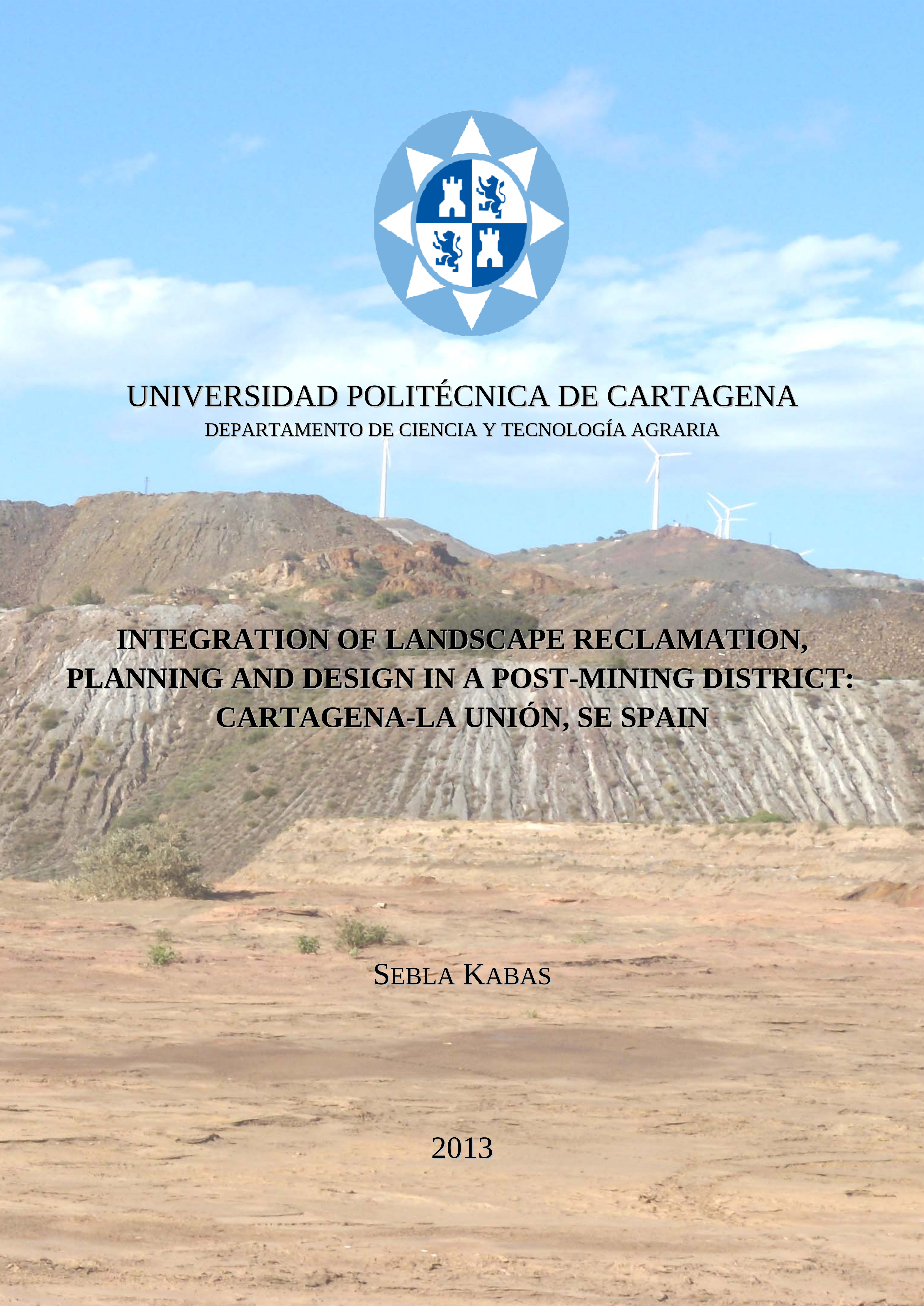


UNIVERSIDAD POLITÉCNICA DE CARTAGENA
DEPARTAMENTO DE CIENCIA Y TECNOLOGÍA AGRARIA

INTEGRATION OF LANDSCAPE RECLAMATION, PLANNING AND DESIGN IN A POST-MINING DISTRICT: CARTAGENA-LA UNIÓN, SE SPAIN

SEBLA KABAS

2013

Universidad Politécnica de Cartagena
Departamento de Ciencia y Tecnología Agraria

Grupo de Investigación Gestión, Aprovechamiento y Recuperación de Suelos y Aguas

Tesis Doctoral

Integration of Landscape Reclamation, Planning and Design in a Post-Mining District: Cartagena-La Unión, SE Spain

SEBLA KABAS

2013

UNIVERSIDAD POLITÉCNICA DE CARTAGENA

DEPARTAMENTO DE CIENCIA Y TECNOLOGÍA AGRARIA

INTEGRATION OF LANDSCAPE RECLAMATION, PLANNING AND DESIGN IN A POST-MINING DISTRICT: CARTAGENA-LA UNIÓN, SE SPAIN

Tesis Doctoral

Trabajo presentado por **SEBLA KABAS** para aspirar al grado de Doctora por la Universidad Politécnica de Cartagena

Dirigida por

DR. ÁNGEL FAZ CANO
DR. JOSÉ ALBERTO ACOSTA ÁVILES

Cartagena, 2013.

To my parents and my brother

ACKNOWLEDGMENTS

Working on the Ph.D. has been a great, but at the same time generally an overwhelming experience. Even it is hard to grapple with the topic itself which has been the real experience of learning. Grappling with how to write papers and proposals, give talks, work in a group, stay up until the sunrise, and still stay focus... In any case, I am indebted to many people for making the time working on my Ph.D.

First of all, to the Project IRIS (no: CP-IP 213968–2) funded by the European Union FP7 for its throughout support which enabled the realization of this work.

I am deeply grateful to my advisor Ángel Faz Cano. To work with you has been a pleasure to me. Thank you for your confidence to give me the opportunity to perform this study, for all your professional and moral support.

Furthermore, I am also very grateful to my co-director José Alberto Acosta Áviles, for his insightful comments both in my work and in this thesis, for his support, and for his positive energy.

In addition I would like to thank to Dr. Arocena and Dr. Mermut, for their professional supports, innovative approaches and helpful comments and advises.

I have been very privileged to get to know and to collaborate with my colleges in GARSA-UPCT who became real friends over the last several years. I have learned a lot from you about life, research, how to tackle new problems and how to develop techniques to solve them. Thank you very much for all your company José, Silvia, Dora, Raúl, María Ángeles, Rosa, Pablo, Melisa, Asuman, Ibrahim, Jennifer, Sara, Ana, Tania and Lola. With you anything would be enjoyable, and it has been so, even making Ph.D.!

Finally, I would like to thank my mom, dad, and brother for their infinite support throughout everything.

Sebla Kabas

Scientific Journals

Acosta, J.A., Faz, A., Martínez-Martínez, S., Zornoza, R., Carmona, D.M., Kabas, S., 2011. Multivariate statistical and GIS-based approach to evaluate heavy metals behavior in mine sites for future reclamation. Journal of Geochemical Exploration 109: 8-17.

Kabas, S., Faz, A., Acosta, J.A., Zornoza, R., Martínez-Martínez, S., Carmona, D.M., 2012. Effects of marble waste and pig slurry on the growth of native vegetation and heavy metal mobility in a mine tailing pond. Journal of Geochemical Exploration 123: 69-76.

Kabas, S., Faz, A., Acosta, J.A., Arocena, J.M., Zornoza, R., Martínez-Martínez, S., Carmona, D.M., 2013. Marble wastes and pig slurry improve the environmental and plant-relevant properties of mine tailings. Environmetal Geochemistry and Health 35 (2).

Kabas, S., Arocena, J.M., Acosta, J.A., Faz, A., Martínez-Martínez, S., Zornoza, R., Carmona, D.M., 2013. Syrian Bean-caper (*Zygophyllum fabago* L.) improves organic matter and other properties of mine wastes deposits. International Journal of Phytoremediation. Accepted.

Kabas, S., Acosta, J.A., Zornoza, R., Faz, A., Carmona, D.M., Martínez-Martínez, S., 2011. Integration of landscape reclamation and design in a mine tailing in Cartagena-La Unión, SE Spain. International Journal of Energy and Environment 2 (5): 301-308.

It is crucial to find sustainable solutions for healing the landscape wounds of post-mining activities all over the world. Early mining operations left degraded lands not in accord with regional ecosystems and lacking socio-economic and cultural values. Increasing awareness of environmental sensitivity identified the minimization need of the environmental consequences of post-mining activities and the importance of returning the degraded land to a beneficial use.

Cartagena-La Unión Mining District, depending upon its long time mining history, has become the subject of these challenges and pending questions for local communities and administrations in Spain. Based on this problematic, to contribute to the landscape reclamation of post-mining areas and to develop new land use functions in those, relevant chapters were organized as follows:

In Chapter 1, objectives and the relevance of the thesis were presented, while the relevant background information was given in the introduction section as Chapter 2.

In Chapter 3, two representative tailings ponds (El Lirio and El Gorguel) in Cartagena-La Unión Mining District were selected and employed for their future reclamation. Thus, their initial characterization was made by analyzing waste samples. Results showed that both ponds were polluted by Cd, Pb, and Zn. High total concentrations of Zn and Pb and high percentage of extractable-Cd in both ponds suggested high risk of mobility via plants uptake, by runoff and leaching. Hereby, it is inferred that the immobilization of these metals should be a priority in the reclamation actions. Additionally a GIS-based approach was adopted to identify the highest risk sites in which the main efforts of reclamation and monitoring would be needed.

Following the initial characterization and the previous experiences of the research group, in order to understand the environmental and plant-relevant benefits of marble waste (MW) and pig slurry (PS) applications to both mine tailings, soil samples from the experimental plots which were designed with different treatments: (1) pig slurry, (2) marble waste, (3) marble waste + pig slurry, and (4) control, were compared in Chapter 4. The prominent difference between two ponds was their acidity level, being pH 5.4 and pH 7.4, in El Lirio and in El Gorguel respectively. Results showed that the characteristics, especially pH, of tailing materials significantly influence the fate of

metals but not improvements to plant-relevant properties such as cation exchange capacity and aggregate stability one year after the application of MW and PS amendments.

After seeing the effect of amendments on soil properties, in Chapter 5 the effectiveness of two amendments (marble waste and pig slurry) on native vegetation growth was investigated after one year of application. Since getting the native vegetation growth substantially in El Gorguel tailing pond, investigation was directed and carried out in this pond. Plant cover, richness, biodiversity, metal in plant tissues, soil physicochemical properties and water and DTPA extractable metal concentrations of bare and rhizosphere soils were analyzed after one year from the application of the treatments. Before the application of amendments, soil was bare and organic matter content was very low. After applications, a native vegetation cover (25–30%) with the highest biodiversity (H=1.1–1.3) and a richness of 10 was obtained in the plots amended with pig slurry. In addition the establishment and development of vegetation improved soil quality and decreased the metal availability, even more efficiently than the direct effect of the amendments. *Piptatherum miliaceum* (L.) Cosson showed the characteristics of Pb phytostabilizer plant species among other native plant species. With this chapter the effectiveness of a vegetation cover for the persistence of the reclamation process in bare mine soils under Mediterranean semiarid conditions was confirmed.

After studying the effects of amendments on soil properties and vegetation cover, the phytoreclamation potential of one outstanding plant species *Zygophyllum fabago* L. (Syrian bean-caper) was investigated in Chapter 6. The omni-presence of *Z. fabago* L. natural colonies in post mining areas prompted this investigation to see its contributions to reclamation of mine wastes deposits´ in southeast Spain. Select plant-related (edaphic) characteristics and bio- and water soluble-Cd, Cu, Pb and Zn in rhizosphere of *Z. fabago* were compared to deposits one year since application of pig slurry and marble waste. As a result of this study addition of marble waste was recommended to encourage colonization by *Z. fabago* in acidic mine wastes deposits.

Within the framework of soil reclamation after getting information of amendments´ effectiveness on soil characteristics - plant evolution and after studying

the reclamation potential of present plant species, landscape reclamation was handled in terms of landscape design and planning. In Chapter 7, development of a conceptual landscape design which attempts to integrate the sustainable reclamation activities, socio-economic and cultural values was discussed theoretically, while this concept was explained by delineating in Chapter 8. Except landscape designs of two mine tailings, highlighting the requirement of a general landscape planning for the problematic areas, in Chapter 9 a conceptual landscape planning approach was developed by addressing the whole post-mining district.

Debido a los graves impactos ambientales que provoca la actividad minera en el paisaje, es fundamental encontrar soluciones sostenibles para la recuperación de aquellos espacios que han sufrido o están sufriendo dichos impactos, y cuyos efectos se pueden observar alrededor del mundo. De especial relevancia son las actividades mineras desarrolladas antiguamente, las cuales, debido a la falta de legislación al respecto, han dejado gran cantidad de zonas degradadas sin ningún valor socio-económico ni cultural, afectando gravemente a los ecosistemas. No obstante, en las últimas décadas la sensibilidad por los problemas ambientales ha aumentado considerablemente, y se ha visto la necesidad de reducir las consecuencias negativas causadas por estas actividades y la importancia de devolver a aquellas zonas degradadas un uso útil y sostenible.

El Distrito Minero de Cartagena-La Unión, debido a su larga historia minera y la gran cantidad de impactos presentes, se ha convertido en un gran desafío ambiental tanto para las comunidades locales como para la administración nacional. En base a esta problemática, y para contribuir a la recuperación del paisaje de las zonas mineras y con el fin de desarrollar nuevas funciones de uso, se procedió a desarrollar esta tesis doctoral, cuyos capítulos se organizan de la siguiente manera:

En el capítulo 1 se presentan los objetivos de la tesis y los aspectos más relevantes de la misma. Por su parte, en el capítulo 2 se realiza una introducción a los impactos generados por la minería.

En el capítulo 3, se presenta la caracterización inicial de los dos depósitos de residuos mineros seleccionados (El Lirio y El Gorguel) y que serán los lugares donde se apliquen las medidas de rehabilitación propuestas en esta tesis. Los resultados mostraron que los dos depósitos estaban contaminados por Cd, Pb y Zn. Además, se observó que las altas concentraciones totales de Zn y Pb y el alto porcentaje de Cd extraíble en ambos depósitos indicaban un alto riesgo de movilidad de los metales a través tanto de la absorción por las plantas como por escorrentía y/o lixiviación. Por lo tanto, y con el objetivo de reducir este riesgo, se concluye que la inmovilización de estos metales debe ser una prioridad en las acciones de recuperación de este tipo de depósitos. Además, en este capítulo, se presenta un enfoque basado en el SIG que permitió identificar aquellos lugares de mayor riesgo en los que los mayores esfuerzos de recuperación deberían ser realizados.

Basado en los resultados de la caracterización inicial y la experiencia previa del grupo de investigación en el que se desarrolló esta tesis, se diseñaron varias parcelas experimentales en ambos depósitos, en las cuales se aplicaron lodo de mármol (MW) y purines de cerdo (PS). Los tratamientos que se realizaron fueron los siguientes: (1) purines de cerdo, (2) lodo de mármol, (3) lodo de mármol + purines de cerdo, y (4) control, los resultados del efecto de estas enmiendas en las propiedades edáficas se presentan en el Capítulo 4. La diferencia más relevante entre ambos depósitos fue su nivel de acidez, cuyos valores fueron de pH 5,4 y pH 7,4 en El Lirio y en El Gorguel respectivamente. Los resultados mostraron, un año después de la aplicación de las enmiendas, que las características, especialmente el pH, de los residuos influyen significativamente en el comportamiento de los metales, aunque no se mejoraron propiedades tales como la capacidad de intercambio catiónico ni la estabilidad de agregados en agua.

Una vez evaluado el efecto de las enmiendas en las propiedades de los residuos mineros, en el capítulo 5 se presentan los resultados de la evaluación del efecto de éstas sobre el crecimiento de la vegetación que colonizó de forma espontánea los depósitos. Debido a que el crecimiento de la vegetación fue sustancialmente mayor en El Gorguel tanto desde el punto de vista de la cobertura vegetal como de la biodiversidad, el estudio fue desarrollado en este depósito. En este caso, se evaluaron los siguientes parámetros: cubierta vegetal, riqueza, biodiversidad, concentración de metales en las plantas (raíz y parte aérea), propiedades fisicoquímicas de los residuos y concentraciones de metales extraíbles en agua y DTPA tanto en los residuos como en la rizosfera. Después de las aplicaciones, se observó que todas las parcelas enmendadas fueron colonizadas por vegetación autóctona, destacando la parcela enmendada con purín, cuyo porcentaje de cobertura fue del 25-30 %, con un valor de biodiversidad de H=1.1-1.3 y una riqueza de 10. Además se demostró que el establecimiento y el desarrollo de la vegetación mejoraban la calidad del suelo y la disminución de la disponibilidad de metales, incluso de manera más eficiente que el efecto directo de las enmiendas. De las plantas estudiadas, fue *Piptatherum miliaceum* (L.) Cosson la que mostró las mejores aptitudes para ser una planta fitoestabilizadora.

En el estudio anterior (capítulo 5) se observó como *Zygophyllum fabago* L. era la especie que colonizaba en primer lugar y con mayor rapidez los depósitos mineros.

Por lo que se profundizó en su potencialidad como especie para ser utilizada en fitoremediación. Para ello, se analizaron las propiedades edáficas tanto en la rizosfera de *Z. fabago* como en los residuos sin vegetación, así como las concentraciones de metales solubles en agua y extraíbles con DTPA un año desde la aplicación de purines y lodo de mármol. De estudio se concluye que la presencia de *Z. fabago* mejora la calidad de los residuos donde se instala, lo que facilita la colonización espontánea de otras especies vegetales y de este modo da comienzo la sucesión vegetal y, posteriormente, favorece la sostenibilidad de una cubierta vegetal estable. Los resultados de este estudio se muestran en el capítulo 6

Finalmente, y en el marco de la recuperación integral de estos espacios altamente degradados, se abordó la regeneración paisajística en términos de diseño y planificación del paisaje. En el capítulo 7 se presenta, en un marco teórico, el desarrollo de un diseño conceptual del paisaje que trata de integrar las actividades sostenibles de recuperación, los valores socio-económicos y los valores culturales. Estos conceptos fueron aplicados a la zona de estudio, desarrollando dos diseños paisajísticos, uno para cada depósito minero, cuyos resultados se presentan de forma detallada en el capítulo 8. Para concluir con la tesis, y poniendo de relieve la necesidad de una planificación paisajística de todo el Distrito Minero de Cartagena-La unión, en el capítulo 9 se presenta la planificación paisajística conceptual que aborda todo el conjunto del Distrito Minero.

CHAPTER 1. Objectives and relevance of the thesis

CHAPTER 2. Introduction

CHAPTER 3. Multivariate statistical and GIS-based approach to evaluate heavy metals behaviour in mine sites for future reclamation

CHAPTER 4. Marble Wastes and Pig Slurry Improve the Environmental and Plant-relevant Properties of Mine Tailings

CHAPTER 5. Effect of marble waste and pig slurry on the growth of native vegetation and heavy metal mobility in a mine tailing pond

CHAPTER 6. Syrian Bean-caper (*Zygophyllum fabago* L.) Improves Organic Matter and Other Properties of Mine Wastes Deposits

CHAPTER 7. A conceptual landscape design approach for the sustainable reclamation activities of a post-mining area in Cartagena, SE Spain

CHAPTER 8. Integration of landscape reclamation and design in a mine tailing in Cartagena-La Unión, SE Spain

CHAPTER 9. Multifunctional greenway approach for landscape planning and reclamation of a post-mining district: Cartagena-La Unión, SE Spain

CHAPTER 1

Objectives and relevance of the thesis

Abstract

It is vital to create sustainable manners for healing the landscape wounds of post-mining activities in all around the world. Sierra Minera Cartagena-La Unión Mining District (SE Spain) has served to mining activities for more than 2.5 millenniums creating deleterious effects on the environment and human health altering soil structure and landscape. Generated mine waste hills, in other words mine tailings - due to their high concentration of heavy metals, the leaching potential of these metals to deeper layers and groundwater, the high affection of erosion processes, the low fertility of the waste and the large surface of the ponds - are subject of environmental problems and pending questions for local communities and administrations in southeast Spain. In order to create sustainable solutions for these mine tailings and gain these problematic areas back, new landscape functions should be given to them, but initially environmental risks should be minimized by sustainable landscape reclamation activities that are required for returning the relevant district to an acceptable environmental condition for the ecosystems and human.

1.1. Relevance and significance of the study

Cartagena-La Unión Mining District in southeast of Spain constituted an important mining focus for more than 2500 years until its closure in 1991. Phoenicians, Carthaginians, Romans, Arabians, and Spaniards have been mining silver, lead, zinc, copper, tin, iron, and manganese in this district (Faz et al., 2001; Conesa and Faz, 2009). Those mineral deposits were likely to be mined for profit, thus, overburden and waste materials (accumulated in tailing ponds) with their consequent environmental risks appear as the fundamental components in the post-mined landscapes (Collins, 2001; Acosta et al., 2011). Tailing ponds contain materials rich in Fe-oxyhydroxides, sulphides, sulphates, and heavy metals (mainly Cd, Pb, and Zn). As a consequence, these soils remain bare and have low soil organic matter content (Conesa et al., 2007b; Acosta et al., 2011). Consequent environmental risks, especially water and wind erosion and mobility of heavy metals in soil-plant systems stand out with propensity to adversely affect both human health and the functioning of ecosystems. Therefore, it is necessary to take actions towards remediation of these risks (Doumett et al., 2008; Ji et al., 2011).

While surface mining has relatively ancient origins, reclamation is a relatively recent phenomenon with a global concern about the potentially damaging effects which can originate with mining (Burley, 2001). In this recent phenomenon, phytoremediation takes its place as a newly emerged reclamation technique in the removal or stabilization of soil heavy metals by the usage of plants providing advantages in costing, in *in situ* applications and in environmental compatibility, among other expensive and often impractical techniques (Sasmaz and Sasmaz, 2009; Pérez-Esteban et al., 2011).

Traditional solutions used in mining areas such as excavation and backfilling works are not feasible and appropriate because of the high amount of pollutants and the big volume of polluted soil of mine tailings in Cartagena- La Unión Mining District. Therefore negative effects of former mining activities can be minimized by *in situ* immobilization of metals creating vegetation covers which can also serve to metal immobilization, called phytostabilization. Restoration of a vegetation cover can fulfil the objectives of stabilization, pollution control, visual improvement and removal of threats to human beings (phytostabilization) (Wong, 2003). Vegetation cover is very effective in reducing surface erosion; can return a large proportion of percolating water to the atmosphere through transpiration, thus reducing the concentration of soluble heavy metals entering watercourses; reduces the visual scars in the landscape, so that successful revegetation may allow recreational use of the land (Tordoff et al., 2000). Several studies on the use of metallophytes for revegetation of metal toxic mine wastes appear in the literature (e.g. Smith and Bradshaw, 1979; Peters, 1984; Wong, 2003). According to these studies, combining metal-tolerant species with proper application of fertilizers and pH adjusters resulted in the successful and rapid revegetation of contaminated soils.

The effects of different amendments (marble waste and pig manure) on heavy metal mobility and on soil characteristics in terms of risk reduction at large-scale from two selected tailing ponds were handled in this study. Also the plant cover establishment, as a consequence of heavy metal immobilization and the improvement of soil properties was determined and heavy metals in plant tissues were analyzed. The results showed that marble waste and pig slurry are useful for improving soil physicochemical characteristics of the tailing ponds such as nitrogen content, stables aggregates etc. Improved soil surface characteristics were followed by colonization of native plant cover from the surroundings.

Related to risks reduction, the results indicated that the application of the amendments results in a decrease of the degradation and therefore a less susceptibility to the erosion processes in both ponds. As expected, total Cd, Cu, Zn and Pb concentrations were above European legislation thresholds and no changes with the application of amendments were found in both tailing ponds. However, the application of marble waste resulted in a reduction of available lead and copper and reduction of solubility of Pb, Cu, Zn and Cd; oppositely, the application of pig slurry alone increased the available Pb and the solubility of all metals in El Lirio tailing pond. The results indicated that *Piptatherum miliaceum* can be used as Pb phytostabilizer plant species in the reclamation of the tailing ponds, while addition of marble waste was recommended to encourage colonization of *Zygophyllum fabago.*

However, because of the fast carbon mineralization and decreasing nutrients content (nitrogen) in 12 months, the application of amendments should be repeated periodically in order to get a sustainable vegetation cover establishment.

