sources of metals in agriculture soils, anthropogenic and lithogenic, but just metals catalogued into the anthropogenic source can be more easily remediated modifying some management practices as reducing the use of phosphate fertilizers, pesticides and controlling the addition of manures and sewage sludge. Thus, multivariable analysis revealed that the management of all studied types of crop promote the contamination by Cd, Cu, Pb and Zn, except in horticultural crop where Cd had a lithogenic origin. The management of fruit, citrus and horticultural crops induced the accumulation of Zn and Co in agriculture soils as same as As in cereal and citrus soils. Finally, citrus crop practice was the major contributor to soil pollution.

Chapter 9

CONCLUSIONS

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Urban areas

➤ Road dust has reported significant differences with natural road dust indicating an enrichment of metals that depends on the city, contrary to urban soils. In urban areas the population density increases metal concentrations in road dust, where Cu, Cr, Pb and Zn are more easily mobilized due to its association to reducible and carbonate phases. Contrary does not affect metal concentration in urban soil. The effect of the population density is more easily observable when it is highly increased.

Fine fractions in road dust are more prone to accumulate metals than soils, especially particles of grain size below 10 μm (PM10) which reported higher risk values being potentially hazardous for human health. Metals that involve higher risk were Cr and Zn by the ingestion and dermal absorption exposure and Ni by inhalation exposure.

Therefore, variations in metal accumulation should be easily observable in higher density population settlements while in little towns is not a useful parameter. The higher metal content of fine particles in road dust than soils suggest an anthropic origin of this metals making the analysis of road dust a useful tool for the risk assessment. In addition, as values of hazard index found for all metals were higher for children than adults and samples were collected in urban parks they should be pointed as great placements to develop monitoring plans for metal risk assessment.

Industrial areas

➤ Using the metal content of the natural area as background, soils and road dust from industrial activities have showed an important enrichment of metals. For example, service industrial soils has reported a moderately pollution in Zn, Pb, Cr, Cu and Ni and a moderate ecological risk. The type of industrial activity determines metals that are in larger concentrations on each industrial complex and its accumulation in soil and road dust. For example, Zn, Pb and Cu dominate in soil for service industrial area and petrochemical activity while in tannery activity the highest concentrations are for Cr, Zn and Pb.

The use of pollution indexes is not enough to assess the hazardous potential of metals in industrial environments because industrial activity increases metal accumulation in road dust and acts as relevance factor to the availability of metals although affect similarly its mobility in soil and road dust. Hence, understanding the distribution and behaviour of each metal at each particular industrial complex and activity is necessary to develop remediation strategies and hazard prevention plans.

Mining areas

➤ The identification of metals sources in urban environments located near to abandoned tailings ponds is a key factor to understand the influence of metal-enriched particles from mining districts in urban soils and road dust. Using the multivariate analysis has been possible to detect that soil and road dust in La Union and Mazarrón are mainly enriched in As, Cd, Pb and Zn by particles which come from the abandoned mine although for Mazarrón road dust the influence of the urban activity was reported as a secondary source of Cr and Cu. Metals risk is also derived to the mobility of metals into the environment and even into the human body. Thus, it was observed that in metals with mining origin its mobility is more affected by its total concentration followed by the organic carbon and carbonate content in urban soil and road dust.

The spread of metal-enriched particles from the mining areas can reach agriculture and natural areas nearby posing a potential risk for human and animal health by the food intake and their incorporation into the trophic chain. Agriculture soils are enriched in As, Cd, Fe, Pb and Zn from the mine wastes. Hence, even though barley plants showed root barrier effect for metals, have accumulated Cr, Pb and As in grains to overreach the

permissible limit in aliment suggested by FAO being highly hazardous if this barley is used as human food.

Ballota hirsuta is an endemic plant of both mining districts that lives in natural soils with high amount of metals. The study of its ability for bio-accumulates and translocate metals to edible parts has been important to evaluate its use in future phytoremediation projects to reclaim abandoned ponds. This specie can accumulate Fe, As and Cr in their tissues transferring a large amount of these metals to leaves without exceeding the toxicity limits for animals, seems a good candidate for phytoremediation plans.

Agricultural areas

➤ Multivariate analysis has been a successful tool in the evaluation of potential source of metals in agriculture soils. Thus, has been found that the management of crops promote the contamination of labour soils. The management of fruit, citrus and horticultural crops induces the accumulation of Zn and Co as well cereal and citrus management induces As enrichment. All soils are also enriched in Cu while horticultural is the most prone to accumulate Pb, that together Cd are the most mobile metals posing a higher risk of plant translocation. The crop management that most metals accumulate is the citrus crop being the major contributor to soil pollution.

General conclusions

➤ Comparing the metal behaviour through the different studied scenes, we can conclude that in urban and industrial environments road dust is a better pollution indicator than soil because is more prone to accumulate metals specially in the fine fraction that is more hazard for human health than the coarse fraction. Metals often found in both sceneries have been Cu, Cr, Pb and Zn although its amount in industrial scene depends on the industrial activity. The amount of metals found in La Unión and Mazarrón towns has been higher than found in the urban scene because the influence of the mining wastes. It is a clear example of the influence of a mining activity into populated areas and the risk that it supposes. The spread of metal-enriched particles from industrial activities or the accumulation of metals in agriculture soils also poses a risk for human health because of deposition and accumulation of metals by plants and its transfer to edible parts that can be eaten by wild animals and human. On this way would be necessary a monitoring plan to

assess metal deposition in agriculture areas near to metal spread sources and develop more sustainable crop managements that minimizes metal inputs in labour soils.

➤ Based on the results priority actions should be developed in the mining scene due to the high concentrations of metals that population is exposed, especially children whom has been demonstrated the highest health risk. However, a deeper health risk study should be carried out in order to evaluate specific actions to carry out. Secondly, in the urban scenery an environmental monitoring in urban parks should be developed, collecting road dust for a period of time to study the variation on metal behaviour, above all in the fine fraction.

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REFERENCES

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