According to Burley (2001) there have been two major focuses in surface mine reclamation. The first focus has concentrated upon the technical aspects concerning the revegetation of the landscape and the science of reclamation as mentioned above and the second focus is in the planning and design arena addressing the creation of usable post-mining land. So based on this second focus an optimal landscape design development for mine tailings which considers the phytostabilization process as a reclamation technique, and integration of reclamation efforts into the landscape design by taking into account not only the scientific considerations and also cultural and human aspects was investigated . Except landscape designs of two mine tailing ponds, based on the landscape planning requirement of the whole problematic area a conceptual landscape planning approach was recommended.

1.2. Objectives

The first main objective of this thesis is to develop an understanding for landscape reclamation of post mining areas, specifically for mine tailing ponds that contain heavy metals to minimize their environmental and human risks by evaluating the effects of different amendments on mine tailing soil properties and on plant cover; and investigating spontaneous colonization of native plant species in terms of phytostabilization as a new emerging soil reclamation technique.

The second major goal of this study is investigation of the assignment of new land use functions to the tailings. Thus, it is aimed to suggest an optimal conceptual landscape design for the tailings and a conceptual landscape planning approach for the entire area to provide the sustainable reclamation progress of the post-mining district.

For these purposes, a multidisciplinary study has been performed that includes the following partial objectives:

1) To evaluate the degree of residual contamination of heavy metals by comparison with guideline values in two representatives tailing ponds of the Cartagena-La Union Mining District:

- By analyzing the relationship between waste properties and total, extractable heavy metals by DTPA and water,
- By spatial analysis, locating hotspots of environmental risk where remediation efforts and monitoring should be focused.

2) To understand the environmental and plant relevant (or edaphic) benefits of inorganic and organic amendments to unproductive mine wastes deposits:

- By monitoring changes in pH, soil organic matter, aggregate stability, cation exchange capacity, and total content, extractability and availability of select metals at 0, 1 week, 6 and 12 months since the application of amendments.
- By interpreting the observations to elucidate natural processes involved in the immediate environmental benefits and risks (e.g., metal leaching to ground water) and improvement to edaphic soil properties (e.g., pH, total N, cation exchange capacity) associated with the applications of marble wastes and pig slurry in mine tailing deposits.

3) To evaluate the evolution in vegetation cover, richness and biodiversity:

- By identifying the most effective amendment for the reduction of the metal uptake by native plants,
- By identifying the most suitable plant species for the reclamation of the study area, in terms of rhizospheric immobilization,
- By evaluating the relationships between metal concentration in soil and plant tissues.

4) Owing to its omni-presence in post mining areas, to investigate the contributions of *Zygophyllum fabago* L. (Syrian bean-caper) to reclamation of mine wastes deposits:

- By quantifying the improvement of selected edaphic characteristics by comparison of properties in mine wastes deposits to rhizosphere materials influenced by the growth of *Z. fabago* in experimental plots subjected to pig manure and marble wastes amendments in SE Spain.
- By investigating the changes to bio-available and water-soluble metals to observe the establishment of ecosystem functions in unproductive deposits of mine wastes with the usage of aggressive endemic pioneer plant species such as *Z. fabago*.

5) To develop a conceptual landscape design approach for degraded areas.

- By examining and discussing the relevant literature review.

6) To create an optimal conceptual landscape design for both mine tailings

- By using the acquired knowledge and results of the realized works and experiments in this study.

7) To develop and extent the conceptual landscape planning approach to the entire post-mining zone.

- By using the multifunctional greenway approach.

1.3. Structure of the thesis

The relevant themes including; mining concept, environmental impacts of mining activities, potential reclamation techniques for tailing ponds, post-mining land use reclamation from the perspective of landscape planning and design are described in the Introduction Section (Chapter 2) of the thesis.

The experimental results obtained during the development of the study and relevant realized studies mentioned above are organized in Chapters 3, 4, 5, 6, 7, 8 and 9 of this document. Each chapter is written in the form of a scientific paper and consists of the following sections: introduction, materials and methods, results and discussion.

Finally, Chapter 10 includes the main scientific conclusions of the work and Chapter 11 the list of references used in the study.

CHAPTER 2

Introduction

Abstract

This introduction section presents the required background aspects of the study mainly including; the general mining concept, mining activities of Cartagena-La Unión, selected tailing ponds of the study and landscape planning-design perspective. The mining concept is detailed by the definitions of mining structures, general environmental impacts of mining activities and potential reclamation techniques of tailing ponds. In the part of Cartagena-La Unión Mining District, study area is described; historical development of mining industries in Cartagena-La Unión is reviewed; and environmental impacts of the post-mining activities in Cartagena-La Unión are presented. In the selected tailing ponds section, El Lirio and El Gorguel tailing ponds were examined in depth. And lastly for being able to make an integration between landscape reclamation efforts and planning-design aspects on tailing ponds, post-mining land-use reclamation was handled with the perspective of landscape planning and design.

2.1. Mining Concept

Mining is a temporarily use of land (QERM, 1995; Burley, 2001a) for extracting minerals of economic value from the earth´s crust for the benefit of mankind and a primary industry contributes the necessary raw materials to a nation’s output of goods and services (The only other basic industries are agriculture and forestry which also produce goods directly derived from the earth’s crust) and it is a vital link in an integrated economic system between the primary industries (mining, forestry, and agriculture) secondary industries (manufacturing), and tertiary industries (sales, distribution, and various other services). According to the varying nature of the minerals and the environmental conditions in which they occur, four classes of mining operations appeared: underground mining, surface mining, alluvial mining and non-entry mining (Collins, 2001).

Surface mining is an endeavor to excavate substrate containing specific chemical and physical properties useful in the manufacture, construction, and development of products. Surface mining is employed to obtain energy related minerals (coal and oil shale), metallic resources (aluminum, copper, iron ore, titanium, gold, lead, nickel, silver, tungsten, uranium, zinc and other metallic resources), and non-metallic resources (limestone, dolomite, molybdenum, sand, gravel, structural soil, organic peat, graphite, salt, sulphur, gemstones, asbestos, gypsum, phosphate, potash, diamonds, and other various materials) (Burley, 2001a). Within the framework of this study the addressed study area would relate to surface mining activities exploited for metallic resources.

Mining practices in the past allowed the mine owners to simply abandon their mines without consideration of reclamation and negative impacts on the environment (Burley, 2001a; Mchaina, 2001; CDMG, 2002). Today, with the ability to disturb and affect large portions of the landscape, there is a deep public concern that surface mines not be abandoned and that resource exhausted surface mines be reclaimed (Burley, 2001a). According to Collins (2001) when reclamation is the subject of mineral producers, the most common reasons for this were legislation (35%), public image (30%), financial gain (20%), return the land to a useful purpose (10%), moral obligation (2.5 %), and research (2.5%).

Generally post-mining landscapes contain certain fundamental structures such as overburden and waste materials (Collins, 2001) as explained in the following section.

2.1.1. Mining Structures

The extraction and beneficiation of ores to produce minerals result in significant waste generation and unwanted by products. Although the mine tailing ponds constitute the main subject of the study, giving descriptions (according to the EPA (1997), EPA (2004), CDMG (2002)) of typical contamination sources in post mining areas are considered to be necessary by force of the theme.

Waste rock and overburden dumps are the leftover material generated as a result of mining and beneficiation activities used to recover a target mineral. Although some consider mine waste piles to be aesthetically pleasing because of their historic nature, these piles are generally difficult to vegetate and may pollute adjacent streams. Generally are constructed on unlined terrain or backfilled in previously excavated areas.

Tailings are created by most beneficiation processes and usually leave the mill as slurry. They contain very small particles which are highly susceptible to erosion or removal by wind and water. Typically, tailings consist of 40 to 70% liquid mill effluent and 30 to 60% solids (Liquids are commonly used in the milling processes.) Most mine tailings are disposed of in on-site impoundments. In the past they were deposited usually in a stream valley. However, slurried tailings are sometimes disposed of as backfill into underground mines to provide ground or wall support. In addition, areas covered by mill tailings are generally difficult to vegetate, due to the high concentration of heavy metals and acidity associated with waste materials high in pyrite.

Polychlorinated biphenyls (PCB)-containing electrical equipment may be found in mines throughout the world because electrical systems in mines follow the same general patterns as any other industry. Since mines generally penetrate the water table, when (PCBs) are spilled or PCB equipment is abandoned underground, the PCBs can be expected to be released into the ground water with no possibility of source retrieval.

Surface impoundments are created to de-water tailings and as a holding area for the tailings. They are also used as evaporation ponds for process waters or waste water cleanup of in situ leach operations.

AMD (Acid Mine Drainage), or highly acidic water rich in metals, forms as a result of a chemical reaction of surface water and/or shallow subsurface water with rocks that contain sulfur-bearing minerals (e.g., pyrite). This reaction causes oxidation to produce ferrous ions and sulfuric acid, which can cause metals to be leached from, rocks that come in contact with the acid. When mixed with ground water, surface water, and soil, AMD may have harmful effects on humans, animals, and plants as it poisons ground and water and destroys aquatic life. AMD is accentuated by mining activities such as extraction and beneficiation.

Heap leaching produces spent ores, spent leach and process solutions, sludge, and slag.

2.1.2. General environmental impacts of mining activities

The surface mining impacts should have a special importance if the land use planning of the post-mining area is questionable. These impacts can be classified into those related to the mine operations which last until the mine closes such as the deterioration of ambient air quality because of dust emissions; and those of permanent character unless proper land reclamation measures are applied. The second category impacts constitute the subject of Cartagena-La Unión Mining District; and in that category the following general impacts are as followed (Pavloudakis *et al.*, 2009; Knoot and de Waal, 2009):

- Alteration of morphology
- Degradation of soil
- Changes in hydrological pattern
- Loss of wild animal habitat
- Degradation of landscape value
- Reduction of property value
- Loss of agricultural land
- Placelessness, people lose their bond to their environment.

In metal mining areas also the contamination and health impacts emerge as negative effects in addition to the mentioned impacts above. Gosar (2004) explains these potential environmental impacts of metal mining in three classes: Physical impacts (destruction of natural habitat, land degradation and instability, changes in river regime, changes in landforms, dangerous structures and dams, abandoned equipment), pollution impacts (AMD, sediment run-off, soil and water contamination, leaching of contaminants, air and dust emissions), occupation health impacts (dust inhalation, handling of residues and products, exposure to toxic materials used on-site, exposure to heat, noise, vibration, radiation, physical risks at the site).

2.1.3. Potential reclamation techniques for tailing ponds

Conventional remedial approaches for metal-contaminated soils to minimize risks usually involve removal and replacement of soil with clean materials (Brown *et al.,* 2005), although it is not considered the most economically or environmentally sound solution available (Alvarenga *et al.,* 2008). Conventional technologies for remediation of mine tailings have focused on physical and chemical stabilization. Physical stabilization entails covering mine waste with an innocuous material, generally waste rock from mining operations, gravel, topsoil from an adjacent site, or a clay capping, to reduce wind and water erosion. These solutions are often temporary in nature because of the impermanence of the capping process (Johnson and Bradshaw, 1977). For example, clay caps in arid and semiarid environments crack from the wetting–

drying cycles and poor consolidation of the tailings due to their high salinity (Newson and Fahey, 2003; Swanson *et al.,* 1997). Chemical stabilization aims to prevent wind and water erosion using a chemical agent such as a lignin sulfonate or a resinous adhesive to form a layer over the tailings. It is also a temporary stabilization technique, as these layers can eventually fail (Tordoff *et al.,* 2000). Recently, reprocessing historic tailing materials using more advanced technologies to reduce metal concentrations and toxicity has been considered as an economic solution in some cases (Warhurst, 2000). However, after reprocess the tailing material will still be left and will need to be stabilized in some way. Thus, since the obtaining of metals from a mining area is a difficult and expensive task, the transformation of metals into harmless species or their removal to a suitable recycled mineral form such as carbonates using marble wastes or lime (Geebelen *et al.,* 2003) is a possible solution for risk reduction in tailing ponds. Formation of insoluble trace element chemical species reduces both leaching though the soil profile and the labile pool available for biological interaction. In SE Spain, marble industries can provide sources of calcium carbonate as marble wastes after cutting processes of the natural stone. In addition, incorporation of organic amendments into contaminated mine soils has been proposed as feasible, inexpensive and environmentally sound disposal practice, as generally such wastes can improve soil physical and chemical properties, and contain nutrients beneficial to microorganisms and plants (Barker, 1997), favoring the reactivation of biogeochemical cycles and the natural establishment of vegetation.

Organic wastes such as sewage sludge or animal manure can be used as slow release of nutrient sources and promote/encourage to the formation of soil aggregates formation (Zanuzzi *et al.,* 2009a). The increment in vegetation cover reduces or even prevents the dispersion of the contamination through wind and water erosion, and improves the aesthetic value of formerly bare areas (Vangronsveld and Cunnungham, 1998). Besides, vegetation itself may contribute to the metal immobilization processes through biological activities in the production of organic matter (Bouwman and Vangronsveld, 2004); this contribution of vegetation is named as phytostabilization and seen as an emerging reclamation technology. The use of organic amendments and materials rich in carbonates has been successfully used to reduce the bioavailability of contaminants and restore the ecological function of contaminated soils with heavy metals (Pérez de Mora *et al.*, 2005; 2006; Alvarenga *et al.*, 2008).

Thus, mine soil stabilization is as an *in situ* remediation method uses inexpensive amendments to reduce environmental risks related to the transfer of metals to soils, waters, biota and population, decreasing heavy metals availability, increasing soil organic matter, nutrients and water retention. This favors the establishment of vegetation which greatly contributes to the reduction of soil erosion and immobilization of metals. Many studies of the effectiveness of soil amendments have been carried out in controlled conditions, utilizing limited volume of amended soils. Relatively there is little information on the long term effectiveness of soil amendments in regulating trace element mobility and transfer under field conditions. The experimental results of a large-scale reclamation using several amendments on the immobilization of heavy metals and improvement in soil properties, vegetation cover and diversity in abandoned tailing ponds from SE Spain affected by former mining activities were shown in this study.

2.2. Cartagena-La Unión Post-Mining District

2.2.1. Geographical description of the district

The study was conducted in the Cartagena-La Unión Mining District located in Murcia Region of southeast Spain (Figure 2.1). The Mining District of Cartagena-La Unión is a coastal mountain range with an approximate E–W trend. It is limited by: in the north, fertile arable lands (Campo de Cartagena); in the east, urban areas and one of the most important lagoons of the Mediterranean Area, Mar Menor Lagoon; in the south, protected areas and Mediterranean Sea; and in the west, industrial areas.

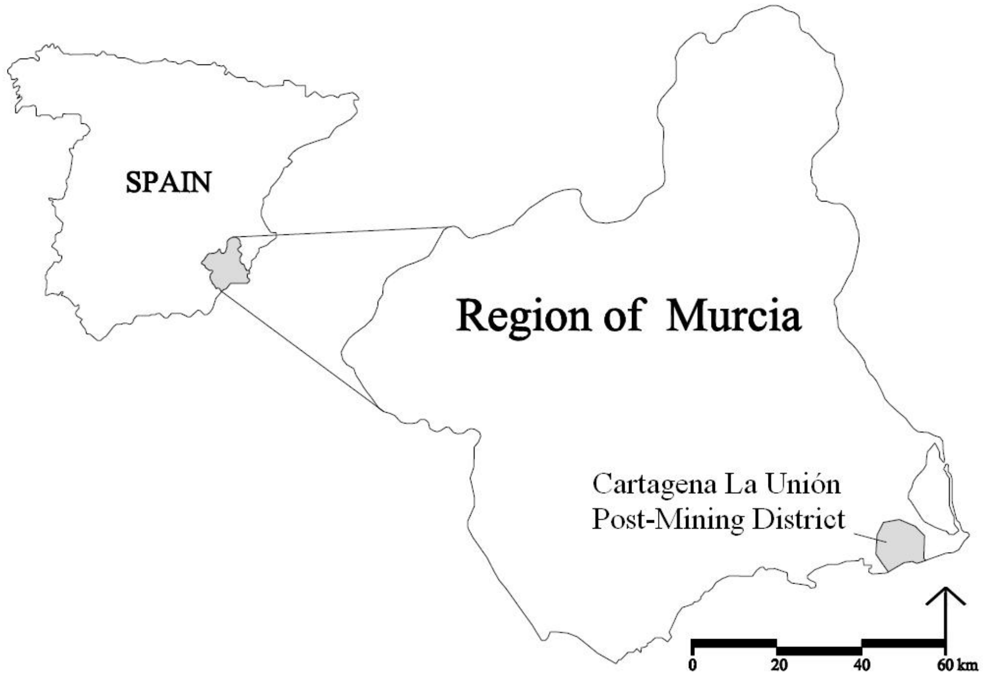


Figure 2.1. Location of Cartagena-La Unión Mining District, SE Spain.

It covers an area of approximately 100 km^2, with a length of 23 km. The highest elevation is the ‘‘Peña del Águila’’ (392 m.a.s.l.). The northern slopes are gentler than southern slopes, the latter end as cliffs on the coast of the Mediterranean Sea.

The climate in Sierra de Cartagena–La Unión is typical semiarid Mediterranean, characterised by an annual mean precipitation of approximately 300 mm, with a range between 250 and 350 mm year^{-1}, distributed in a few intensive rainfall events. The southern slope is wetter than the northern due to air-moisture condensation from the Mediterranean Sea. The area shows a temperature range between 4.0 ºC (January) and 29.34 ºC (August) from 2008 and 2012. The annual average temperature is 18 ºC. Wind is always present in the study area, mainly ‘‘Levante’’ (a wet wind with an E–W trend). The lowest wind speed is registered in autumn (15.6 km h^{-1}) and the fastest in spring (22.4 km h^{-1}). The potential evapotranspiration is approximately 900 mm year^{-1}. Vegetation is composed mainly by shrubs, although small areas are being reforested with *Pinus* *halepensis*. A lot of endemism has been reported. Native plants in some cases grow on tailing ponds (Conesa *et al.*, 2006).

The district includes five population nuclei with around 20,000 total populations while the surroundings of the district have a population of more than 200,000 inhabitants including the city of Cartagena and the rest of its municipality. During the summer, the population dramatically increases due to the tourists who come to the Mar Menor Lagoon and the Mediterranean Sea beaches.

2.2.2. Historical review of the mining industry in the Cartagena-La Unión

The Cartagena-La Unión Mining District was among the most important mining centers in the country in obtaining lead, silver and zinc. For more than 2500 years, different civilizations such as the Iberians, Greeks, Phoenicians, Carthaginians, Romans, Visigoths, Arabs and Spanish exploited mineral resources in these areas. However, that mining activity had varying time periods of importance till the end of 1991.

Initially mining activities occurred intrinsically depending to the civilizations populated in the southeast Spain, creating different technological, economical, social and cultural characteristics and traditions for each period (Conesa, 2005). Generally, the history of local mining activity can be divided into several historical periods, depending on production levels and existing technology.

The first data about the development of mining in the area is attributed to the Iberians. Then, Phoenicians, Greeks and Carthaginians extracted minerals through inclined galleries and wells (SMMPE, 1983; Sáez, 1998). In the year 209 BC Cartagena fell under the Roman ruling, and was managed creating a great splendor for the city port and for the mining industry which provided them valuable metals such as iron, lead and silver.

The techniques of extraction and subsequent processing of the mineral were developed qualitatively and quantitatively in Roman period. Thus, galleries of great length with an average depth of 80 m were excavated (SMMPE, 1983).

In the year 425 AD, Roman rule was ended by conquer of vandals and began a period in which mining activity almost ceased completely. After the

"Reconquista" and during the eighteenth century, the Sierra Minera of Cartagena-La Unión suffered an almost total cessation of mining due to the serious depopulation (Manteca and Berrocal, 1997). In the early nineteenth century everything continued as before limiting the work to dig in old dumps. However, in 1820 and 1821 several provisions were declared and enacted in order to promote mining activity, offsetting the previous privileges granted by monarchs and somewhat encouraging private initiative. Thus, mining in the Cartagena-La Unión District was enhanced and driven by improvements in production systems; new and more efficient kilns were built and the first washing gravimetric plant was installed. Thus, the mineral laws were increased and also included the foundries (SMMPE, 1983). Hereby the Cartagena-La Unión Mining District became one of the largest producers of lead from the late nineteenth century to the early twentieth century (Figure 2.2).

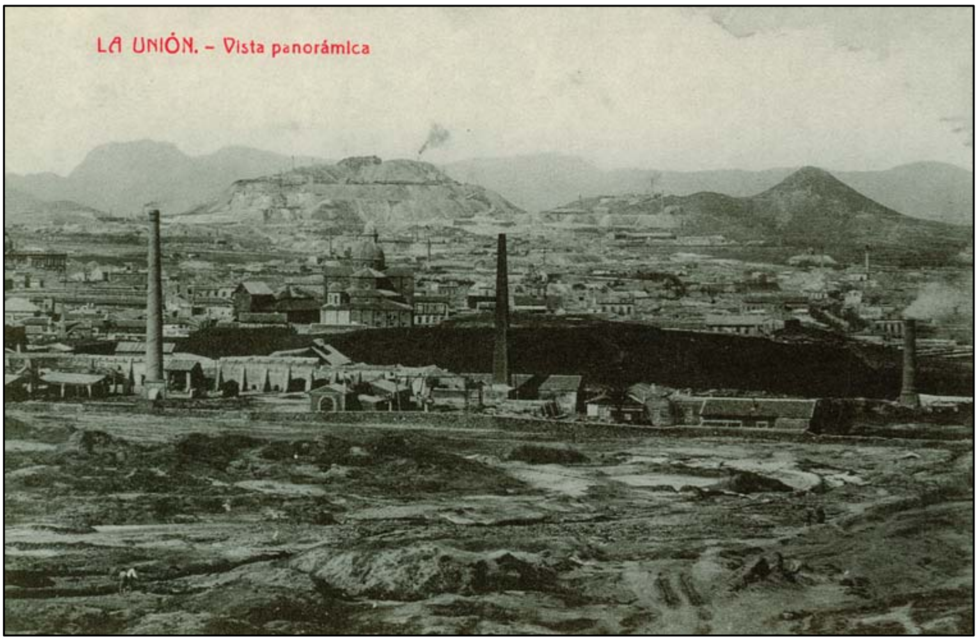


Figure 2.2. Thriving Cartagena-La Unión Mining District.

Then the degradation of landscape pictured an utter desolation view. Besides, mineral dust and gases from the smelters affected negatively the various places of the mountains that were not damaged by mining activities (Vilar and Egea, 1990). International economic fluctuations affected significantly the local mining. After World War, the severe crisis hit the region and wiped out the small-sized industrial, mining and metallurgical companies leaving the Peñarroya (Spain) behind as the main protagonist of the regional mining during the twentieth century (SMMPE, 1983; Vilar and Egea, 1990). Recovery of mining in the 40's was related to the use of new differential flotation techniques for obtaining minerals. Because of the low-grade ores, mining was paid poorly. An enormous amount of soil was needed to move in order to get a saleable tonnage of ore that can compensate the expenses of operating (Vilar *et al.*, 1991).

In 1944 Mining Law re-applied the concepts of public ownership of mining; thereby the State increased the degree of intervention in the sector. Peñarroya (Spain) completes the process of concentration of ownership of mining with the start of plowing in open pits. The efficiency of production techniques in the latter period accelerated the depletion of the resources. To give an idea of the enormous impact of contemporary mining it is possible to say that in just 50 years, from 1940-1990, it was exploded almost about the same amount within the previous two thousand years. The economical boom began its decline in the eighties due to the fall in mineral prices and the depletion of resources. As a result, in late 1991 mining in the Sierra de Cartagena-La Unión was finally ceased (Manteca and Berrocal, 1997) (Figure 2.3).

Over the years, 12 open-pits were excavated, 3,000 wells and kilometres of mining galleries were drilled, and hundreds of piles of mining waste and spoil were excavated and deposited.

The mines constituted the only economic activity during hundreds of years for local people. Despite this situation created a monocultural socio-economic character in the region, nevertheless other economic alternatives to mining were not proposed by successive governments. Mining dependence caused significant population fluctuations with a decline from 30,000 in 1900 to 13,900 in 1991 when the mining ceased. Thus, these aspects left a strong mark in the idiosyncrasy and character of La Unión’s citizen (Conesa *et al.*, 2008a).

Figure 2.3. Cartagena-La Unión Mining District of today.

2.2.3. Environmental impacts of mining activities in Cartagena-La Unión

The environmental impacts of the long-history of mining activities in southeast Spain include large areas of soils characterized by strong acidification processes, high salinity and accumulation of metals. These mining activities have generated high amounts of sterile materials for many years; the wastes are accumulated in pyramidal structures called tailing ponds (Figure 2.4).

Figure 2.4. Tailing ponds in the Sierra Minera of Cartagena-La Unión.

Throughout the area there are 85 tailing ponds as a result of gravimetric and flotation plants of mineral washing by the intensive mining activity carried out during the past century containing materials of high Fe-oxyhydroxides, sulphates, and potentially leachable elevated contents of heavy metals (mainly Cd, Pb, Cu and Zn) due to extreme acidic conditions. Although tailing ponds were abandoned when the activities of washing gravimetric and flotation plants stopped some decades ago, the environmental and human health impacts remain the same.

These tailings are existing critic problems due to their composition of constituent materials and due to their location. As a source of pollution the heavy metals contained by tailings, acid materials, acid mine drainage can reach to the natural or populated areas by erosion or collapses because of the geotechnical instability, adversely affecting the soil, water, plants, animals and human populations as well as infrastructures close to them. In fact, a large area of the Cartagena-La Unión Mining District is dominated by areas where natural soils have been lost, because they have been collected in the opening of mine pits, operating mineshafts, covered by mining waste or contaminated by the discharge of effluents.

Although these abandoned tailing ponds have different heterogeneous physical and chemical properties, the generation of acidic waters and high levels of heavy metals is generally their common characteristics (Chambers and Sidle, 1991; Michelutti and Wiseman, 1995; Dudka and Adriano, 1997). As a consequence, mine soils have null vegetation due to very poor properties, including extremely low soil organic matter (Conesa *et al.*, 2006; Ottenhof *et al.*, 2007; Zanuzzi *et al.*, 2009a).

In addition, these tailings constitute potential risks of instability such as collapse or slip related to the subsidence of the pond, due to the accumulation of water on its surface, seismic situations or adverse weather (Fundación Sierra Minera, 2001). Related to stability, it is possible to see some examples threatening the public safety. In the year 1972, the mine tailing Brunita collapsed due to the strong rainfalls, spreading the materials in nearby areas and causing to lose one´s life (Orozco *et al.* 1993). According to Ortega *et al.*, (1993) some of the mine tailings are more than 20 m in height and cover an average area of 40,000 to 80,000 m^2, are unstable and difficult to eliminate.

Most tailings have gullies, landslides and a high degree of erosion, while do not have a proper drainage system. Besides, they provide solid and fine materials to runoff which can produce acid mine drainage. The lack of vegetation in the most tailing ponds increase the risk of wind and water erosion and transport of contaminated material to the surroundings (Ortega *et al.*, 1993).

The effects on vegetation and wildlife are the direct consequences of the occupation of open pits, mine tailings and destruction of soil structure that eradicate natural plant cover, destroy the habitats of fauna and ultimately cause to their extinction. The risk of erosion, by water and wind, is also one of the most important environmental problems. The effects of the erosion of mineral tailings are manifested with the contamination of soil, riverbeds, the marine environment and the stability loss of these structures. The intensity of the winds is the factor that determines the risk of wind erosion which mostly impacts the areas without vegetation. Tailing ponds are mainly affected because of their fine particle size, lacking of vegetation and the oxidation of sulfides to sulfate. These compounds form a soil surface with a very low-density which can be eroded by wind and, sometimes, can be transported long distances (Ros, 1997). Similarly, surface waters and the marine environment, mainly the Mar Menor Lagoon and the Mediterranean coast were polluted by the effects of water erosion (CAAMA, 1999; García *et al.*, 2003; Faz *et al.*, 2004).

Runoff not only produces the erosion of materials but also supports the formation of acid waters. These waters are generated by the reaction of sulphide-bearing rocks, pyrite (FeS_2), sphalerite ((Zn, Fe)S) and galena (PbS), with water, oxygen and bacteria, this process is also known as acid mine drainage as described before in the section of mining structures. The high corrosive power of acid mine drainage aggravated by the heavy metal content has different negative effects such as degradation of aquatic systems (especially in the Mar Menor Lagoon), removal of vegetation, introduction of heavy metals in the food chain, toxicity of the soil and loss of agricultural capacity.

With regards to groundwater, alteration of the groundwater level by disruption of water table in the open pits and upwelling or seepage of acid water is another undesired effect of the mining (Figure 2.5).

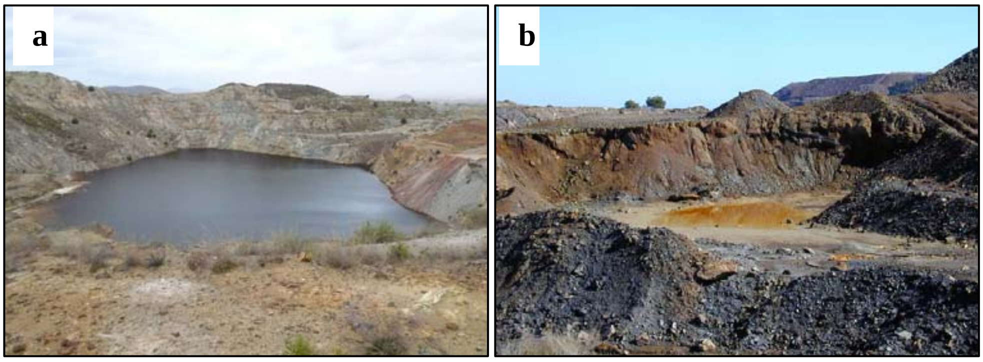


Figure 2.5. (a) Groundwater contamination risk; (b) Effects of water erosion.

In addition, the presence of these tailing ponds also reveals a high risk for public health, since heavy metals are also constitute a pollution factor for air suspension, sediments on beaches of public use, or bioaccumulation by ingestion of herbivores in the mining site.

The impacts associated with surface mining operations also cause alterations in the visual impact of the landscape by making physiographic modifications and changing the landscape quality negatively (Ros, 1997; Ross, 1999; García *et al.*, 2004) (Figure 2.6).

Figure 2.6. Landscape in Cartagena-La Unión Mining District.

In brief, the environmental impacts caused by the waste produced by mining and metallurgical activities result in negative effects on the soil, water resources (surface, groundwater and marine water), landscape, atmosphere, biota and the human (Zanuzzi, 2007).

2.3. Selected tailing ponds of the study: El Lirio and El Gorguel

Two tailing ponds affected by mining activities were selected, El Lirio and El Gorguel. Except the pH (pH 5.4 and 7.4 for El Lirio and El Gorguel respectively) these ponds have similar properties typical for waste deposits in the area (Acosta *et al.,* 2011). The selection of these two ponds was based on their access facilities (both are easily accessible for sampling and carried out future reclamation actions), physico-chemical characteristics (both ponds present the common characteristics of the ponds located in the mine district: salinity, absence of vegetation, high metal concentrations and low organic carbon content), hydrological conditions (both ponds are located in dry watercourse and are affected by runoff water as most of the pond in the mine district), slope (the slope of the pond surface is flat which will allow futures reclamation activities), distance from towns (the distance from towns is less than 2 km, and therefore is easily accessible for population which would be interested to visit these areas after reclamation) and surrounding landscapes (the surrounding area of the ponds) which is covered a surface of 60-70 % of the soil by the native vegetation including *Zygophyllum fabago, Brachypodium retusum, Phragmites communis, Stipa tecnacissima, Calicotome intermedia, Dorycnium pentaphyllum, Thymus hyemalis,* and *Lavandula dentate* etc. According to Conesa *et al.* (2008a) some of the thicket plant species are endemic in the zone such as *Tetraclinis articulata* and therefore have a high botanic interest. Thus, the conclusions that can be extracted from these zones can be applied to the rest of the areas, at the same post-mining district, or in other areas from different metallic mining activities under the same environment. In Figure 2.7, the aerial photography of the selected tailing ponds were shown, while the evolution of the tailing ponds in the last 50 years is shown in Figure 2.8.

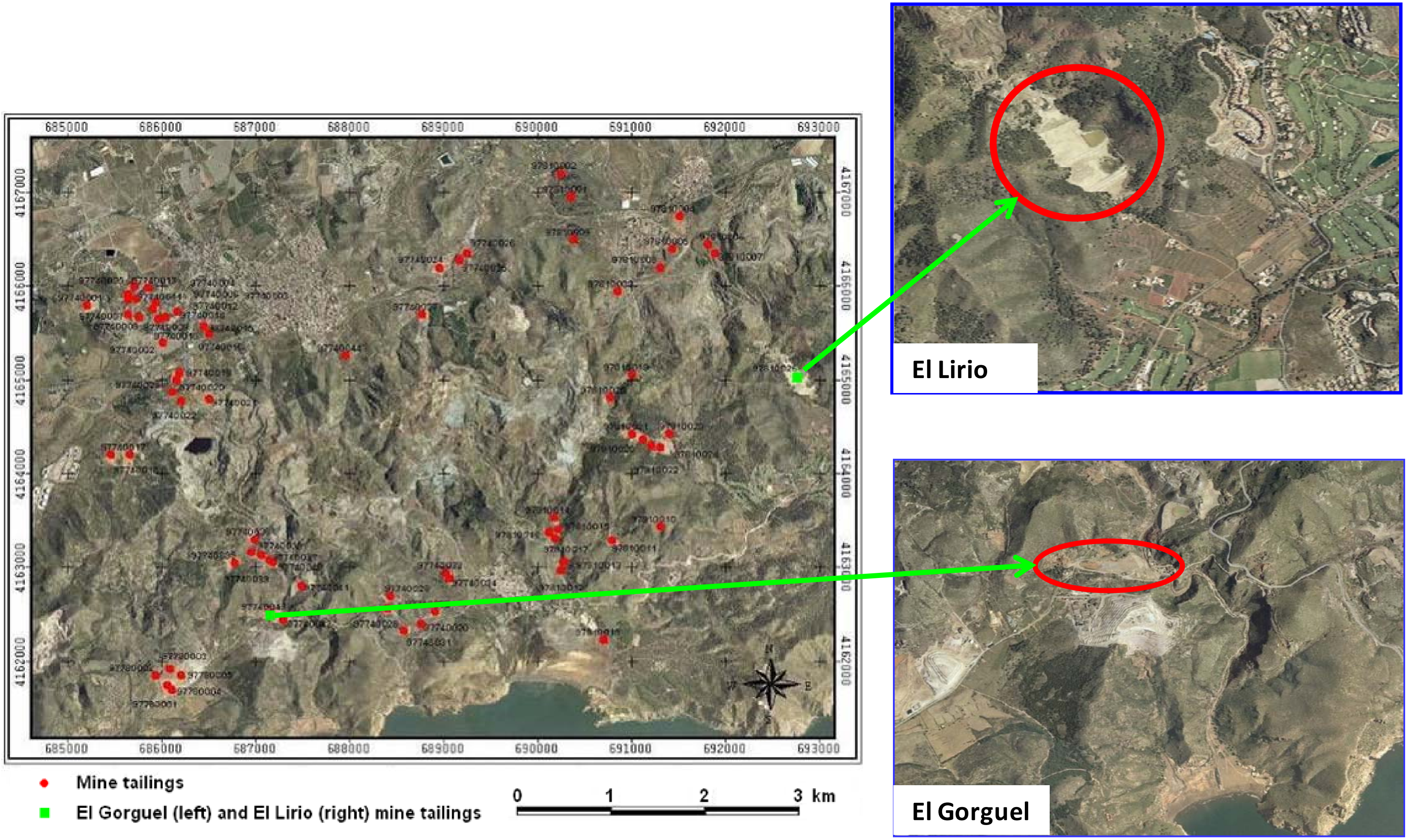


Figure 2.7. Representative tailing ponds from the Cartagena-LaUnión Mining District.

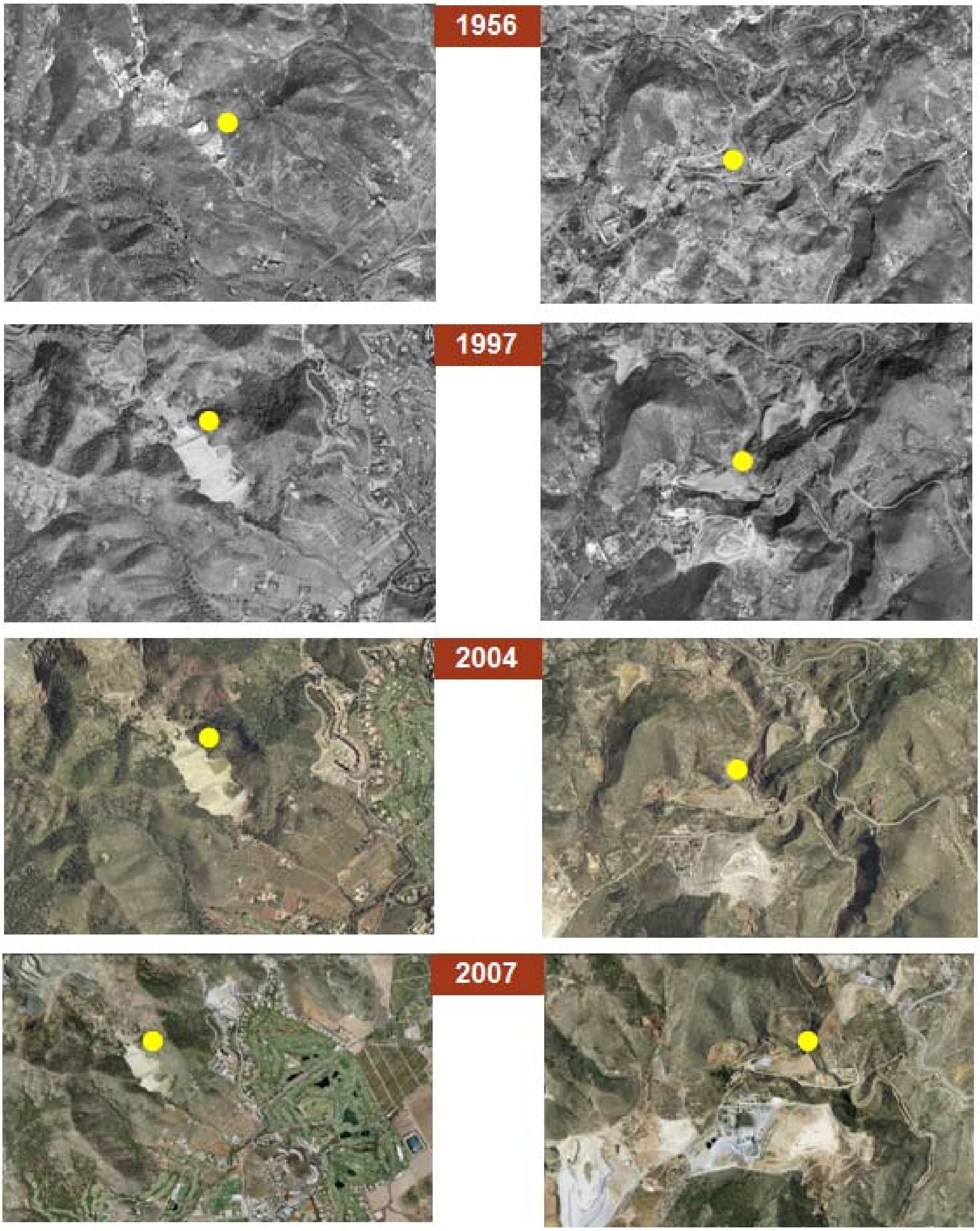


Figure 2.8. Historical evolution of the tailing ponds EL Liro and El Gorguel.

Figures 2.9-2.10 show the panoramic views of each tailing ponds before this study. These tailing ponds were abandoned after mining activities, being intensely polluted, with absence of vegetation, and poor soil structure.

Figure 2.9. Current panoramic view of El Lirio.

Figure 2.10. Current panoramic view of El Gorguel.

In order to evaluate the interne structure of the selected tailing ponds a geophysical evaluation was carried out, the main results of this evaluation is summarized as follow (Faz *et al.*, 2012):

At El Lirio mining tailing pond 2D ERI electrical sections revealed that the electrical resistivity values generally increased with depth from surface to the bedrock, while very low to intermediate values were found to be associated with the tailings (Figures 2.11A, 2.11B). Mine wastes stored in El Lirio tailing pond had electrical resistivity (ER) <8 Ohm.m and were much lower than the resistivity measured for bedrock (>150 Ohm.m). Mining tailings with ER <8 Ohm.m occupied the centre of tailing pond with a thickness of 20 m in El Lirio tailing pond. Results of particle size analysis revealed that materials with low ER (<8 Ohm.m) were composed of fine-textured (< 0.4 mm in diameter) materials.

Materials in the pond with intermediate ER values between 8 and 150 Ohm.m were located at the perimeter as well as near the bottom overlying the bedrock. Particle size analysis indicated a coarse (0.1-1.0 mm in diameter) distribution for these materials with intermediate ER values (8-150 Ohm.m). The obtained RMS error was 7.3% for the electrical sections.

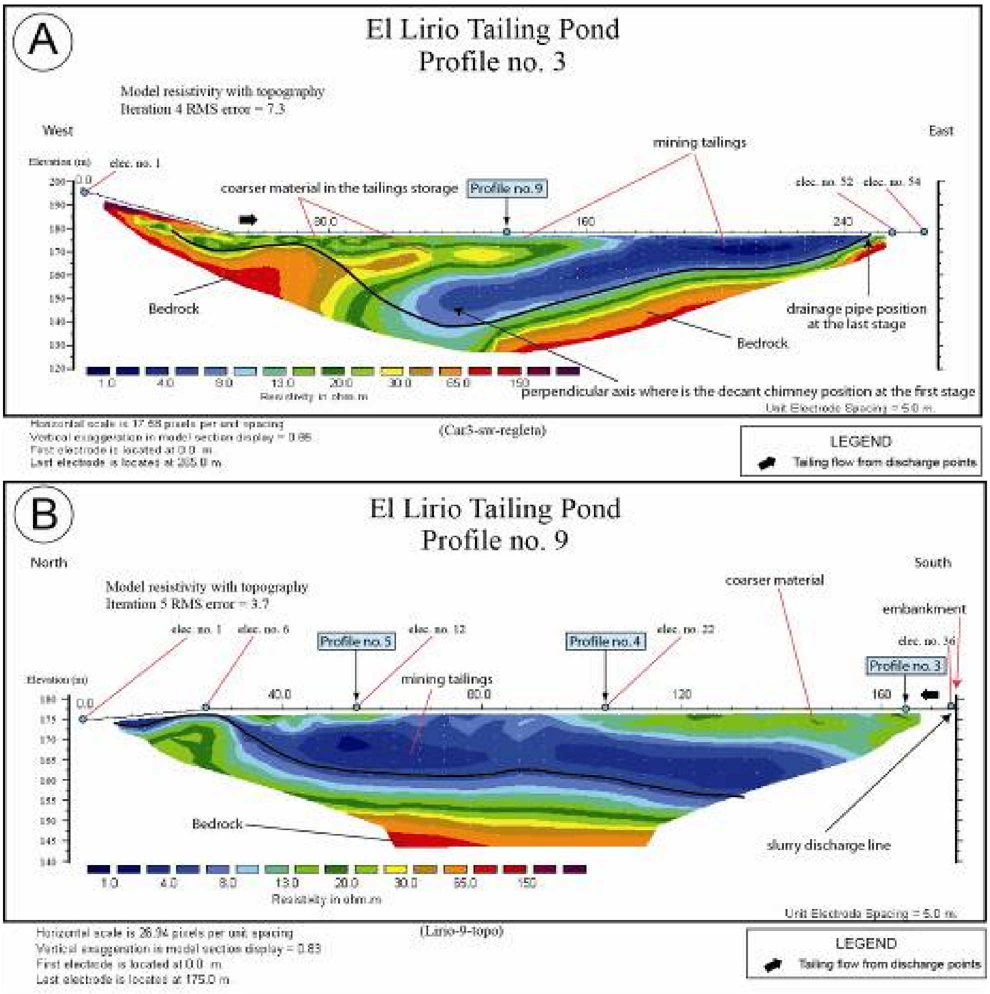


Figure 2.11. Resistivity sections of crosswise (A) Profile no. 3, and (B) lengthwise Profile no. 9, in El Lirio tailing pond.

At El Lirio tailing pond, there were alternating regions of materials with low (<8 Ohm.m) and intermediate (8-150 Ohm.m) electrical resistivity values between electrode positions 100 to 160 at elevations 160 to 140 m (or depths of ~ 15 -35 m) in the crosswise Profile 3 (Figure 2.11A). Materials with ER values < 8 Ohm.m intersected the surface between electrode positions 175 to 255 in Profile 3

(Figure 2.11). From the lengthwise 2D resistivity section in Profile 9, it was noticeable that the materials with resistivity <8 Ohm.m were below materials with intermediate ER values (8-150 Ohm.m) especially at electrode positions 30 to 65, and 100 to 160 (Figure 2.11B). In Figure 2.11A, these materials with intermediate ER (8-150 Ohm.m) were located towards the southern and western perimeter in El Lirio mine tailing pond. The black contour line denotes the interpreted boundary between bedrock and deposits of mine tailings.

Figure 2.12 depicts the electrical section of lengthwise ERI Profile 1 in El Gorguel. This profile has a length of 175 m in which the electrodes were placed every 2.5 m. This section was obtained with a fitting absolute error of 10.8% after 5 iterations. This picture shows a moderate electrical resistivity layer whose electrical resistivity values ranges from 6 to 65 Ohm.m. This shallow layer goes from the position x = 0 to x = 112 m. Its thickness ranges from 2-3 m, in the most western area, to 4-5 m in the eastern one. Underlying this shallow layer appears the most electrically conductive layer with electrical resistivity values below 8 Ohm.m. This layer depicts a steady increase in thickness to the eastern part of Profile 1 where at the position x = 30 m its thickness is about 14 meters. On the right-hand corner of Profile 1 the thickness of this conductive layer is about 10 meters. On the electrical section it has been drawn a white dotted line which reflects a boundary between the conductive layer and the most resistive one. The last one reveals a steady raise of the electrical resistivity value (> 25 Ohm.m) as this layer deepens. On Figure 2.12 it can be noted the crossing points with other ERI profiles by means of vertical black arrows.

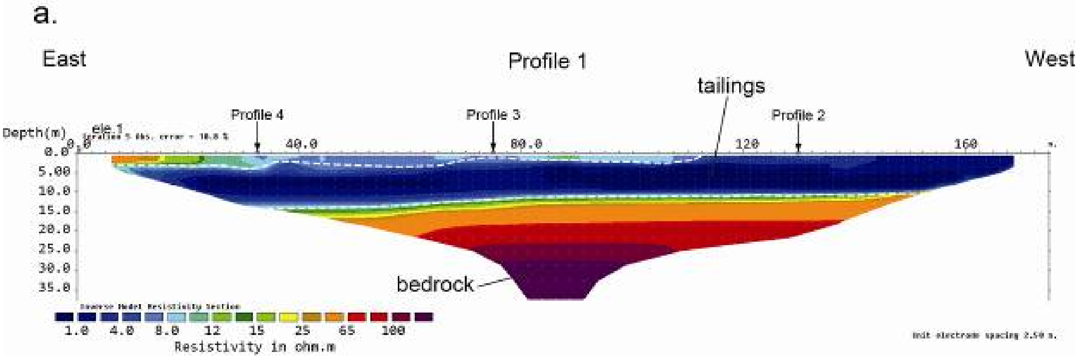


Figure 2.12. Electrical resistivity section of the ERI profile 1 with the final model and interpretation.

Figure 2.13 represents the electrical sections of Profile 2. This profile has a length of 70 m in which the electrodes were placed every 2 m. This ERI profile was laid out with North-South orientation. Its electrical section was obtained with a fitting absolute error of 10.4% after 6 iterations. As noted above, this profile shows a shallow layer which overlays the most conductive layer and goes from the position x = 0 to x = 22 m. Its thickness reaches the maximum value under the position x = 16 m where it is about 2.5 meters thick. This layer has an electrical resistivity value ranging from 6 to > 100 Ohm.m. Underlying the last layer appears the most electrically conductive layer whose thickness ranges from 11 meters, on its southern flank, to 14 meters on the right-hand corner of the electrical sections. In fact, this maximum thickness is encountered on the electrical section at the position x = 44 m. These conductive layer overlays a more resistive layer whose electrical resistivity values gradually increase as it deepens. These electrical resistivity values range from 6 Ohm.m to above 100 Ohm.m.

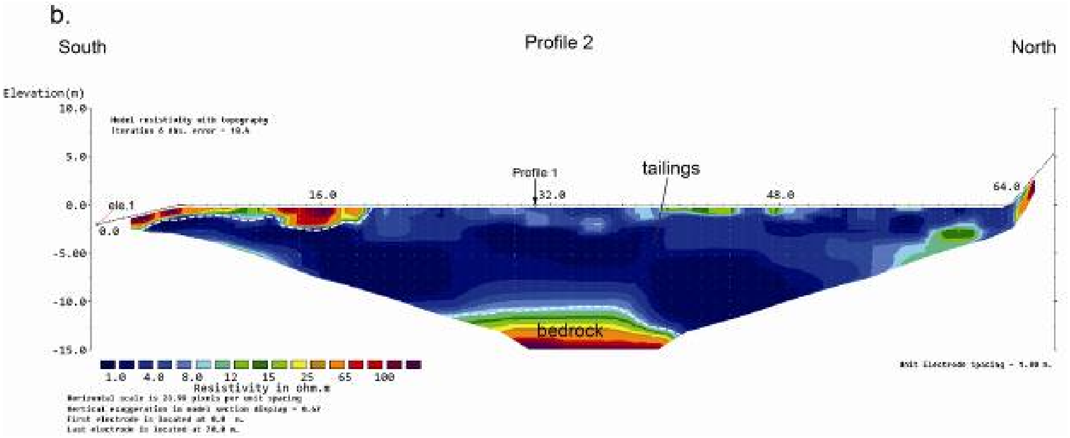


Figure 2.13. Electrical resistivity section of the ERI profile 2 with the final model and interpretation.

Figure 2.14 represents the electrical sections of Profile 3. This profile has a length of 70 m in which the electrodes were placed every 2 m. This ERI profile was laid out with North-South orientation. Its electrical section was obtained with a fitting absolute error of 8% after 4 iterations. On its electrical section it can be seen the same upper electrically-moderate layer as it was described above. However, this layer has a longer extent that it had on the previous profile where it goes from the position x = 0 to x = 67 m. On the other hand, its thickness is almost constant hence it being around 2 meter. The electrical resistivity value goes from 6 Ohm.m to 65 Ohm.m where the smallest electrical resistivity values take place between the position x = 47 and x = 60 m. One more time, underlying the shallow layer it comes out a more electrically conductive layer with electrical resistivity values below 6 Ohm.m. Fig. 7 depicts as this layer slightly dips to South where it reaches 14 meter thick at the position x = 29 m. On the electrical section has been marked the position of the drill hole showing the depth it needed to enter in contact with the bedrock (about 11 meters depth). The tailing-bedrock contact has been marked by a white dotted line.

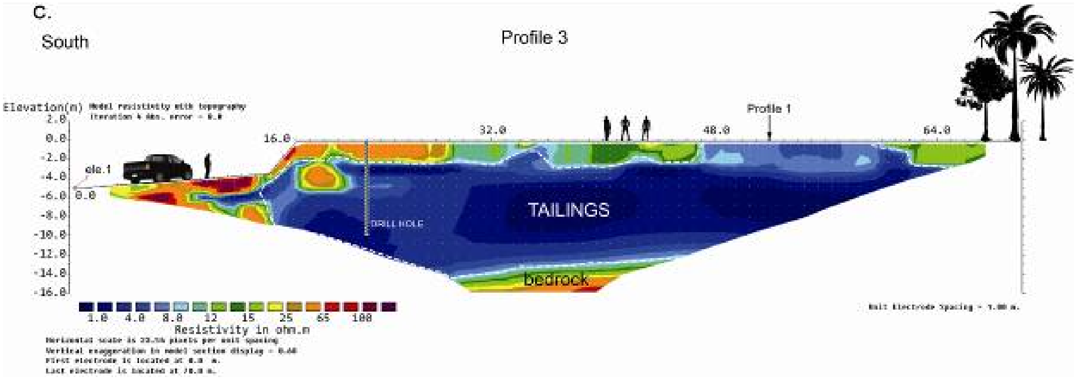


Figure 2.14. Electrical resistivity section of the ERI profile 3 with the final model and interpretation.

Figure 2.15 represents the electrical sections of Profile 4. This profile has a length of 70 m in which the electrodes were placed every 2 m. This ERI profile was laid out with North-South orientation. Its electrical section was obtained with a fitting absolute error of 4.8% after 5 iterations. Unlike the previously described electrical section this one shows a thicker upper layer. This bigger thickness can be found in the following areas on the electrical section: from x = 19 to x = 28 m; from x = 34 to x = 37 m; and from x = 44 to 67 m. This thickness can reach a value around 4 meters with electrical resistivity values ranging from 6 to 100 Ohm.m. This shallow layer presents its highest electrical resistivity values from x = 6 to x = 16 m where they are above 100 Ohm.m. Underlying the last layer there is another layer which has a thickness of about 15 meters at the position x = 33 m.

This layer depicts electrical resistivity values below 8 Ohm.m. Under this conductive layer it looks like a more electrically resistive layer comes out on the electrical section between the positions x = 29 and x = 41 m.

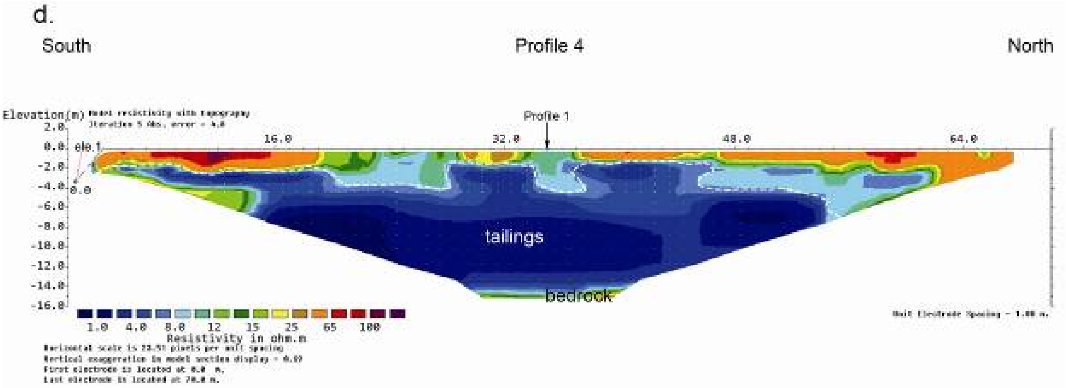


Figure 2.15. Electrical resistivity section of the ERI profile 4 with the final model and interpretation.

2.4. Planning and design perspective: Post-mining land use reclamation

Once the mineral is extracted and the mine is closed, then commensurate with the surface mining, reclamation activities should be realized. Reclamation in surface mining is usually the process of successfully converting a material resource exhausted environment into a site that can fulfill a new use. Illustrating the relationship between surface mining and reclamation, it is best to consider surface mining as just a transitional land-use where the pre-mining environment may have been farmland or some other land use, then the landscape is mined to obtain the resource, and eventually the land can be used for the previous land use or another land use (Burley, 2001a).

At that point it is important to clarify the related terminology as restoration refers to reinstatement of the pre-mining ecosystem in all its structural and functional aspects; rehabilitation means the progression towards the reinstatement of the original ecosystem and reclamation converts the land to a new land-use and creates new ecological conditions, it does not attempt to restore the landscape to its historical trajectory. In fact restoration of a mining area is almost impossible, because turning back to its historical trajectory or bringing the overall ecosystem with its all functions back is not thoroughly possible (Mchaina, 2001; Fisher, 2006) as mentioned by Schulz and Wiegleb (2000), a pre-mining situation does not exist and even if it did, it could never be restored. The concept of reclamation combines all measures needed to make surface-mined landscapes productive and visually attractive again (Mchaina, 2001; Fisher, 2006).

The goal of reclamation is to create a self-sustaining ecosystem on site. Additionally in recent years in the context of reclamation producing landforms that are visually similar to their surroundings has also received an important attention (Dilts, 2007).

Mine reclamation should generally seek to return disturbed areas to at least the same status (ie. having a similar suitability and range of land use options) as existed prior to mining. However, there will undoubtedly be areas (such as tailings dams or final voids) in which rehabilitation to the pre-existing land use suitability will be impractical, and other areas where land existed in a degraded condition or was subject to poor land management practices. In such cases, other beneficial post-mining land use options need to be identified and agreed (QERM, 1995; SMRE, 2000).

It should be noted that both mining and reclamation ultimately aims towards the same ideal: contributing to a higher standard of living and, therefore, a better quality of life for society in general, thus the necessity of mine reclamation (Collins, 2001).

There can be many land-use choices in post-mining planning and design. Each land-use type may embody essential design principles to guide some aspects of mining operations and post-mining development. The land-uses and issues that should be examined by individuals participating in post-mining land-use planning and design should include (Burley, 2001a):

1. Stabilization of disturbed landscapes
2. Agricultural land, both cropland and pastureland/rangeland
3. Forested land
4. Wildlife habitat
5. Recreational land
6. Housing

7. Commercial/industrial land
8. Naturalized/rehabilitated native landscapes
9. Art
10. Managing landscape for visual quality
11. Second mining
12. Cultural and historic aspects of land development.

The over-riding principles in the determination of postmining land uses are that (QERM, 1995):

1. Land should be returned to its pre-mining land suitability as a minimum requirement
2. The agreed land use should be stable, selfsustaining and maintenance free.

McHarg (1969) stresses that any land-use designed within the natural processes that maintain a healthy self-sustaining environment is simply a rational, non-emotional decision (Collins, 2001).

According to Wang *et al.,* (2001) a landscape ecosystem has three basic functions: biological production function that supports agricultural land use and improvement of biological yield as much as possible, environmental service function supports greening and tourist areas and cultural support function that supports the relevant housing and urban infrastructure constructional area. Application of these functions is depends on the characteristics of the areas.

Post-mining areas provide excellent case studies with regard to ecosystem development starting at point zero on a landscape scale, that’s why surface mines are used for educational purposes at the university level in the studio classroom in landscape architecture programs across the United States and Canada for the last 20 years (Nieratko and Burley, 2003; Hüttl and Gerwin, 2005).

It is also possible to use didactic, educative, cultural and historical values as prominent values in the post mining land use in order to increase public awareness and knowledge about environmental issues and challenges, these values should enable people to gain an understanding of how their individual actions affect the environment (Toorn, 2007). So, instead of consuming green areas by destroying natural or virgin lands, if the degraded lands can be redeveloped by adequate reclamation activities, the potential problems of the future can be discarded (De Sousa, 2003; Kabas *et al.*, 2011).

CHAPTER 3

Multivariate statistical and GIS-based approach to evaluate heavy metals behavior in mine sites for future reclamation

Abstract

Soil contamination by metals has become a widespread serious problem in many parts of the world. Two tailing ponds (Lirio and Gorguel) from an abandoned Pb-Zn mine for a future reclamation were selected, surface samples were taken and analyzed for waste properties and total, extractable by DTPA and water-soluble Pb, Cu, Zn and Cd content. Results showed that both ponds were polluted by Cd, Pb, and Zn. High total concentrations of Zn and Pb and high percentage of extractable-Cd in both ponds suggested high risk of mobility via plants uptake. Due to high concentrations of soluble Zn and percentages of soluble Cd, especially in Lirio pond, these metals could be mobilized by runoff water and reach streams or leach to waste deep layers and contaminate soil and even groundwater. Thus, the immobilization of these metals should be a priority in reclamation actions.

Statistical analyses showed that, for Lirio pond, soluble Cd and Zn and extractable Cd, Zn and Pb concentrations were increased by the presence of organic matter, due likely to formation of soluble organic ligands. Clay and electrical conductivity also increased soluble and extractable Zn concentrations, which could be attributed to adsorption of metals for clays combined by the effect of competition for sorption sites with cations and metal-complexation with anions. Finally, soluble Pb was controlled by pH. Therefore, it is recommended the use of alkaline amendment, which will increase the pH and immobilize the metals preventing the effect of organic matter. However, in Gorguel pond, the concentration of soluble and extractable Zn, Pb and Cd were dependent on pH and salinity. Since the pH of this pond is high, it is not necessary to increase it. Oppositely, the reclamation program should include actions to reduce soluble salts generated by oxidation process, which would reduce heavy metal mobility.

A GIS-based approach was adopted to identify highest risk sites, where main efforts of reclamation and monitoring should be realized. Three locations in the Lirio pond and two in the Gorguel pond were selected according to their environmental risk, north, south and west edges for Lirio and west and centre for Gorguel.

3.1. Introduction

Soil contamination by metals has become a widespread serious problem in many parts of the world, including the Mediterranean environments. Heavy metals in soil may come from agricultural activities, urbanization, industrialization, and mine activities. Among these, mine activity is considered as one of the most dangerous anthropogenic activities in the world. This results in changes in landscapes, destruction of habitats, contamination of soil and water, and degradation of land resources (European Environmental Bureau, 2000). Even after the cessation of the mining works, huge tailing ponds as a result of the accumulation of the wastes in pyramidal structures remain in the area with the consequent environmental risk.

In order to reduce the damages against environment that these tailings produce, reclamation actions are necessary. These must be based on preliminary studies about waste properties, heavy metals content and their relation in the free environment. Markus and McBratney (2001) and Ferguson (1998) suggest that the determination of the level of pollution and understanding of spatial variability of topsoil heavy metal concentration in tailing ponds is critical for environmental management and remediation. The evaluation of the spatial variability of waste properties is essential to achieve a better understanding of complex relations between the factors (Goovaerts, 1998). This is very importante for successful land management (Burgos *et al.,* 2008).

With the rapid growth of computer technology and new statistical methods of analysis such as the geostatistic (Burgos *et al.,* 2008), geographical information system (GIS) is becoming one of the most important tools for studying environmental geochemistry problems (Zhang and Selinus, 1998). This is due to the spatial heterogeneity of the soil and the wastes, in terms of covariates, such as its characteristics, affecting the contaminating process.

Multivariate analysis methods provide techniques for classifying the interrelationship of waste properties and heavy metals. One of the most commonly used technique in environmental studies, included in multivariate statistical methods, is the principal component analysis (Mendiguchía *et al.,* 2004; Tariq *et al.,* 2006). Principal component analysis is a technique whereby a complex data set is simplified by creating one or more new variables or factors, each representing a cluster of interrelated variables within the data set. This technique has been widely used to evaluate the relations between metal concentration and soil properties (Gutierrez-Galindo *et al.,* 2007; Peris *et al.,* 2008; Acosta *et al.,* 2009), and could be used to understand the influence of waste properties in the behavior of metals in tailing ponds.

In Murcia province, southeast of Spain, past mining activities have generated large amounts of unconfined wastes, where there are 85 mine tailing ponds due to intensive mining activities that occurred during last century, especially in the Sierra de Cartagena-La Union. Although mining activity was abandoned several decades ago, however, tailing ponds still remain in the area. The environmental impact of such structures, generally results from their low pH, high metal content, low organic matter and scarce or null vegetation (Conesa *et al.*, 2006; Ottenhof *et al.,* 2007). High incidence of wind and water erosion events (Zanuzzi *et al.,* 2009a), negatively affect soil, water, vegetation, fauna, and human populations in the surrounding areas.

In the area studied, several researches have been addressed, both under laboratory (Conesa *et al.,* 2007a; Conesa *et al.*, 2009) and field conditions (Zanuzzi *et al.,* 2009a; Ottenhof *et al.,* 2007) for reclamation of these areas. However, these researches were pilot experiments realized in pots or plots. For large scale reclamation of the tailing ponds, and using the recommendations arisen from previous studies, it is essential to evaluate the spatial distribution of metals, which will allow identify vulnerable areas where the main remediation efforts and monitoring should be focused.

The objectives of this research were to: 1) evaluate the degree of residual contamination of heavy metals by comparison with guideline values in two representatives tailing ponds of the Cartagena-La Unión Mining District, 2) analyze the relationship between waste properties and total, extractable heavy metals by DTPA and water and, 3) locate hotspots of environmental risk by spatial analysis, where remediation efforts and monitoring should be focused.

3.2. Material and methods

3.2.1. Study area and sampling

The study was conducted in El Lirio and El Gorguel mine tailings. For the physico-chemical characterization of wastes at the two ponds, a sampling was carried out in April 2009 according to a regular sampling grid with a distance between samples of 100 m using Geographic Information System - GIS. Aerial orthophotos were used to design the grid so that sampling was representative of all the surface area of each pond (Figure 3.1). Samples were taken from the 0-15 cm depth.

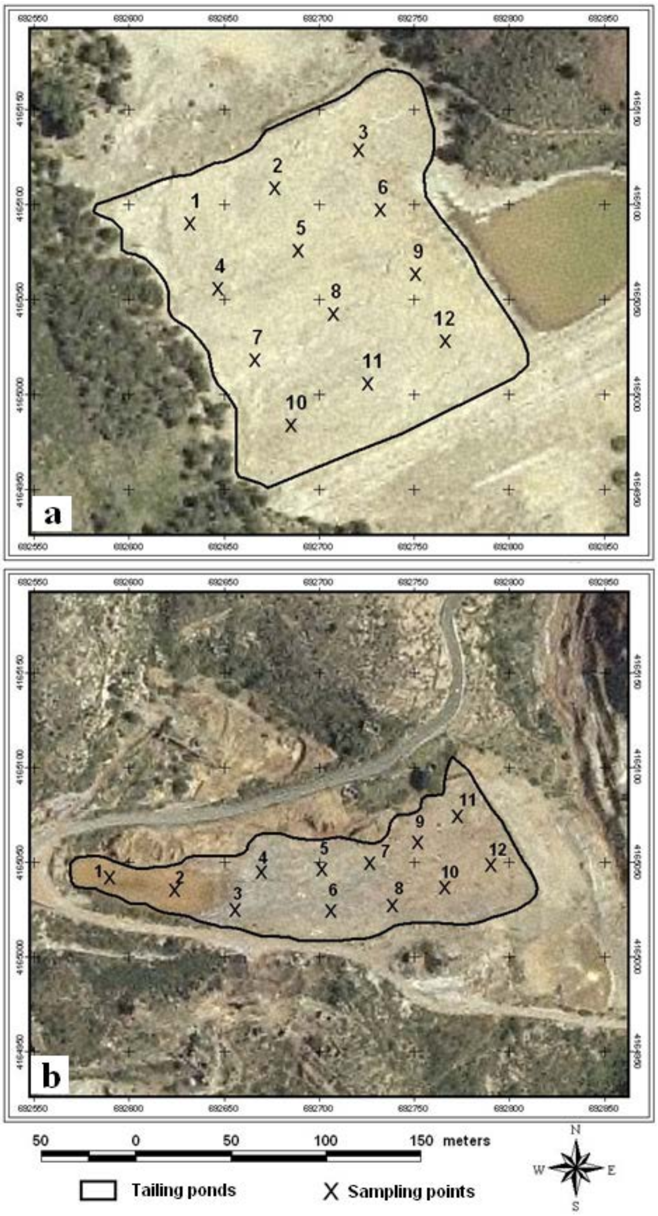


Figure 3.1. Design of soil sampling grids for El Lirio (a) and El Gorguel (b) tailing ponds.

3.2.2. Analytical methods

The samples were air-dried for 7 days in the lab, passed through a 2-mm sieve, homogenized, and stored in plastic bags at room temperature prior to laboratory analyses.

The analyses for this study were determined as follow: pH and electrical conductivity (EC) were measured in a 1:1 and 1:5 deionised water/soil ratio solution, respectively, according to Peech (1965); organic carbon (OC) and total nitrogen (TN) according to Duchaufour (1970), cation exchange capacity (CEC) following the method of Chapman (1965); particle size analysis carried out by using the FAO-ISRIC system (2006) after the combination of pipette Robinson and sieving. For the quantification of the total metals in each sample, a subset of each one was ground, and an acid digestion (nitric-perchloric) was used (Risser and Baker, 1990). For soil extractable metals, DTPA (diethylene triamine pentaacetic) was used (Lindsay and Norwell, 1978; Norvell, 1984). Soluble metals were determined according to Ernst (1996). Measurements of metals were carried out using flame atomic absorption spectrophotometer (AAnalyst 800, Perkin Elmer), detection limits of the metals were: Pb (1.5 mg kg^{-1}), Cu (0.30 mg kg^{-1}), Cd (0.08 mg kg^{-1}) and Zn (0.15 mg kg^{-1}).

Reference soil SO-4 from the Canadian Certified Reference Materials Project (Bowman *et al.,* 1979) and reagent blanks were used as the quality control samples during the analyses. The recovery of metals in the analyses was within <4% for Cd, <2 % for Cu, <3% for Zn, and <1% for Pb compared to this reference sample.

3.2.3. Multivariable statistical and spatial analyses

Prior to statistical analysis, the data set distribution was evaluated using Kolmogorov–Smirnov method; when the distribution was not normal, the data were log-transformed (Romic and Romic, 2002), before statistical treatment. Descriptive statistics (mean, median, standard deviation and range) of metals and soil properties were performed applying the Excel for Windows software package. We used the t-test to determine the existence of significant differences among waste properties and metals in the two ponds.

Correlation matrix and Principal Component Analysis (PCA) were used to evaluate heavy metal-waste properties relations. The Pearson correlation coefficient, *r*, was used to measure the relationship between two quantitative variables (metals and waste properties); PCA was used to study the correlations among heavy metals and properties and their grouping into a few factors. After grouping, the metals and properties within each factor are more highly correlated with metals and properties in that factor than with metals and properties in other factors. In this case, varimax rotation was applied because it minimizes the number of metals and properties with a high loading on each component and facilitates the interpretation of results (Micó *et al.*, 2006). Statistical calculations were performed using SPSS 15.0 for Windows (Norusis, 1993).

Metals concentrations and waste properties were used as the input data for distribution maps. The software used for the mapping and spatial analysis was Arcview 3.1. An interpolation method called the inverse distanced weighted method was adopted for the interpolation of the data (Burrough and McDonnell 1998; Celine *et al.*, 2006).

3.3. Results and discussion

3.3.1. Tailing ponds characterization and degree of pollution

As shown in Table 3.1, pH values of the samples from Lirio were statistically lower than those from Gorguel pond, being strongly acid (5.39) and slightly alkaline (7.41), respectively (Soils Survey Division Staff, 1993).The wastes from Lirio are depleted in bases (Cobertera, 1993), corroborated by the absence of calcium carbonate on both ponds (Conesa *et al.*, 2006). The rest of properties were similar for both ponds, except for cation exchange capacity, being higher in Lirio pond and due to different mineralogical composition, since the amount of organic carbon is low (Urbano, 2001) and equal for both ponds. According with the results from Conesa (2006), in Gorguel only three minerals were identified: quarz (SiO_2), gypsum ($CaSO_4$ $2H_2O$) and chlorite ($(Mg,Al)_6(Si,Al)_4$ $O_{10}(OH)_8$); oppositely, Zanuzzi (2007) reported the following minerals in Lirio: quarz (SiO_2), gypsum ($CaSO_4$ $2H_2O$), clinochlorite ($(Mg_5Al)(Si_3Al)O_{10}(OH)_8$), goethite ($FeO(OH)$), faujasite ($Na_{58}(Al_{58}Si_{134}O_{384})._{240}H_2O$) and magnetite ($Fe_3O_4$). According to Soil Survey Division Staff (1993), these ponds were considered as saline (EC > 2 dS m^{-1}). The mean values of the particle size fractions ranged from 60.2-60.4% sand, 32.5-30.1 % silt, and 7.35-9.55% clay; being classified as sandy loam (F.A.O.-I.S.R.I.C., 2006), which makes it moderately permeable, with low water retention capacity.

There were no significant differences in total and DTPA-extractable concentrations of trace-element between the Lirio and Gorguel; only significant higher concentrations of soluble Cd, Zn, and Pb were observed in the Lirio, due likely to the low pH of this pond. The mean metal total concentrations provided a broad assessment of waste quality of the ponds. Concentrations for all samples and metals in both ponds were higher than those reported as local background by Martínez and Pérez (2007) (Table 3.1). In addition, mean Pb (6322-7923 mg kg^{-1}), Zn (16397-18075 mg kg^{-1}) and Cd (14.9-16.3 mg kg^{-1}) total concentrations in both ponds (Lirio-Gorguel) were markedly higher than Spanish, Dutch, and Danish intervention values. However, values for Cu (166-156 mg kg^{-1}) did not exceed those levels (Table 3.1). Lirio and Gorguel ponds were especially high in Pb and Zn compared with mentioned guideline values. Total Pb, Cu and Cd were lower and Zn content was higher to those reported by Rodriguez *et al.* (2009) in the tailings of a Pb-Zn mine from Ciudad Real, Spain. However, they were slightly higher to those found by Conesa *et al.* (2006) from the same ponds; this can be due to the surface covered for the sampling in that study was much smaller than the one used in our study, which allowed us to find samples with higher metal concentrations.

In both tailings, the concentrations of Zn and Pb extractable by DTPA were found high compared to other metals, and suggested that high concentrations of these metals can be taken by plants creating risk for the food chain (Pastor *et al.*, 2007). After calculating the percentages of DTPA-extractable metals with respect to their total concentrations, the highest percentages were reported for Cd, 38 and 27 % in the Lirio and Gorguel; while for Zn were 11.9 and 6.2 %, and for Pb they were 7.3 and 2.3 %. This means that Cd is the metal with highest risk as it is more mobile to enter food chain. With regards to Cu, the percentage extracted by DTPA reached 4.5 % and the mean concentration was <10 mg kg^{-1} in both ponds, indicating that this metal is not environmentally problematic in the area studied. However, due to some factors would be able to affected the complexing capacity of the DTPA, such as organic matter, content of oxides and hydroxides of metals, pH and others (Sims and Johnson, 1991), the results of DTPA-extracted metals in the acid and heavy polluted samples must be carefully interpreted (National Research Council, 2003).

Table 3.1. Waste properties and heavy metals concentration of the selected tailing ponds.

	El Lirio tailing pond			**El Gorguel tailing pond**		
	Mean (S.D.)[†]	**Median**	**Range**	**Mean (S.D.)[†]**	**Median**	**Range**
pH	5.39(1.33)a	5.46	3.71-7.67	7.41(0.43)b	7.59	6.54-7.9
EC (dSm^{-1})*	3.63(1.39)a	2.93	2.53-7.39	4.8(2.3)a	3.90	2.67-9.35
TN (%)*	0.01(0.01)a	0.01	0.00-0.02	0.02(0.02)a	0.01	0.00-0.06
OC (%)*	0.37(0.16)a	0.37	0.13-0.67	0.42(0.23)a	0.40	0.15-0.71
CEC	18.8(8.78)a	15.5	8.75-34.8	8.39(5.18)b	5.24	3.73-18.1
Sand (%)	60.2(26.2)a	62.0	3.00-87	60.4(17.8)a	58.1	33.7-88.9
Silt (%)	32.5(21.9)a	30.5	8.55-1.11	30.1(15.3)a	32.5	6.15-54.8
Clay (%)	7.35(6.89)a	5.21	1.11-26.1	9.55(6.74)a	8.21	3.16-29
Soluble metal concentration (mgkg^{-1})						
Cadmium	1.37(1.53)a	0.80	0.01-4.54	0.23(0.40)b	0.04	0.00-1.22
Copper	0.24(0.15)a	0.21	0.11-0.62	0.49(0.08)b	0.50	0.36-0.59
Lead	2.90(2.83)a	1.30	0.06-7.11	0.20(0.16)b	0.15	0.05-0.56
Zinc	336(551)a	169	1.14-2010	24.8(60.1)b	1.46	0.33-204
DTPA extractable metal concentration (mgkg^{-1})						
Cadmium	5.71(7.47)a	2.91	0.11-24	4.48(4.10)a	3.00	0.77-13.7
Copper	7.43(8.47)a	4.30	0.33-28	7.39(8.45)a	3.84	1.05-25.9
Lead	463(461)a	283	70-1403	178(298)a	30.0	2.34-982
Zinc	1951(2499)a	953	74-7578	1121(1626)a	531	121-5344
Total metal concentration						
Cadmium	14.9(16.3)a	11.7	0.34-53	16.3(9.07)a	14.1	3.95-31.0
Copper	166(40.3)a	154	130-281	156(55.4)a	154	65.9-256
Lead	6322(4265)a	4535	1426-14252	7923(5197)a	7548	1501-
Zinc	16397(11151)a	14650	4995-43021	18075(7536)a	18870	4790-
Guidelines of maximum allowed concentration of heavy metals and local background (mgkg^{-1})						
	Spain[1]	Denmark[2]	Netherlands[3]	Local background[4]		
Cadmium	1-3	5	12	0.32		
Copper	50-210	500	190	12.6		
Lead	50-300	400	530	9.3		
Zinc	150-450	1000	720	41.4		

*E.C.: electrical conductivity, T.N.: total nitrogen, O.C.: organic carbon. C.E.C.: cation exchange capacity.

[†] Within the same row, different letters indicate significant differences ($P<0.05$) between means in the different tailing ponds after a T-test.

[1] Real Decreto 1310/1990, allowed level in agricultural soil, interval: soil pH<7 and pH>7.

[2] Ministerial Decree (1999), intervention values.

[3] Ministery of Housing, (1994), intervention values.

[4] Martínez and Pérez (2007), background values.

As observed for metals concentrations extracted by DTPA, mean values of soluble Zn were the highest for tailings, 336 and 24.8 mg kg^{-1}. In the case of Pb, an opposite trend was observed. Despite the high total and extractable concentration of Pb in both ponds, the soluble fraction was very low, even lower than Cd in the Gorguel pond; this shows the low solubility of this metal, also reported by other authors (e.g. Burgos *et al.,* 2006; Conesa *et al.,* 2008b), demonstrating that Pb is not highly mobilized in the environment. The amounts of soluble Cd showed the highest percentage in comparison with its total concentration, 9.19 and 1.41 % for the Lirio and Gorguel respectively, followed by the Zn>Cu>Pb sequence. Autier and White (2004) concluded that Cd is more mobile in soil than most of other heavy metals, and Liu *et al.* (2005) also reported that Cd and Zn were more mobile than Cu in an area affected by Pb/Zn mine spill.

3.3.2. Behavior of heavy metals and their relation with waste properties

The results of Pearson correlation and the PCA (principal component analysis) for the Lirio pond are reported in Tables 3.2 and 3.3. According to the PCA results, 5 factors were considered since their eigenvalues were higher than one unit. The communalities shown by the variables, considering these 5 factors, ranged from 78% for total nitrogen to 99% for total Zn, therefore all the elements were consequently well represented.

The Cu, Pb, Cu and Zn extracted by DTPA method, total Cu, Cd and Zn, soluble Cd and Zn, EC and OC were associated in the first principal component (PC1), which explained 35% of the total variance. Since many variables were included in this factor, it is not easy to interpret the relations between them. However, the correlation matrix (Table 3.2) allowed reaching some conclusions. 1) Total Zn, Cd and Cu were positively correlated, indicating a common behavior in the pond (Manta *et al.,* 2002). 2) As the correlation coefficients reported in Table 3.2, an increase of total Zn and Cd concentrations promoted an increase in the concentrations of soluble and extractable fractions of these metals. 3) The positive correlation between OC and soluble Cd and Zn indicated that an increase of concentration of the soluble fraction of these metals is associated to an increase in OC, due likely related to the formation of soluble organic ligands which would increase the solubility of these elements (Almas *et al.,* 1999). 4) Soluble Zn was also positively affected by clay (not present in PC1) and EC, while negatively affected by sand (not present in PC1), which could be attributed to the effect of competition for the sorption sites of clay by cations and metal-complexation with anions coming from salts that increases soluble Zn concentration (Paalman *et al.,* 1994; Hatje *et al.*, 2003).

Supported by correlation coefficients (Table 3.2), an increase of organic matter also enhanced a higher concentration of Cd, Cu and Zn extractable by DTPA (Rauret, 1998). DTPA-extracted Zn and Cu were also positively affected by the increase of clay (not present in PC1) and salinity. An increase of clay percentage in the soil increases the amount of sorption sites for cation (Norvell, 1984).

PC2 explained 22 % of the total variance and loaded positively on total Cu, clay, silt and negatively on sand (Table 3.3), supported by the correlation coefficients between total Cu and those soil constituents (Table 3.2). This suggests that Cu is mainly bound to clay and silt in Lirio pond.

PC3 was positively correlated with total and soluble Pb and negatively with pH. As shown in Table 3.2, there is a significant negative correlation between pH and soluble Pb ($r = -0.75$, $p<0.05$), which means that Pb solubility tends to increase at lower pH. pH is generally acknowledged to be the main governing factor concentrations of soluble metals (Ross, 1994, Brallier *et al.,* 1996), however, no correlation was found with the rest of the metals.

PC4 was dependent upon OC, TN and soluble Cu, and accounted for 11.2% of the total variance (Table 3.3). The negative correlation with soluble Cu is due to the formation of strong association of Cu in organic complexes (Alvim *et al.,* 2000), which causes a decrease in the concentration of soluble form. PC 5 only included the cation exchange capacity (CEC) indicating that the variability of this property is not associated with any other property or metal. This trend was not expected, since CEC is normally strongly correlated with organic matter and clay content, with variable charges able to adsorb cations (Bhagat and Verma, 1991; Ganuza and Almendros, 2003; Oorts *et al.,* 2003).

Data from the Gorguel pond was treated in the same way as for Lirio (Tables 3.4 and 3.5). With regards to PCA, four factors or components were retained, accounting for more than 85 % of the total variance. The communalities showed that the variables displayed high values.

Table 3.2. Pearson correlation coefficients between metals and waste properties in El Lirio tailing pond.

Cu-Soluble	**-0.58***											
Pb-Soluble	-0.30	0.21										
Zn-Soluble	0.56	-0.25	0.15									
Cd-DTPA	**0.92****	-0.33	-0.32	0.55								
Cu-DTPA	**0.78****	-0.48	-0.12	**0.83****	**0.79****							
Pb-DTPA	0.43	-0.09	0.39	**0.80****	0.43	**0.62***						
Zn-DTPA	**0.86****	-0.45	-0.17	**0.78****	**0.89****	**0.98****	**0.61***					
Cd-Total	**0.63***	0.01	-0.38	**0.70***	**0.80****	**0.68***	0.44	**0.75****				
Cu-Total	0.55	-0.28	0.18	**0.88****	0.48	**0.76****	0.57	**0.69***	**0.58***			
Pb-Total	-0.32	0.24	**0.64***	0.23	-0.24	-0.02	0.05	-0.11	-0.06	0.40		
Zn-Total	**0.76****	-0.25	-0.35	**0.79****	**0.84****	**0.91****	0.57	**0.92****	**0.88****	**0.69***	-0.17	
pH	0.34	-0.08	**-0.70***	0.15	0.44	0.28	0.06	0.32	0.56	0.02	-0.56	**0.58***
E.C.	0.55	-0.40	0.00	**0.84****	0.43	**0.74****	0.48	**0.66***	0.54	**0.63****	0.21	**0.68***
T.N.	0.29	-0.42	0.17	0.57	0.23	0.51	0.38	0.43	0.20	0.56	0.47	0.32
O.C.	**0.72****	**-0.71****	-0.43	**0.67***	**0.61***	**0.79****	0.41	**0.76****	0.54	0.57	-0.25	**0.76****
C.E.C.	0.01	-0.26	0.09	0.27	0.03	0.36	-0.07	0.28	0.10	0.39	0.33	0.17
Sand	-0.23	0.08	0.18	**-0.59***	-0.25	**-0.60***	-0.17	-0.47	-0.48	**-0.72****	-0.37	**-0.60***
Silt	0.11	0.01	-0.22	0.45	0.17	0.51	0.05	0.38	0.39	**0.58***	0.33	0.52
Clay	0.52	-0.35	0.01	**0.83****	0.43	**0.64***	0.51	**0.58***	**0.59***	**0.89****	0.37	**0.61***
LIRIO	Cd-s.	Cu-s.	Pb-s.	Zn-s.	Cd-d.	Cu-d.	Pb-d.	Zn-d.	Cd-t.	Cu-t.	Pb-t.	Zn-t.

* Significant correlation to $p < 0.05$; ** Significant correlation to $p < 0.01$, . s:soluble, d:DTPA, t:total

Table 3.3. Varimax-rotated factor matrix for Lirio tailing pond.

LIRIO	**1**	**2**	**3**	**4**	**5**	**Communalities**
pH	0.33	0.07	**-0.79**	-0.07	-0.23	0.80
EC	**0.65**	0.52	0.10	0.26	0.15	0.81
TN	0.19	0.51	0.32	**0.68**	-0.15	0.78
OC	**0.54**	0.42	-0.34	**0.61**	-0.10	0.97
CEC	0.12	0.22	0.19	0.11	**0.89**	0.90
Sand	-0.23	**-0.94**	0.11	-0.02	-0.12	0.97
Silt	0.12	**0.91**	-0.18	-0.07	0.18	0.91
Clay	0.50	**0.69**	0.18	0.31	-0.11	0.87
Cd-Soluble	**0.79**	-0.01	-0.24	0.44	0.00	0.88
Cu-Soluble	-0.20	0.01	0.11	**-0.95**	-0.18	0.98
Pb-Soluble	-0.01	-0.09	**0.96**	-0.12	-0.05	0.94
Zn-Soluble	**0.79**	0.49	0.24	0.13	-0.05	0.93
Cd-DTPA	**0.87**	0.00	-0.30	0.15	0.05	0.86
Cu-DTPA	**0.83**	0.36	-0.06	0.30	0.19	0.94
Pb-DTPA	**0.76**	0.07	0.40	0.05	-0.36	0.88
Zn-DTPA	**0.89**	0.22	-0.12	0.27	0.16	0.95
Cd-Total	**0.80**	0.33	-0.32	-0.20	0.00	0.89
Cu-Total	**0.64**	**0.62**	0.28	0.16	0.14	0.92
Pb-Total	-0.14	0.52	**0.71**	-0.18	0.17	0.85
Zn-Total	**0.86**	0.37	-0.32	0.05	0.04	0.99
Eigenvalues	7.01	4.48	3.06	2.24	1.24	
% of variance	35.05	22.38	15.32	11.20	6.19	
Accumulative %	35.05	57.43	72.75	83.96	90.15	

The first component, which explained 37% of the total variance, was positively correlated with Cu, Pb and Zn extractable by DTPA, soluble Zn, Pb and Cd, and EC, and negatively correlated with pH. The negative correlation between pH and EC ($r = -0.57$, $p<0.05$) (data not shown) is explained by the fact that when the pH decreases the salts are increased (Wong *et al.*, 2003). However, the low range of pH and the high amounts of EC (Table 3.2) suggest that the salinity is not only dependent on pH, and its variability is affected by other factors (e.g. topography of the pond).

The absence of total metals concentrations in PC1, and the lack of correlation between them and pH (Table 3.4) indicated that only soluble and extractable forms of the metals depended on pH and salinity. However, as it has been shown previously (Table 3.2), the pH of this pond is quite high. Therefore no current actuation to increase pH will be necessary; however a monitoring plan should be carried out in order to prevent the decrease of pH. The reclamation program should include activities to reduce the salinity, which would influence the amount of both heavy metal mobility and the stress on vegetation.

The PC2 (Table 3.5) presented positive scores for total Cu, Pb and Zn, clay and silt, and negative for soluble Cu and sand. These results are supported by the correlation coefficients shown in Table 3.4. Likely the minerals in the clay and silt fractions have elements such as Cu, Pb and Zn in their composition. In the Mining District of Cartagena-La Union, Pb and Zn occur mainly in galena, sphalerite, sulfates, and Pb- or Zn-bearing oxide minerals (manganese, iron) (Oen *et al.,* 1975). Heavy metals and trace elements are generally more strongly retained in the fine fractions than in coarsest ones (Adriano, 2001). Higher clay content may increase metal retention and thus enhances the natural attenuation capacity of the soil (Burgos *et al.,* 2008). The presence of negative score of soluble Cu in this component could indicate that Cu is bound to clay and silt.

The PC3 included organic carbon (OC), total nitrogen (TN) and cation exchange capacity (CEC), indicating that organic matter is the main constituent affecting the adsorption capacity of the soil (Brady and Weil, 2001); in addition, the presence of OC and TN in this component (PC3) indicates that most amount of nitrogen in this pond is associated to the organic matter.

The PC4 loaded on total and extractable Cd, accounted for 11.6 % of the total variance. Pearson correlation coefficient between these variables ($r=0.66$, $p>0.05$) showed that when extractable Cd increases its concentration is mainly due to an increment in its total concentration.

Table 3.4. Pearson correlation coefficients between metals and waste properties in El Gorguel pond.

Cu-Soluble	0.15											
Pb-Soluble	0.84**	-0.16										
Zn-Soluble	0.93**	0.22	0.78**									
Cd-DTPA	0.45	-0.19	0.71**	0.46								
Cu-DTPA	0.97**	0.09	0.80**	0.88**	0.34							
Pb-DTPA	0.84**	0.34	0.55	0.68*	0.00	0.87**						
Zn-DTPA	0.98**	0.19	0.80**	0.96**	0.38	0.97**	0.82**					
Cd-Total	-0.12	-0.26	0.08	-0.15	0.66*	-0.18	-0.40	-0.20				
Cu-Total	0.34	-0.47	0.27	0.21	0.25	0.41	0.18	0.28	0.49			
Pb-Total	0.29	-0.63*	0.32	0.10	0.30	0.35	0.16	0.19	0.34	0.87**		
Zn-Total	0.55	-0.35	0.55	0.47	0.53	0.57	0.24	0.50	0.53	0.88**	0.79**	
pH	-0.93**	-0.17	-0.62*	-0.82**	-0.27	-0.92**	-0.88**	-0.89**	0.18	-0.41	-0.34	-0.49
E.C.	0.80**	-0.12	0.98**	0.73**	0.51	0.79**	0.67*	0.79**	-0.04	0.18	0.23	0.44
T.N.	-0.32	0.38	-0.55	-0.26	-0.35	-0.34	-0.16	-0.29	0.09	-0.16	-0.43	-0.35
O.C.	-0.20	0.22	-0.52	-0.28	-0.41	-0.20	0.04	-0.23	0.16	0.14	-0.11	-0.14
C.E.C.	0.36	0.15	0.02	0.24	0.00	0.31	0.41	0.28	-0.11	0.31	0.31	0.24
Sand	-0.34	0.69*	-0.44	-0.16	-0.31	-0.42	-0.21	-0.27	-0.15	-0.75**	-0.94**	-0.71**
Silt	0.41	-0.53	0.48	0.22	0.19	0.54	0.37	0.38	-0.08	0.60*	0.79**	0.61*
Clay	-0.03	-0.63*	0.08	-0.10	0.38	-0.11	-0.28	-0.16	0.57	0.61*	0.70*	0.51
GORGUEL	Cd-s.	Cu-s.	Pb-s.	Zn-s.	Cd-d.	Cu-d.	Pb-d.	Zn-d.	Cd-t.	Cu-t.	Pb-t.	Zn-t.

* Significant correlation to $p < 0.05$, ** Significant correlation to $p < 0.01$, s: soluble, d: DTPA, t: total

Table 3.5. Varimax-rotated factor matrix for Gorguel tailing pond.

GORGUEL	1	2	3	4	Communalities
pH	**-0.93**	-0.23	-0.22	0.08	0.97
EC	**0.75**	0.09	-0.54	0.18	0.90
TN	-0.21	-0.44	**0.77**	0.10	0.84
OC	-0.13	-0.09	**0.93**	0.02	0.89
CEC	0.37	0.33	**0.57**	-0.16	0.60
Sand	-0.21	**-0.94**	0.25	0.01	0.99
Silt	0.32	**0.80**	-0.36	-0.23	0.92
Clay	-0.18	**0.68**	0.16	0.50	0.77
Cd-Soluble	**0.98**	0.13	-0.07	0.07	0.99
Cu-Soluble	0.30	**-0.73**	0.32	-0.15	0.75
Pb-Soluble	**0.77**	0.17	-0.49	0.30	0.95
Zn-Soluble	**0.93**	-0.05	-0.13	0.13	0.90
Cd-DTPA	0.37	0.13	-0.36	**0.76**	0.87
Cu-DTPA	**0.96**	0.22	-0.09	-0.05	0.98
Pb-DTPA	**0.88**	0.06	0.13	-0.35	0.91
Zn-DTPA	**0.98**	0.05	-0.11	0.01	0.97
Cd-Total	-0.20	0.25	0.13	**0.89**	0.90
Cu-Total	0.24	**0.83**	0.25	0.30	0.89
Pb-Total	0.15	**0.96**	0.00	0.15	0.97
Zn-Total	0.44	**0.68**	0.00	0.46	0.87
Eigenvalues	7.41	5.12	2.95	2.33	
% of variance	37.07	25.62	14.75	11.66	
Accumulative %	37.07	62.69	77.44	89.11	

3.3.3. Spatial variability of waste parameters and identification of environmental risk areas

As shown in the previous section, the physicochemical properties of the mine tailing (i.e. pH, OC, EC, and clay) control the presence of most of the soluble and extractable metals in the ponds. The Lirio pond maps (Figures 3.2 and 3.3) showed similar distribution for electrical conductivity, organic carbon, clay, and silt with both high contents in the north and east edges of the pond (Figure 3.2). This pattern was also the same for total and extractable concentration for all the metals and soluble Zn and Cd. On contrast, the highest concentrations of soluble Pb are located in the south side of the pond associated with the lowest pH values (Figure 3.3). In the west side, available concentrations for all metals were high.

The topography of the pond surface contributed to the distribution of the metals. The most depress part of the pond is located in the north and east where fine particles such as clay, silt and organic matter are accumulated, likely transported by water transport.

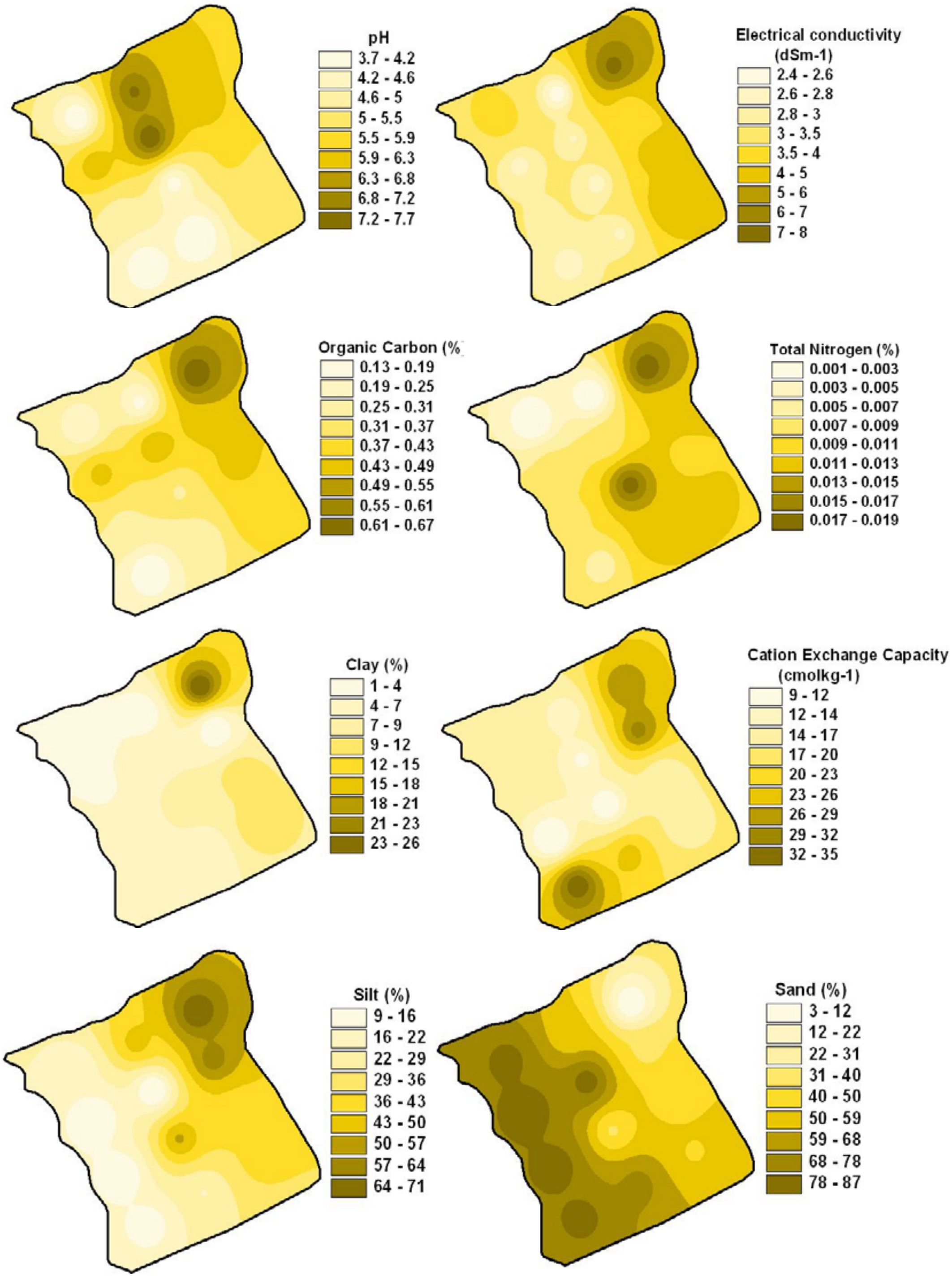


Figure 3.2. Spatial distribution of waste properties in El Lirio tailing pond.

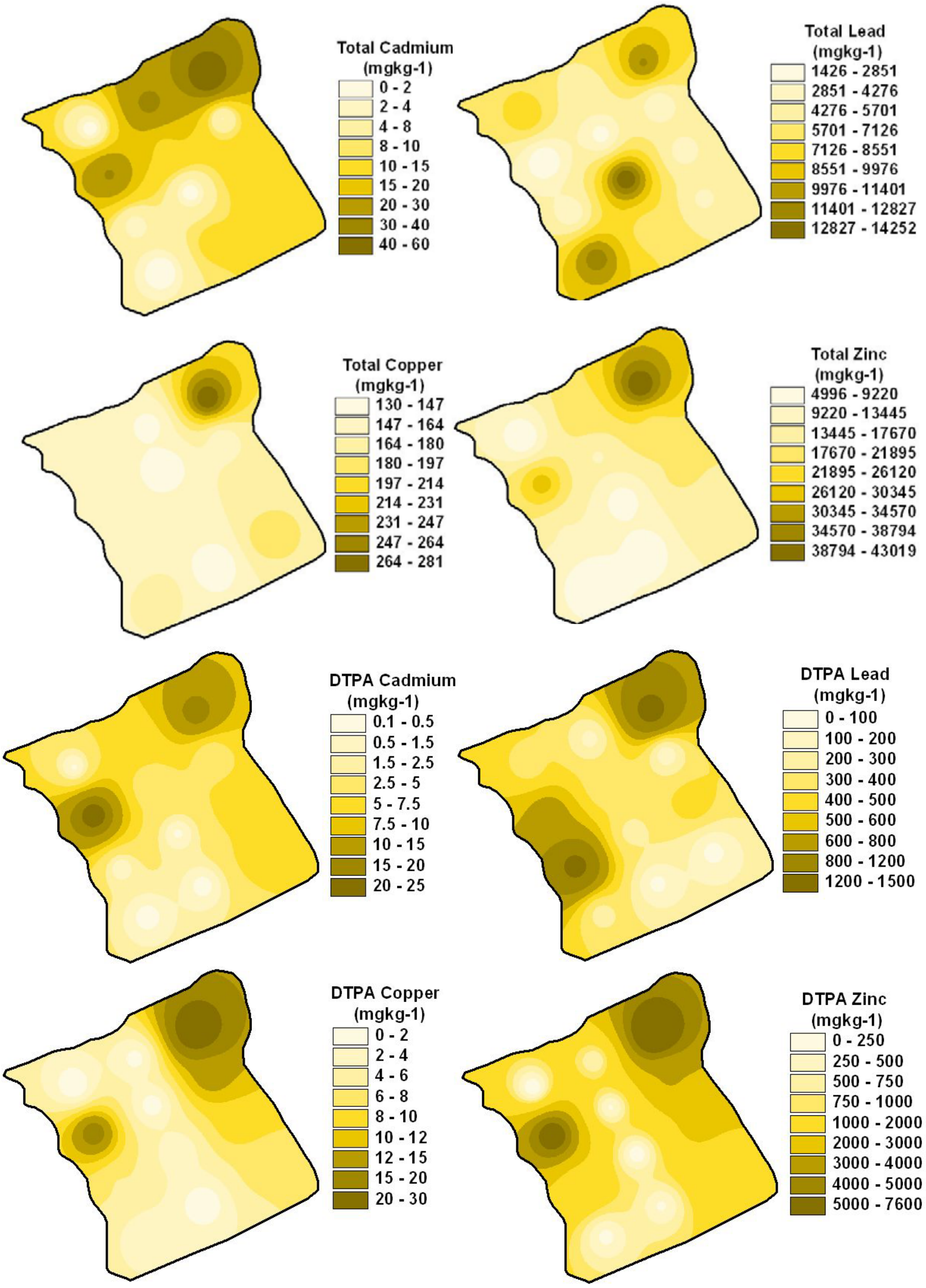


Figure 3.3. Spatial distribution of heavy metals in El Lirio tailing pond.

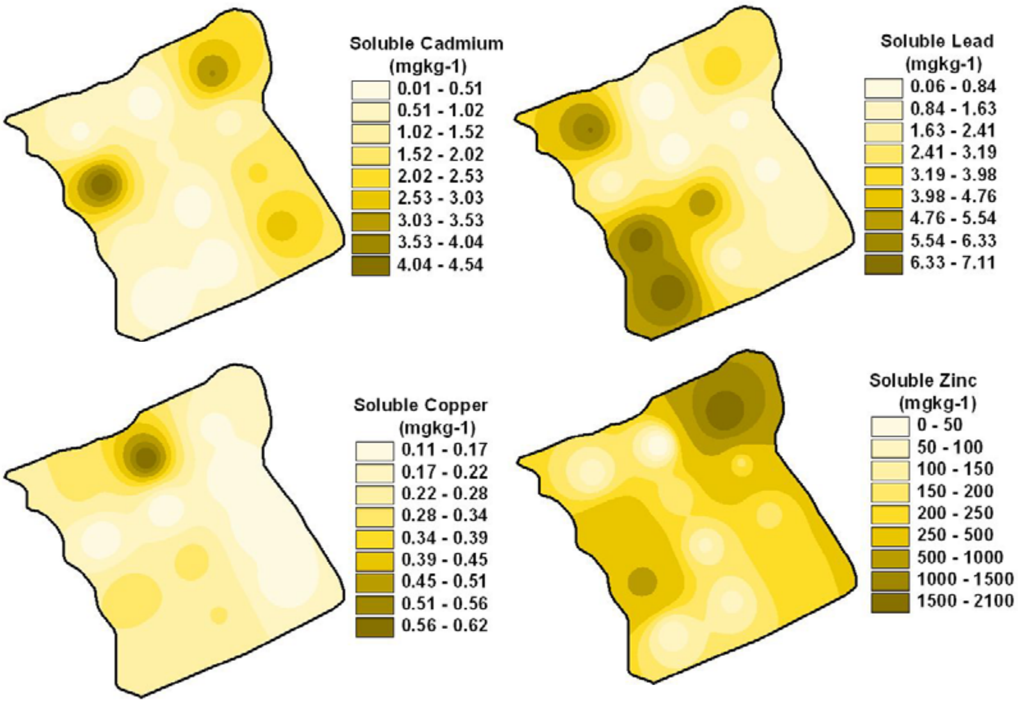


Figure 3.3. Spatial distribution of heavy metals in El Lirio tailing pond (cont.)

In addition, the effect of the main direction of flows of the surface water streams following the slope enhances the pollution spreading due to acidic drainage to these parts of the pond. The geographic distribution of characteristics and heavy metals for the Gorguel tailing pond are shown in Figures 3.4 and 3.5. The pH and EC showed a similar distribution pattern with inverse values; i.e. the lowest pH and the highest EC values were reported in the centre of the pond. The spatial variations of clay and silt were also similar. The highest percentages of clay and silt were found in the west and the lowest in the east (Figure 3.4).

The variations in total concentrations for all the metals showed a very similar pattern (Figure 3.5). The heavily contaminated areas occur in the west of the pond, associated with high percentages of clay and silt. However, the highest soluble and extractable concentrations for all the metals, except soluble Cu, were located in the centre of the pond, associated to the lowest pH values, high salinity, and low organic matter.

The main mechanism affecting the metal distribution in the Gorguel tailing pond is its physicochemical properties, especially the pH and EC for soluble and extractable metals, and the texture (clay, silt and sand) for the total concentration. The topography of the pond surface affects the particle sizes distribution and as a consequence the distribution of total metal concentration in the west part of the pond. No relation was found between the main runoff directions with soluble and extractable concentration for all the metals.

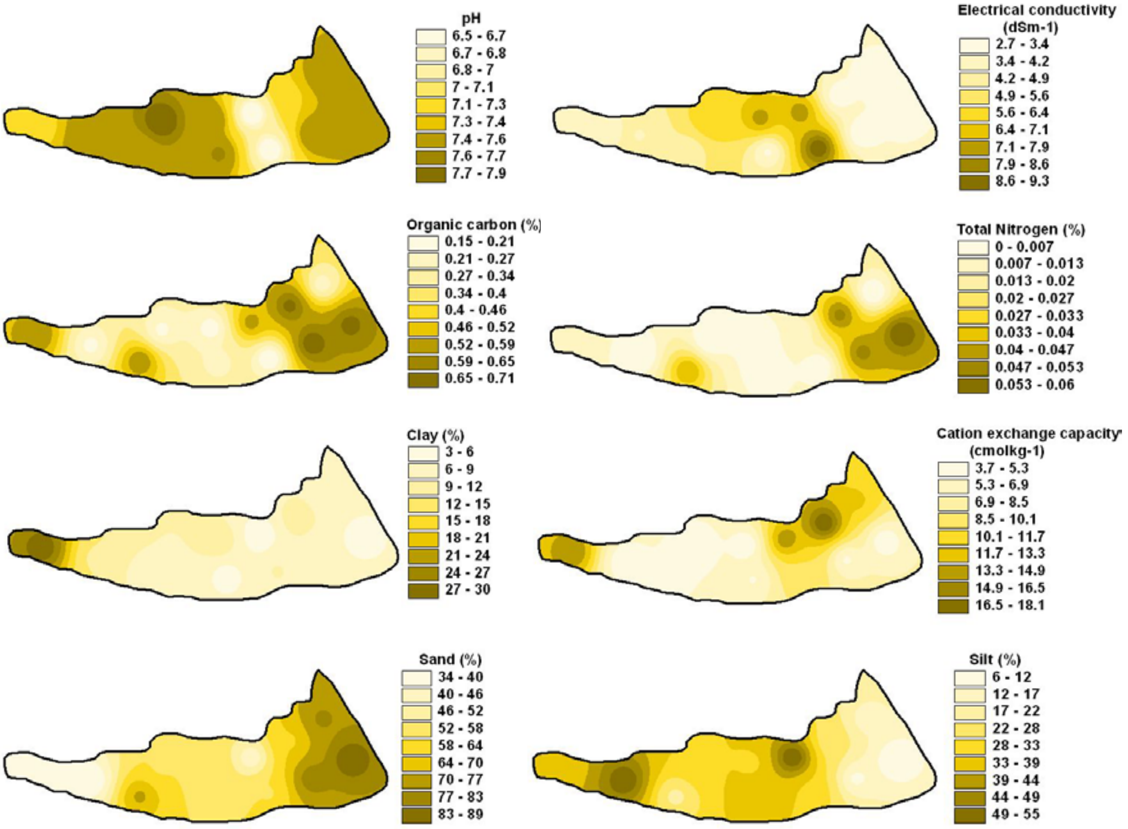


Figure 3.4. Spatial distribution of waste properties in El Gorguel tailing pond.

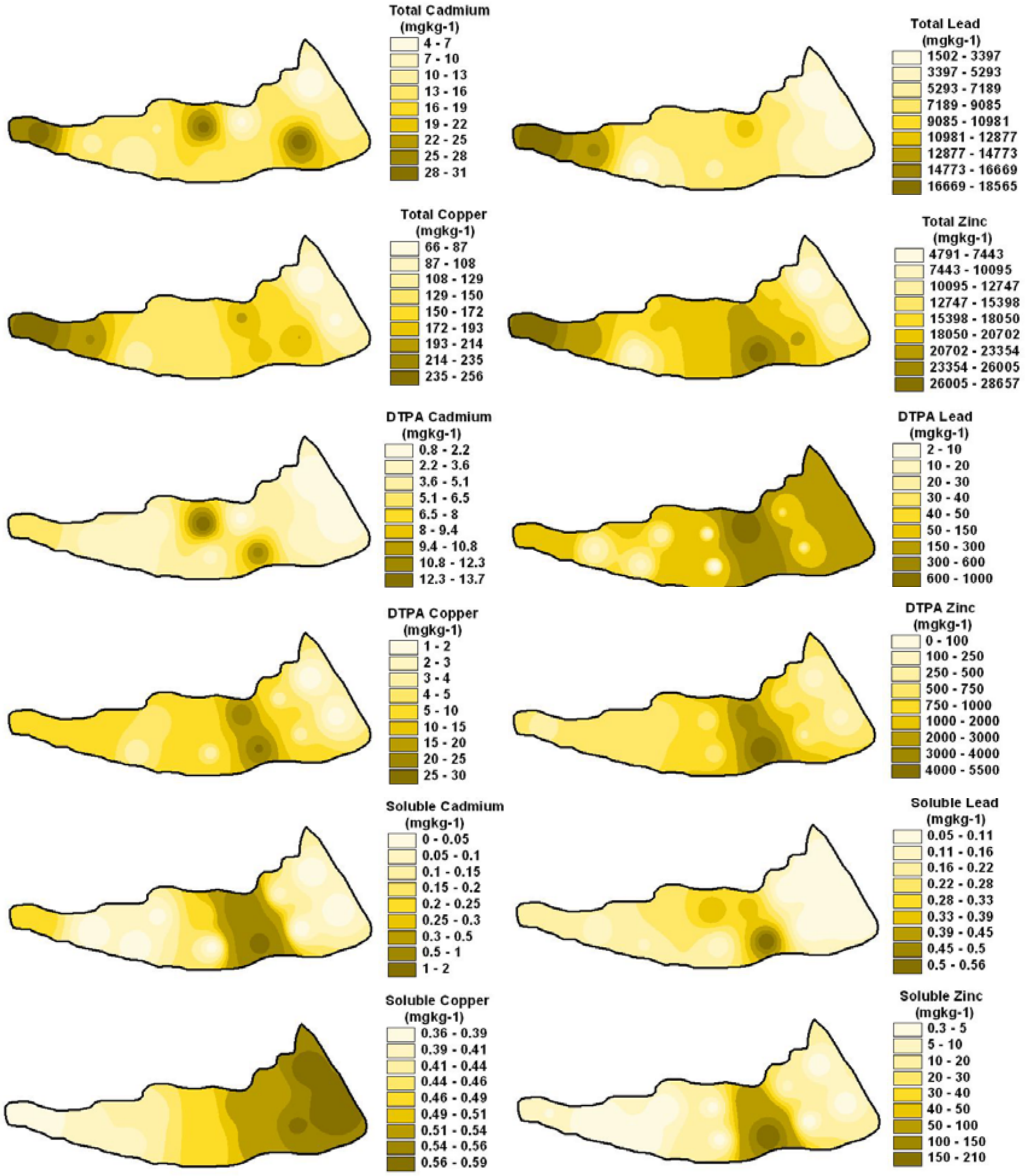


Figure 3.5. Spatial distribution of heavy metals in El Gorguel tailing pond.

3. 4. Conclusions

Most of the waste properties of the ponds studied were similar, although pH values from the Lirio were lower than those from the Gorguel pond. This characteristic is responsible for higher concentrations of soluble Cd, Zn, and Pb in the Lirio than in Gorguel, showing a higher risk of heavy metals mobility. Total and extractable concentrations of all metals were similar in both ponds. Total Pb, Zn, and Cd were markedly higher than the threshold values, suggesting that reclamation programs should be carried out in both ponds.

Concentrations of Zn and Pb extractable by DTPA and percentage of extractable Cd were very high, which suggests high risk of mobility via plants uptake with the subsequent risk for the food chain. Mean concentration of soluble Zn and percentage of soluble Cd were the highest in both ponds, especially for the Lirio. These metals could be transported by runoff water that may reach streams or contaminate soils and even groundwater under the ponds and surrounding areas.

In the Lirio tailing pond, concentrations of soluble Cd and Zn and extractable Cd, Zn and Pb were increased by organic matter, likely forming organic ligands. Soluble and extractable Zn is also positively affected by clay and electrical conductivity, which could be attributed to adsorption of metals by clays combined with the effect of competition for cation sorption sites and metal-complexation with anions, causing an increase in soluble and extractable metal concentrations. Soluble Pb is controlled by pH.

In the Gorguel pond, soluble and extractable forms of Zn, Pb, and Cd depend on pH and salinity. However, the pH of this pond is rather high. Measures should be taken to prevent a decrease in pH. Reclamation program should include activities to reduce the salinity, so that the heavy metal mobility could be reduced.

Spatial distribution analysis in the Lirio tailing pond are: (1) Concentrations of all metals and soluble concentrations of Cd and Zn are in the north edge; (2) Extractable concentrations of all the metals were in the west edge; and (3) The soluble Pb concentrations were in south edge. For the Gorguel tailing pond: (1) The highest total concentrations for all metals were found in the west edge and (2) Highest extractable concentrations for all metals and the highest soluble Pb, Cd and Zn concentration were in the center. The spatial distribution of metals in the ponds is affected by the physicochemical properties and topography of ponds surface.

CHAPTER 4

Marble Wastes and Pig Slurry Improve the Environmental and Plant-relevant Properties of Mine Tailings

Abstract

Poor soil fertility is often the biggest challenge to the establishment of vegetation in mine wastes deposits. We conducted field trials in the El Gorguel and El Lirio sites in SE Spain, two representative tailing ponds of similar properties except for pH, to understand the environmental and plant-relevant benefits of marble waste (MW) and pig slurry (PS) applications to mine tailings. Low pH (5.4) tailings (El Lirio) exhibit reduction of up to 4-fold in bio-availability of metals as shown by the DTPA-Zn, Pb, water-soluble Zn, Pb and up to 3x for water-soluble Cd. El Gorguel tailing has high pH (7.4) and did not exhibit significant trends in the reductions of water-extractable Zn, Pb, Cd and Cu. Improvements to the edaphic (plant-relevant) properties of tailings after the amendments are not as sensitive to pH compared to the environmental characteristics. The two sites had increases in aggregate stability, organic matter (total N and organic C) although total N is higher in the El Gorguel (up to 212 μg N kg^{-1}) than the El Lirio (up to 26 μg N kg^{-1}). However, cation exchange capacities are similar in both sites at 15.2 cmol$_{+}$ kg^{-1}. We conclude that the characteristics, especially pH, of tailing materials significantly influence the fate of metals but not improvements to plant-relevant properties such as cation exchange capacity and aggregate stability one year after the application of MW and PS amendments.

4.1. Introduction

Mine tailings or deposits of mine wastes left after intensive extractions of metals and other mineral resources often contain high levels of potentially toxic metals and very poor soil fertility. In southeast (SE) Spain, mine waste materials have extreme acidities (pH <2.0), electrical conductivity up to 20 dS m^{-1} and contain as much as 8,000 mg Pb kg^{-1} soil (Conesa *et al.,* 2007a). Environmentally, these mine wastes are hazards due to their susceptibility to water and wind erosions and leaching potential of high acidity and toxic metals into rivers and other bodies of water (Zanuzzi *et al.,* 2009a). Inhospitable plant-relevant (or edaphic) properties include low organic C (<3 g C kg^{-1} soil), low N content (<0.03 % N) and limited cation exchange capacity (< 2 $cmol_+$ kg^{-1} soil) (Conesa *et al.,* 2006; Ottenhof *et al.,* 2007).

Establishment of vegetation is one of the most environmentally-friendly means to manage risks associated with these mine wastes deposits. However, plants require a hospitable habitat with available water and essential nutrients to support growth and life requirements of plants and associated organisms (Alveranga *et al.,* 2009; Zanuzzi *et al.,* 2009a).

In reclamation of mine wastes, SOM is often increased through addition of organic amendments such as composts, sewage sludge and animal manures while lime addition is used to increase the low pH of materials in mine wastes deposits. Application of pig slurry or liquid hog manure at 100 m^{-3} $year^{-1}$ for 20 years increased N contents of agricultural soil in Canada by 1,200 kg N ha^{-1} (Angers *et al.,* 2010). In some cases, application of 100 t ha^{-1} sewage sludge or municipal sewage wastes, with a pH of 8.2, to the mine soils increased the pH from <4.0 to pH > 6.0 (Alveranga *et al.,* 2008).

From other studies, environmental and edaphic benefits were observed from the simultaneous applications of industrial and organic wastes into mine waste deposits in SE Spain (Zanuzzi *et al.,* 2009a; Arocena *et al.,* 2012; Zornoza *et al.,* 2012), which means the immobilization of metals; decreases in metal solubility and bioavailability; and increases of carbon, nitrogen and other nutrients. Twenty four months after the application of pig manure, soil acidity decreased from pH 2.9 to pH 7.3 with the addition of calcium carbonate in the form of waste cuttings generated by the marble construction industry (Zanuzzi *et al.,* 2009a). Application of marble and pig manure significantly reduced soluble Cd (0.07-0.17 mg kg^{-1}) and Zn (0.8-1.73 mg kg^{-1}) compared with un-amended treatment at 0.64 and 6.8 mg kg^{-1} for Cd and Zn, respectively (Zornoza *et al.*, 2012). In addition, development of granular soil structure is evident in mine waste materials amended with marble and organic wastes (Arocena *et al.*, 2012). However, Zornoza *et al.* (2012) did not report any significant build up of SOM after 5 years since marble wastes and organic amendments to mine soils although significant increases in enzymes such as phosphodiesterase (210 %) and urease (500 %) were observed in plots treated with pig manure. The nature of mine wastes materials may have played a role in the differential accumulations of SOM in mine tailings.

The initial properties of waste materials may explain the seemingly variable environmental benefits of marble and organic wastes additions to mine waste deposits. Zanuzzi (2007) reported significant reductions of extractable Cd, Pb and Zn contents after application of marble waste in a tailing pond with an initial pH of 7.3. Contrarily, Zornoza *et al.* (2012) did report that reduction in a tailing pond amendment with marble waste with an initial pH of 2.7. Although the application of organic wastes is practiced in reclamation of soils, further information related to the effect of soil initial characteristics (such as pH, SOM and total metal contents) is needed to fully understand the ecological benefits of inorganic and organic amendments to mine and other metal-contaminated soils. For example, contrary to what it is often observed for solid animal manure, application of liquid pig manure does not always increase soil C content due to the possible mineralization of native C (Angers *et al.*, 2010) that may be inherently variable among soils.

The objective of the study was to understand the environmental and plant-relevant (or edaphic) benefits of inorganic and organic amendments to unproductive mine wastes deposits. Specifically, we monitored changes in pH, SOM, aggregate stability, cation exchange capacity, and total content, extractability and availability of select metals at 0, 1 week, 6 and 12 months since the application of amendments. We interpreted our observations to elucidate natural processes involved in the immediate environmental benefits and risks (e.g., metal leaching to ground water) and improvement to edaphic soil properties (e.g., pH, total N, cation exchange capacity) associated with the applications of marble wastes and pig slurry in mine tailing deposits.

4.2. Materials and Methods

4.2.1. Study area

The study was conducted in El Lirio and El Gorguel tailing ponds. Main initial characteristics of the tailings are shown in Table 4.1.

Table 4.1. Main initial characteristics of El Gorguel, El Lirio, and used amendments, mean (standard deviation).

Parameters	El Gorguel	El Lirio	PS	MW
pH	7.41(0.43)	5.39(1.33)	7.8	8
Electrical conductivity (dS m^{-1})	4.8(2.3)	3.63(1.39)	39.1	2.2
Density (g mL^{-1})	-	-	1	-
$CaCO_3$ (%)	-	-	-	98
Moisture (%)	-	-	96	1
Total Nitrogen (%)	0.02(0.02)	0.01(0.01)	5.1 (g L^{-1})	-
NH_4^+-N (g L^{-1})	-	-	4.5	-
NO_3^--N (mg L^{-1})	-	-	22	-
Total organic Carbon (%)	0.42(0.23)	0.37(0.16)	18.7(g L^{-1})	-
Phosphate (mg L^{-1})	-	-	623	-
Sulfate (mg L^{-1})	-	-	47.8	-
Total Cadmium (mg kg^{-1})	16.3(9.07)	14.9(16.3)	BDL (mg L^{-1})	0.05
Total Copper (mg kg^{-1})	156(55.4)	166(40.3)	19.3 (mg L^{-1})	0.36
Total Zinc (mg kg^{-1})	18,075(7,536)	16,397(11,151)	28 (mg L^{-1})	0.26
Total Lead (mg kg^{-1})	7,923(5,197)	6,322(4,265)	BDL (mg L^{-1})	BDL

PS: pig slurry
MW: marble waste
BDL – below detection limit

4.2.2. Field experiments

A field experiment comprising plots amended with marble wastes (MW) and pig slurry (PS) were conducted on the El Gorguel and El Lirio mine wastes deposits at the Cartagena-La Unión Mining District in Murcia (SE Spain). The MW and PS were waste materials associated, respectively with the construction and pig industries in Spain, and have properties useful to the remediation of mine waste soils (Kabas *et al.*, 2012; Acosta *et al.*, 2011) (Table 4.1). The PS came from a pig farm in Pozo Estrecho (SE Murcia) and can be a good source of SOM with 5.1 g total N L^{-1} and 18.7 g organic C L^{-1}, while the predominantly 5-10 µm-sized MW was acquired from Cehegín area (NE Murcia) quarry and contains 98% $CaCO_3$ (Table 4.1).

The treatments were control, marble waste (MW), pig slurry (PS) and marble waste + pig slurry (MW+PS), a schematic representation of the experimental plots is showed in Figure 4.1. Plot sizes ranged from 1,300 to 2,300 m^2 and from 3,500 to 3,750 m^2 in the El Gorguel and El Lirio sites, respectively. The differences between sizes of the plots were due to the availability of the total amount of each amendment. The first activity was tilling the first 50 cm of the surface soil in order to prepare it for the application of the amendments (control plot was also tilled). This activity is realized to prevent the difficulties in the application of amendments because of the formation of very hardened crusting in 2 - 20 cm thickness due to the presence of cementing agents such as oxides and hydroxides of iron. In the MW treatment, 4 kg MW m^{-2} were applied on the soil surface and then mixed in the 0-30 cm layer using a "rotavator". Marble waste (4 kg MW m^{-2}) were applied on soil surface followed by PS application (3 L PS m^{-2}) and after 24 h, amendments were ploughed into 0-30 cm layer in the MW+PS treatment (Figure 4.2). In the PS treatment, 3 L PS m^{-2} were added while the Control plots were neither treated with MW nor PS amendments. The amount of PS amendment followed the legislated threshold for total N addition to avoid nitrate contamination of groundwater (Council Directive 91/676/EEC) while MW was equivalent to the quantity of lime required to neutralise potential acidity from sulphide contents of the materials (Sobek *et al.*, 1978). The experimental plots were not seeded or planted and were left un-vegetated to encourage colonization by native pioneer plant species.

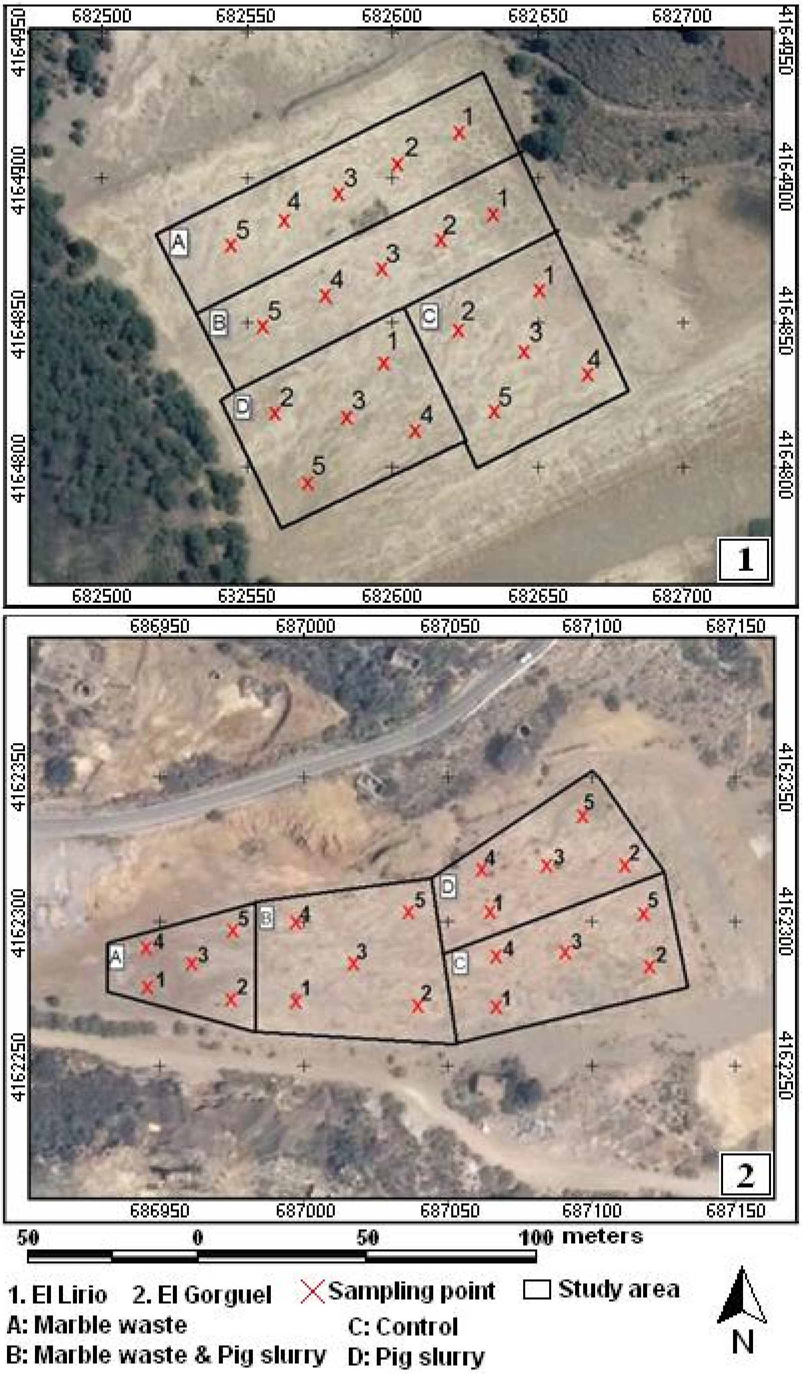


Figure 4.1. The scheme of four field-scale plots of tailings with different treatments.

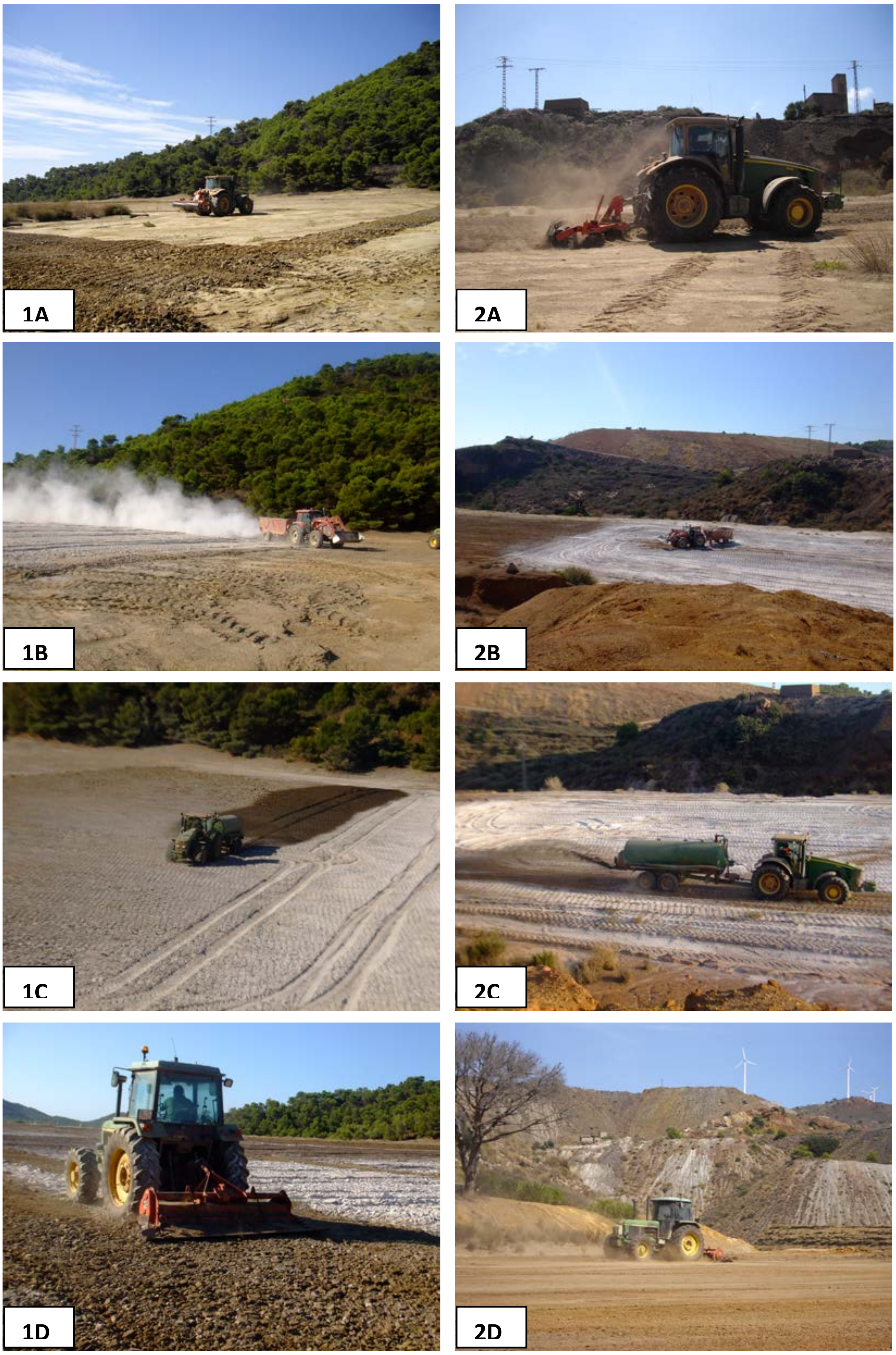


Figure 4.2. El Lirio (1), El Gorguel (2). A: Tilling, B: Application of marble waste, C: Application of pig slurry, D: Incorporation of amendments.

4.2.3. Sampling and analytical methods

In each site, soil samples were collected at the start of the experiment from the tailing without amendments (0 mo), and 1 week (0.25 mo), 6 (6 mo) and 12 months (12 mo) after the application of MW and PS amendments to track short-term changes to tailings properties. Five tailing samples from 0-30 cm within each area of treatment application were collected randomly. Samples were air-dried, passed through a 2-mm sieve and stored in plastic bags at room temperature prior to laboratory analysis.

Eh and pH were determined in de-ionised water (1:1 w/v) (Soil Survey Staff, 2004). Electrical conductivity (EC) was measured in solution extracted from a mixture composed of 1:5 w/v soil:de-ionised water ratio (Andrades, 1996). Total carbon (OC), total nitrogen (TN) and total sulphur (TS) were determined by a CHNS elemental analyzer (EA-1108, Carlo Erba). Untreated ground samples were used to determine the total (TC) and samples subjected to overnight reaction with 1N HCl to dissolve the carbonates were used to estimate total organic carbon (TOC). Inorganic carbon (IC) was the difference between TC and TOC. Aggregate stability was evaluated using the wet aggregate stability method (Soil Survey Staff, 2004). Two techniques were employed to determine the cation exchange capacity (CEC) of tailings: (1) for tailings with no carbonates, we followed Merino *et al.* (1998) where an unbuffered solution of 1M NH_4Cl was used to replace the adsorbed cations, and (2) for samples containing carbonates, CEC was estimated from $BaCl_2$ solution buffered with triethanolamine at pH 8.1 (Roig *et al.*, 1980). The extract is reacted with 0.5 M $(NH_4)_2SO_4$ where Ba^{2+} displaces NH_4^+ and precipitates as $BaSO_4$. CEC is the difference between the weights of extracted $BaSO_4$ of the blank and the sample. Total metals in samples were estimated after soil digestion in $HNO_3/HClO_4$ mixture at 210 ºC for 1.5 h in open vessel with reflux (Risser and Baker, 1990). The bio-available metal fractions were determined using the diethylene triamine pentaacetic acid (DTPA) (1:2 soil-extractant ratio) for samples with pH>6, and EDTA (1:5 soil-extractant ratio) for samples with pH<6 (Lindsay and Norwell, 1978). Water soluble metals were determined using a 1:5 tailing/MilliQ water mixture, shaked 6 hours, centrifuged and filtered (Ernst, 1996). Metal concentrations in extracts and digests were estimated using atomic absorption spectrophotometer (AAnalyst 800 Perkin Elmer). In the determination of total metal contents, the Certified Reference Material BAM-U110 (Federal Institute for Materials Research and Testing, Germany) was used as quality control sample.

4.2.4. Statistical analyses

The effectiveness of MW and PS amendments as tailing amendments in various times of sampling were separately evaluated for the El Gorguel and El Lirio and tailing ponds due to the inherent differences in soil pH (i.e., pH 7.4 and 5.4 for the El Gorguel and El Lirio sites, respectively). A two-factor (i.e., amendments and times of sampling) analysis of variance was conducted to compare the means of treatments at various times of sampling. The results of statistical analysis were grouped into two parts: (1) dependent variables with significant ($p < 0.05$) interaction between treatments and time, and (2) dependent variables with significant differences ($p < 0.05$) due to treatments.

4.3. Results

4.3.1. Total, DTPA and water-extractable metals

Total contents of metals show significant differences with treatments in both the El Gorguel and El Lirio tailing ponds (Table 4.2), DTPA Cu, DTPA Pb, water extractable Cd, water extractable Cu, water extractable Pb in El Gorguel and DTPA Zn, DTPA Pb, water extractable Pb in El Lirio are reported in Figures 4.3 and 4.4 because their contents were also affected by the time factor. In both tailing ponds, total Cd is higher in MW (29.6 mg Cd kg^{-1} in El Gorguel; 48.5 mg Cd kg^{-1} in El Lirio) and MW+PS (28.3 mg Cd kg^{-1} in El Gorguel; 40.0 mg Cd kg^{-1} in El Lirio) treatments compared with control and PS plots.Total Cu is higher in PS (228 mg Cu kg^{-1} in El Gorguel; 164 mg Cu kg^{-1} in El Lirio) and control (226 mg Cu kg^{-1} in El Gorguel; 180 mg Cu kg^{-1} in El Lirio) plots than in other plots.

Total Pb in MW+PS treatment of El Gorguel (3740 mg Pb kg^{-1}) is lower than other treatments, while in El Lirio total Pb content in PS (6012 mg Pb kg^{-1}) is significantly higher than in other plots. Total Zn content shows a similar distribution in all plots of El Gorguel, while PS plot of El Lirio shows the lowest Zn content (3582 mg Zn kg^{-1}).

DTPA-extractable Cd contents in the PS treatments of both tailing ponds (2.4 mg Cd kg^{-1} in El Gorguel; 2.6 mg Cd kg^{-1} in El Lirio) are significantly lower than other treatments including control plots (3.1 mg Cd kg^{-1} in El Gorguel; 11.9 mg Cd kg^{-1} in El Lirio) (Table 4.2). While DTPA-Zn in amended plots (467 mg kg^{-1} in MW; 475 mg kg^{-1} in MW+PS; 466 mg kg^{-1} in PS) is significantly higher than in control of El Gorguel (Table 4.2), the opposite trend is observed in El Lirio as having a significantly higher content in Control plot when compared with amended plots (Figure 4.3).

DTPA-Cu content shows different behavior among tailing ponds. It varies with treatment and time for the El Gorguel (Figure 4.3), while the control has the highest (5.12 mg Cu kg^{-1}) content in the El Lirio (Table 4.2). DTPA-Pb content show lower values in 6 mo, and higher values in 12 mo, except 12 mo of MW+PS plot in El Lirio in MW and MW+PS plots from both ponds (Figure 4.3).

Water-extractable Cd in MW and MW+PS treatments are higher than control (Figure 4.4) after 12 mo, while the opposite behaviour is observed in the El Lirio (Table 4.2).

Water-extractable Cu shows different trends among ponds; in MW plot of the El Gorguel 0 and 0.25 mo are significantly higher than water-extractable Cu in other treatments and times of sampling (Figure 4.4), on the other hand in MW and MW+PS plots of El Lirio water-extractable Cu contents are significantly lower than PS and control (Table 4.2).

Water-extractable Pb in the period from 6 to 12 mo in the amended plots of the both tailing ponds decreases in contents in contrary to the control plots (Figure 4.4). In the El Lirio except for 0 mo, MW and MW+PS treatments have lower water-extractable Pb than control plot at various times of sampling (Figure 4.4). Water-extractable Zn in 12 mo in the amended plots of both ponds presents an opposite trend among tailings and treatments, while in MW and MW+PS plots the content of water-extractable Zn increases in the El Gorguel, in the same plots of the El Lirio decreases, but in PS plots it decreases in the El Gorguel while increases in the El Lirio (Figure 4.4). In the El Lirio at all sampling times amended plots have lower water-extractable Zn contents than control plot (Figure 4.4).

Table 4.2. Total, DTPA-extractable and water-extractable metals within a year since the application of treatments in the El Gorguel and El Lirio tailing ponds. Values are mean ±standard deviation (*n* = 20).

Treatments	Total Cd	Total Cu	Total Pb	Total Zn	DTPA Cd	DTPA Zn	DTPA Cu	Water-Extract Cd	Water-Extract Cu
					(mg kg^{-1})				
El Gorguel									
MW	29.6a[†] (1.4)	208a (8.0)	4373a (129)	11651a (187)	6.2c (0.49)	467a (18)	-	-	-
MW+PS	28.3a (1.09)	208a (6.3)	3740b (134)	11757a (241)	3.9b (0.19)	475a (18)	-	-	-
PS	26.6ab (1.03)	228b (6.4)	4326a (98)	10729a (771)	2.4a (0.21)	466a (18)	-	-	-
Control	24.1b (0.86)	226ab (7.5)	4402a (178)	11668a (273)	3.1ab (0.25)	429b (14)	-	-	-
El Lirio									
MW	48.5c[†] (3.09)	149a (6.3)	3613ab (196)	10933a (390)	9.2b (1.17)	-	1.81a (0.14)	0.96a (0.26)	0.05a (0.01)
MW+PS	40.0b (1.60)	148ab (5.6)	3268a (116)	10178a (424)	9.6b (1.06)	-	1.40a (0.10)	0.40a (0.09)	0.04a (0.001)
PS	13.0a (0.56)	164bc (4.8)	6012c (207)	3582b (234)	2.6a (0.44)	-	1.60a (0.20)	2.65b (0.40)	0.13b (0.02)
Control	17.6a (0.89)	180c (6.3)	4133b 214)	12285c (382)	11.9b (0.90)	-	5.12b (0.64)	7.70c (0.45)	0.11b (0.02)
Soil guidelines for maximum allowed concentration and local background of metals (mg kg^{-1})[‡]									
Spain	1-3	50-210	50-300	150-450					
Denmark	5	500	400	1000					
Netherlands	12	190	530	720					
Local Background	0.3	13	41	9					
Drinking water threshold values for select metals (μg L^{-1})[‡]									
USA	5	1300	15	5000					
WHO	3	2000	10	not avail					

[†] Within each tailing pond and column, means followed by similar letter are not significantly different, $p > 0.05$

- Not applicable, this metal exhibits treatment x time interaction, $p < 0.05$

[‡] Soil and water quality guidelines for select metals are adapted from Real Decreto, 1310/1990, Ministerial Decree (1999), Ministry of Housing (1994), Martínez and Pérez (2007), USEPA (2007), WHO (2011)

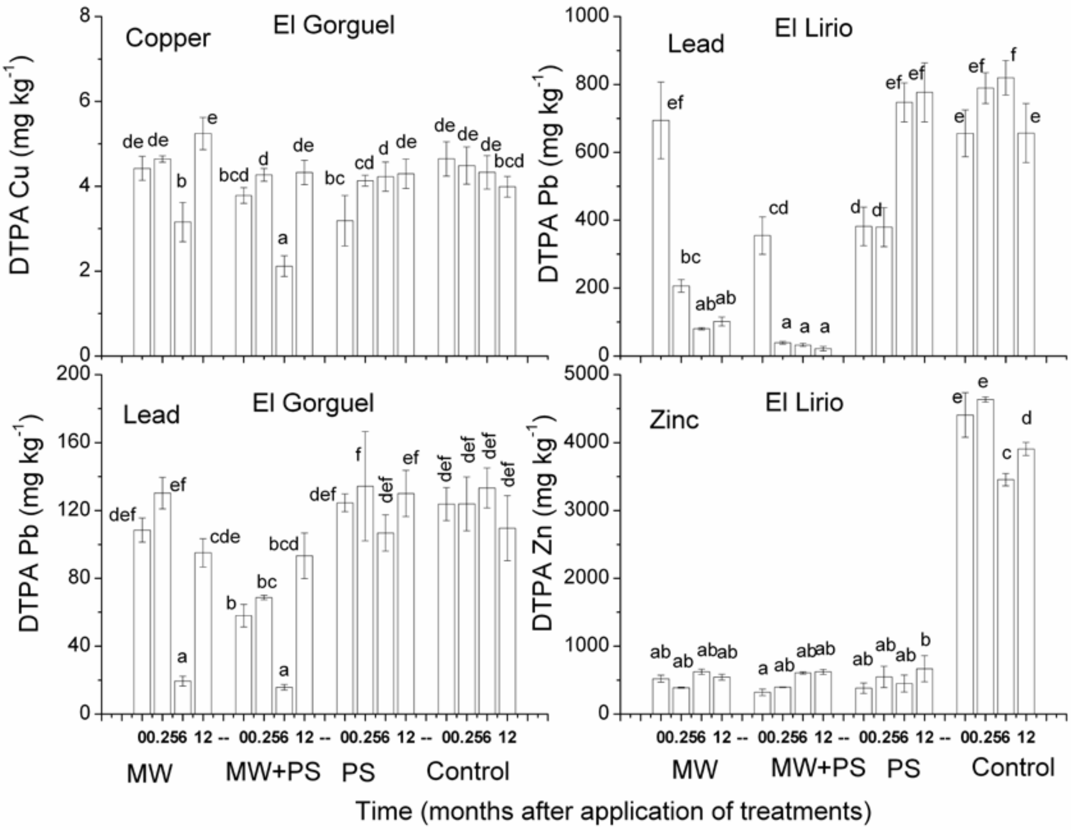


Figure 4.3. Means (and standard error) of DTPA-extractable metals showing significant changes with MW and PS amendments within a year since the application of treatments (i.e., treatment x time has $p < 0.05$) in the El Gorguel and El Lirio tailing ponds, $n = 5$.

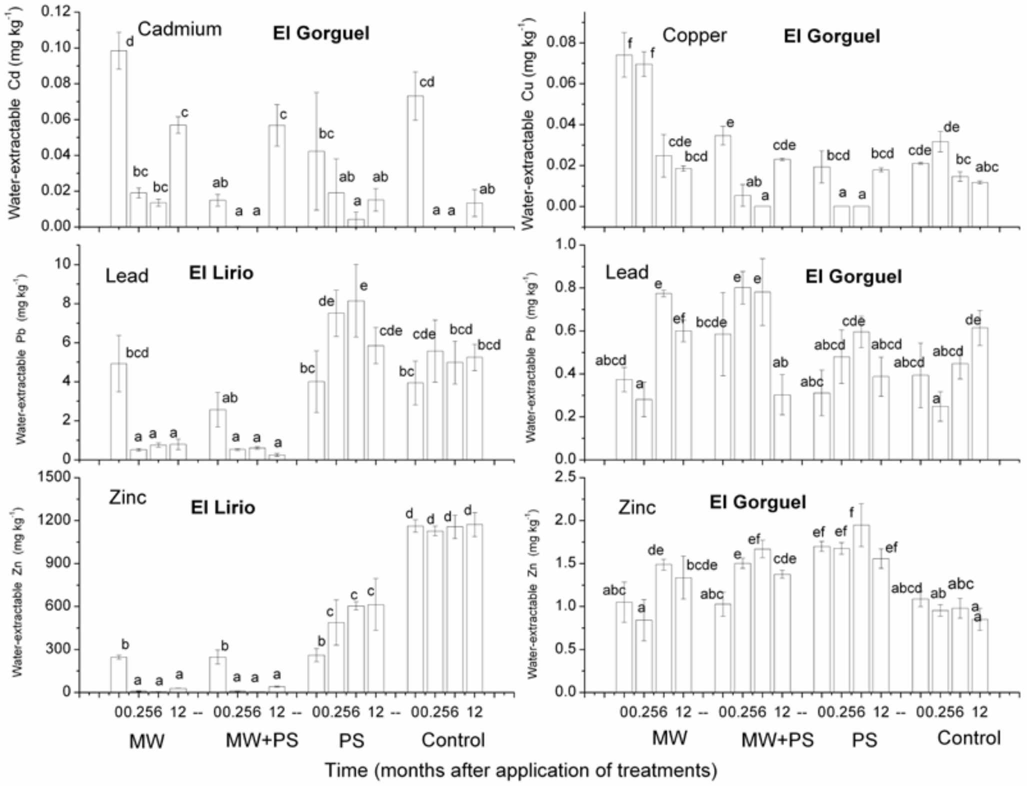


Figure 4.4. Means (and standard error) of water-extractable metals showing significant changes with MW and PS amendments within a year since the application of treatments (i.e., treatment x time has $p < 0.05$) in the El Gorguel and El Lirio tailing ponds, $n = 5$.

4.3.2. Soil pH and other plant-relevant properties

Plant-relevant properties of mine wastes that varied with treatments and times are summarized in Table 4.3 (El Gorguel) and Table 4.4 (El Lirio) while Table 4.5 reports improvements to other properties with treatments.

In the both tailings, pH in MW and MW+PS plots shows increases with time especially in the 6 mo of the applications when compared with their 0 mo. This trend is more prominent in El Lirio pond due to its initial low pH. Both control plots show the lowest pH values among all treatments (Tables 4.3 - 4.4). Electrical conductivity (EC) was highest (13.5 dS m^{-1}) after12 mo of MW application in El Gorguel. At 0 mo in MW plot in El Lirio has the highest EC (6.4 dS m^{-1}), while the rest of samples showed no significant differences (Tables 4.3 - 4.4). Total nitrogen in 6 mo of MW+PS plots of both tailings show the highest values (212 μg kg^{-1} in El Gorguel; 26.4 μg kg^{-1} in El Lirio) among all plots and times (Tables 4.3 - 4.4).

Table 4.3. Soil properties showing significant changes with MW and PS amendments within a year since the application of treatments in the El Gorguel tailing pond, Values are mean ±standard deviation (*n* = 5).

Treatments	Time	pH	EC (dS m^{-1})	Total N (µg kg^{-1})	Total C (mg kg^{-1})	Org C (mg kg^{-1})
MW	0	7.8c[†] (0.10)	7.6c (2.2)	50.3a (36.9)	16.4bcd (0.87)	13.2bc (0.06)
MW	0.25 mo	7.9cd (0.07)	5.6bc (1.1)	35.8a (4.9)	18.0cd (0.18)	11.0abc (0.60)
MW	6 mo	8.2d (0.02)	5.5bc (0.34)	0.00a	19.2d (0.36)	14.7c (0.58)
MW	12 mo	7.8c (0.05)	13.5c (1.6)	15.7a (6.56)	17.7bcd (0.59)	12.6bc (0.17)
MW+PS	0	7.9cd (0.03)	3.9ab (0.83)	1.7a (1.7)	17.4bcd (1.5)	14.3bc (0.03)
MW+PS	0.25	7.8c (0.03)	4.1ab (0.44)	180c (2.3)	16.8bcd (1.5)	12.1abc (0.67)
MW+PS	6 mo	8.1d (0.04)	3.2ab (0.17)	212c (59.0)	15.0bcd (1.6)	10.8abc (0.67)
MW+PS	12 mo	7.8c (0.04)	4.5ab (0.85)	150bc (33.5)	15.4bcd (2.2)	11.2abc (0.85)
PS	0	7.5b (0.18)	2.6ab (0.32)	3.5a (1.3)	14.4abc (3.7)	11.4abc (0.01)
PS	0.25 mo	7.7bc (0.07)	4.1ab (1.0)	114b (9.2)	13.8abc (1.2)	10.1ab (0.74)
PS	6 mo	7.6bc (0.09)	2.4a (0.15)	131bc (22.4)	13.7ab (2.0)	11.1abc (0.23)
PS	12 mo	7.8c (0.02)	2.5a (0.01)	55.7b (11)	18.7cd (1.2)	16.0c (0.14)
Control	0	7.6bc (0.12)	3.3ab (0.65)	0.00a	14.1abc (1.8)	11.0abc (0.03)
Control	0.25 mo	6.5a (0.09)	5.4bc (2.3)	31.2a (6.6)	10.6a (0.53)	8.2ab (0.29)
Control	6 mo	6.8b (0.03)	2.9ab (0.38)	16.8a (0.41)	11.6ab (0.66)	8.0ab (0.58)
Control	12 mo	7.7bc (0.11)	3.0ab (0.34)	21.9a (13.4)	10.4a (0.96)	7.8a (0.24)

[†] Within each column, means followed by similar letter are not significantly different, treatment x time $p > 0.05$

Table 4.4. Soil properties showing significant changes with MW and PS amendments within a year since the application of treatments in the El Lirio tailing pond, Values are mean ±standard deviation (*n* = 5).

Treatments	Time	pH	EC (dS m^{-1})	Eh (mV)	Total N (μg kg^{-1})	Total C (mg kg^{-1})	Org C (mg kg^{-1})
MW	0	5.5a[†] (0.44)	6.4c (1.1)	312c (12)	0.00a	2.4a (0.52)	2.1abc (0.33)
MW	0.25 mo	7.5b (0.12)	3.5ab (0.69)	241b (5)	0.00a	4.9bc (0.53)	2.2 abc (0.16)
MW	6 mo	7.7b (0.06)	2.9ab (0.49)	181a (14)	7.6ab (0.30)	5.3bc (0.39)	2.9c (0.37)
MW	12 mo	7.2b (0.26)	3.5ab (0.43)	182a (12)	5.6ab (1.75)	5.0bc (0.64)	2.8bc (0.20)
MW+PS	0	7.2b (0.24)	2.2a (0.25)	302c (6)	0.00a	3.5ab (0.41)	2.8bc (0.22)
MW+PS	0.25 mo	7.6b (0.13)	3.1ab (0.48)	241b (3)	16.9c (2.1)	5.8bc (0.48)	3.9c (0.34)
MW+PS	6 mo	7.8b (0.05)	2.6a (0.28)	141a (15)	26.4c (2.4)	5.9c (0.72)	3.8c (0.72)
MW+PS	12 mo	7.2b (0.16)	3.3ab (0.37)	211ab (20)	24.3c (5.6)	4.7b (0.68)	2.4 abc (0.20)
PS	0	5.0a (0.60)	2.5a (0.27)	405d (37)	0.00a	2.5a (0.24)	2.3 abc (0.12)
PS	0.25 mo	4.0a (0.20)	2.8ab (0.30)	408d (17)	24.3c (2.6)	2.6a (0.17)	2.6abc (0.17)
PS	6 mo	4.1a (0.15)	2.4a (0.13)	383d (17)	9.9b (2.3)	2.8a (0.09)	2.7bc (0.08)
PS	12 mo	3.6a (0.08)	3.2ab (0.25)	397d (26)	10.5b (1.2)	2.4a (0.08)	1.90a (0.09)
Control	0	5.3a (0.27)	3.8ab (0.53)	344cd (9)	0.00a	2.1a (0.17)	2.0ab (0.18)
Control	0.25 mo	5.0a (0.22)	4.2b (0.73)	336cd (15)	0.00a	1.8a (0.19)	1.7a (0.14)
Control	6 mo	5.2a (0.13)	4.6b (0.96)	264bc (11)	2.9a (0.19)	2.5a (0.21)	2.5 abc (0.21)
Control	12 mo	5.3a (0.31)	3.9ab (0.60)	234b (17)	3.2a (0.62)	2.6a (0.20)	2.1ab (0.19)

[†] Within each column, means followed by similar letter are not significantly different, treatment x time $p > 0.05$

Total carbon increased with the application of MW in the El Lirio. In addition, the TC content was statistically higher in the amendment plots with MW compared with control plot (Table 4.4). Application of pig slurry did not increase the TOC in MW+PS and PS plots from the El Gorguel, except in the PS 12 mo treatment, where TOC was statistically the highest (16.0 mg C kg^{-1}) (Table 4.3). In contrast, only MW+PS sampled at 0.25 and 6 mo showed an increase in TOC, being statically higher than TOCin other treatments (Table 4.4).

Table 4.5. Eh, Total Sulfur and Cation Exchange Capacity within a year since the application of treatments in the El Gorguel and El Lirio tailing ponds. Values are mean ±standard deviation (*n* = 20).

Treatments	Eh (mV)	TS (mg kg^{-1})	CEC (cmol(+) kg^{-1})
El Gorguel			
MW	163 ab[†] (7.3)	31 c (1.03)	6.7 b (0.38)
MW+PS	168 bc (8.2)	28 ab (0.84)	8.6 c (0.75)
PS	175 c (8.7)	26 a (1.12)	15.2 d (0.67)
Control	156 a (7.4)	30 bc (1.06)	4.8 a (0.30)
El Lirio			
MW	-	20 a (0.68)	14.1 a (0.81)
MW+PS	-	17 b (0.44)	15.2 a (0.37)
PS	-	20 a (0.70)	8.3 b (0.43)
Control	-	23 c[†] (0.79)	12.5 c (0.45)

TS: Total Sulfur

CEC: Cation Exchange Capacity

[†] - within each tailing pond and column, means followed by similar letter are not significantly different, $p > 0.05$

- not applicable, this property exhibits treatment x time interaction, $p < 0.05$

In the El Gorguel site, Eh, total sulphur and cation exchange capacity while the latter two properties in the El Lirio tailing pond vary with treatments but showed no interaction between MW and PS amendments within a year after application of treatment (Table 4.5).

The PS treatment has an Eh value of 175 mV and is higher than Control (156 mV) and total sulphur content (26 mg S kg^{-1}) lower than Control (30 mg S kg^{-1}) in the El Gorguel site (Table 4.5). In the El Lirio site, Control has the highest total sulphur at 23 mg S kg-1 compared to other treatments (17-20 mg S kg^{-1}). Cation exchange capacity (CEC) in the control plot at El Gorguel pond is lowest at 4.8 cmol$_+$ kg^{-1} compared to other treatments (6.7 – 15.2 cmol$_+$ kg^{-1}). In the El Lirio site, CEC (cmol$_+$ kg^{-1}) in the MW (14.1) and MW+PS (15.2) treatments are higher than in control (12.5) (Table 4.5).

Aggregate stability varies with treatments and times of sampling (Figure 4.5). In both El Gorguel and El Lirio sites, water stable aggregates in the MW, MW+PS and PS treatments at 6 and 12 mo are significantly higher than in control plots.

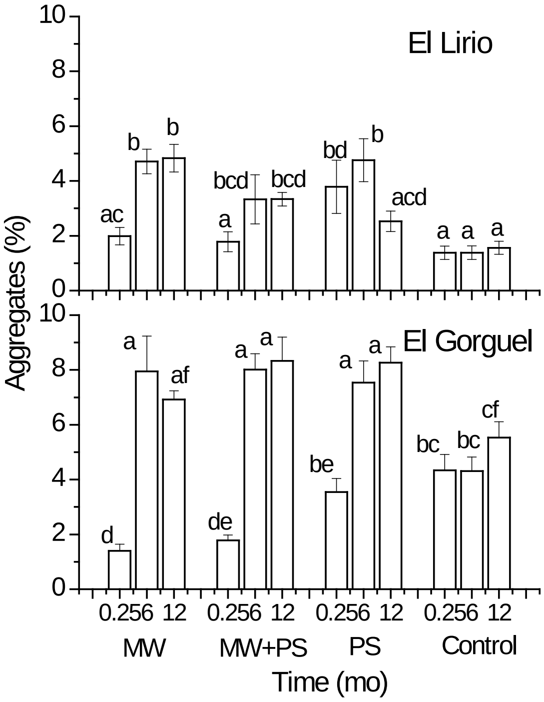


Figure 4.5. Means (and standard error) of aggregate stability with MW and PS amendments within a year since the application of treatments (i.e., treatment x time has $p < 0.05$) in the El Gorguel and El Lirio tailing ponds, *n* = 5.

4.4. Discussions

4.4.1. Total metal contents in tailing ponds

The total contents of Cd, Pb and Zn in the initial waste materials at the El Gorguel and El Lirio tailing ponds are above the environmental thresholds for soils in Spain, Denmark and the Netherlands (see Table 4.2). Currently, several local public organizations are working on tailing mine reclamation to develop legislations to mandatory establish vegetation on these tailing ponds to minimize potential environmental hazards (Conesa *et al.*, 2008b; Fundación Sierra Minera, 2007). Thus, results from this study may prove useful to the design of management plans for these tailing ponds and perhaps, in similar waste deposits in other parts of the world.

However, the high standard deviations of the total concentrations of metals in the El Gorguel and El Lirio (Table 4.1), showed the high variability of the total metals contents in these tailing ponds, which is due to the heterogeneous waste composition used in the formation of the ponds. These tailing ponds were formed from the waste generated from the extraction of metallic ores such as galena, sphalerite, carbonates, sulfates and lead- and zinc-bearing oxides (Oen *et al.*, 1975). During the extraction process, the wastes were dumped and created the various layers in the tailing ponds. Depending on the market demands, Pb, Zn or Fe were extracted in different periods creating different composition of the tailing ponds, e.g. when Zn was extracted Pb was left behind and consequently enriched in the waste deposits.

4.4.2. Environmental benefits of marble waste and pig slurry applications

Taking into account the inherent high variability of the total metals concentrations in the El Gorguel and El Lirio ponds (Table 4.1), we can affirm that the difference observed in total concentrations of metals between plots in both tailing ponds (Table 4.2) is not due to the effect of the amendments applications but to the variations in composition of the waste stored in the ponds. This is logical explanation because the concentration of metals in the amendments can only be expected to increase < 1 mg kg^{-1} of metals in the amended plots from MW and PS applications in both tailing ponds.

In addition, statistical analysis showed that there are no changes in the total concentration of any metal in the course of time (Table 4.2). However, the high pH (7.4) of waste materials in the El Gorguel might have prevented the dissolution of added $CaCO_3$ (or the MW), 9200 and 5200 kg of MW for MW+PS and MW plots respectively, and thus, the statistically insignificant decreases in total metals among various treatments might be partially due to dilution effect.

In the El Lirio site, the low pH (5.4) induces other processes such as partial dissolution of added $CaCO_3$ that may influence Zn and Cd retention/removal in waste materials (González-Alcaraz *et al.,* 2013), as Zn and Cd normally exhibit similar behaviour in the environment (e.g., Degryse *et al.*, 2009). At equilibrium, Zn, Cd, Pb and Cu often exhibits a “pH-dependent labile fraction” (Degryse *et al.*, 2009) – or simply more Zn, Cd, Pb and Cu ions are mobile and can be lost at low compared to high pH conditions. In contrast (e.g., El Gorguel), precipitation of metal-carbonates may have occurred at pH > 6.5 (Hamon *et al.*, 2002; Kumpiene *et al.*, 2008).

We argue that the significant increased in pH coupled with less concentration in total Zn, and to a limited extent total Pb, upon MW and PS+MW amendments led to much lower amounts of DTPA- and water-soluble Zn and Pb (except for 0 mo MW and MW+PS) than control in the El Lirio site. Hamon *et al.* (2002) attributed the decrease in concentration of Zn in solution as pH increases to the precipitation of $ZnCO_3$. However, the Zn and Pb sorption on organic matter (from PS addition) should not be ignored as metal solubility is influenced by pH, organic matter and total metal contents (McBride *et al.*, 1997). In addition, Zn removal from MW+PS plot may be partly due to Zn-organic chelate, where ligands are supplied by the PS treatment, although Zn normally forms weak bonds with SOM due to its electronic configuration (McBride *et al.*, 1997).

In contrast, contents of DTPA-Zn in the El Gorguel site did not vary with time after MW and PS amendments and are higher than control, perhaps due to high pH of the initial waste materials. Kabata-Pendias (2004) summarized that Zn (and Pb) have higher mobility at low pH compared to high pH. In addition, DTPA-Pb and water-extractable Pb in the El Gorguel site did not have well-defined changes with MW and PS amendments.

Effect of pH is also observed from the reduction in the bio-available and water-extractable Cd and Cu in the two tailing ponds. The concentration of DTPA-Cd in PS plot is 4X less compared to control plot in the El Lirio, while this reduction is not seen in the El Gorguel site (Table 4.2). In the MW treatment, DTPA-Cd is higher than control in the El Gorguel site. Similar trends are true for water-extractable Cd where consistent reductions compared to control are observed in the El Lirio site but not in the El Gorguel pond (Table 4.2 and Figure 4.4). Amounts of DTPA-Cu in the El Lirio site are significantly reduced by the MW and PS applications and in contrast with the El Gorguel site except for MW+PS 6 mo sample. Trends in water-extractable Cu are similar to DTPA-Cu for the two tailing ponds.

Although the water-soluble Zn and Pb are still above the US EPA (2007) 5 mg Zn L^{-1} and 15 μg Pb L^{-1} guidelines (see Table 4.2), the 4-fold reductions in bio-available (i.e., DTPA-Zn and Pb) and readily available (or water-soluble) Zn and Pb in the El

Lirio site constitute the most significant improvements to the environmental properties of mine wastes after MW and PS amendments. Similar argument can be extended for the reduction in water-extractable Cd due to MW and PS amendments in the El Lirio site. Understanding the bioavailability of trace metals (e.g., DTPA-Zn, Pb, Cd and Cu) is one of the major issues in environmental studies because “the risk to both the environment and human health of a given trace element is a function of its mobility and phytoavailability” (Kabata-Pendias, 2004).

4.4.3. Marble waste and pig slurry improve plant-relevant properties of mine wastes

Additions of PS to mine tailings increase total N in the two sites. In addition, MW increases soil pH in the El Lirio site. However, total N contents in the PS amended plots in the El Gorguel site, except for 0 mo, are much higher (56 – 212 μg N kg^{-1}) than similar plots in the El Lirio sites (9.9 – 26.4 μg N kg^{-1}). Carbonates that are initially present (high pH) likely initiated the more efficient build up of organic matter in the El Gorguel site than El Lirio. Application of PS did not increase TOC in the El Gorguel except for PS 12 mo plot, which can be due to the presence of vegetation in this plot one year after application (Kabas *et al.*, 2012). Only the content TC was increased in MW+PS 0.25 mo and 6 mo at the El Lirio, organic matter from PS amendments binds with calcium carbonates to form stable organic matter-calcite pedofeatures (e.g., organo-calcite infills and caps) as revealed by soil thin section analysis of tailings amended with MW and PS (Zanuzzi *et al.*, 2009a; Arocena *et al.*, 2012). Similar mechanisms might be responsible to higher total N in MW+PS than PS treatment in the El Lirio site.

The beneficial consequence of enhanced accumulation of total N (and organic matter) to plant growth is reflected in increased CEC upon MW and PS applications in the El Gorguel (6.7 – 15.2 cmol(+) kg^{-1}) and El Lirio (8.3 – 15.2 cmol(+) kg^{-1}) sites. The highest values of CEC in both ponds are related to the highest organic carbon contents in the PS plot for El Gorguel and MW+PS plot for El Lirio (Tables 4.3 and 4.4). Increased CEC is important because these exchange sites hold cations (e.g., Ca, Mg, K and Na) that are essential to plant growth (e.g., Brady and Weil, 2007) such as those pioneer species, some of which like *Piptatherum miliaceum* (L.) Cosson have potential to stabilize Pb in soils (Kabas *et al.*, 2012), observed in the study sites. The root systems of pioneer species are expected to continually add organic matter, thus increasing CEC and water holding storage capacity to render tailings materials suitable to growth of soil microorganisms especially in the rhizosphere zones (Arocena *et al.*, 2012). We also attributed the increases in aggregate stability to the cohesive forces resulting from the interactions between plants and organisms in root zone of pioneer species. Aggregate stability is considered a pathway for the stabilization of organic carbon in soil systems (Six *et al.*, 2004).

4.5. Conclusions

It is concluded that after one year since the applications of marble wastes and pig slurry, initial pH of tailing materials determines the improvement to the environmental properties in tailing ponds, significant reductions to the DTPA- and water-soluble Zn, Pb are limited to the El Lirio site only. Unlike in the El Gorguel site, water-extractable Cd and Cu and DPTA-Cu did not vary with treatment and times in the El Lirio site. However, pH seems to have a minor regulatory role with respect to changes to key plant-related properties of tailings, because most of the studied edaphic properties are affected by the treatment and time, except (TS and CEC), in both tailing ponds. Organic matter (total N and organic C), cation exchange capacity and aggregate stability are increased at both the El Gorguel and El Lirio sites. Use waste materials with high calcium carbonates (like marble waste) and sources of C and N (pig slurry) are beneficial to enhance the environmental and edaphic properties of tailing deposits.

CHAPTER 5

Effect of marble waste and pig slurry on the growth of native vegetation and heavy metal mobility in a mine tailing pond

Abstract

The effect of marble waste and pig slurry on the growth of native vegetation and heavy metal mobility in an abandoned Pb-Zn-Cd tailing pond (southeast Spain) has been investigated. Different treatments were carried out in four plots, (1) pig slurry, (2) marble waste, (3) marble waste + pig slurry, and (4) control. Plant cover, richness, biodiversity, metal in plant tissues, soil physicochemical properties and water and DTPA extractable metal concentrations of bare and rhizosphere soils were analyzed after one year from the application of the treatments. The pond materials contain large amounts of Fe-oxyhydroxides, sulphates, and heavy metals. Before the application of amendments, soil remained bare and organic matter content was very low. After applications, a native vegetation cover (25-30 %) with the highest biodiversity (H=1.1-1.3) and a richness of 10 was reached in the plots amended with pig slurry. The establishment and development of vegetation improved soil quality and decreased the metal availability, even more efficiently than the direct effect of the amendments. Among indigenous vegetation, *Piptatherum miliaceum* (L.) Cosson showed the characteristics of Pb phytostabilizer plant species. This study confirms the effectiveness of a vegetation cover for the persistence of the reclamation processes in bare mine soils under Mediterranean semiarid conditions.

5. 1. Introduction

The Cartagena-La Unión Mining District (SE Spain) constituted an important mining focus for more than 2500 years until its closure in 1991. Phoenicians, Carthaginians, Romans, Arabians, and Spaniards have been mining silver, lead, zinc, copper, tin, iron, and manganese in this district (Conesa and Faz, 2009; Faz *et al.*, 2001). Those mineral deposits were mined for profit, thus, overburden and waste materials (accumulated in tailing ponds) with their consequent environmental risks appear as the fundamental components in the post-mined landscapes (Acosta *et al.*, 2011; Collins, 2001). Tailing ponds contain materials rich in Fe-oxyhydroxides, sulphides, sulphates, and heavy metals (mainly Cd, Pb, and Zn). As a consequence, these soils remain bare and have low soil organic matter content (Acosta *et al.*, 2011; Conesa *et al.*, 2007a). Consequently, environmental risks, especially water and wind erosion and mobility of heavy metals in soil-plant systems stand out with propensity to adversely affect both human health and the functioning of ecosystems. Therefore, it is necessary to take action towards remediation of this contamination (Doumett *et al.*, 2008; Ji *et al.*, 2011).

While surface mining has relatively ancient origins, reclamation is a relatively recent phenomenon with a global concern about the potentially damaging effects which can originate with mining (Burley, 2001). In this recent phenomenon, phytoremediation takes its place as a newly emerged reclamation technique in the removal or stabilization of soil heavy metals by the usage of plants providing advantages in costing, in *in situ* applications and in environmental compatibility, among other expensive and often impractical techniques (Pérez-Esteban *et al.*, 2011; Sasmaz and Sasmaz, 2009). As a general rule, for creating a self sustaining landscape by the help of phytoremediation, native species which are appropriate to that specific condition are preferred to exotic plants, owing to their characteristics of preventing introduction of non-native and potentially invasive species that may result in decreasing regional plant diversity and endanger the harmony of the ecosystem (Kabas *et al.*, 2011; Lasat, 2000; Mendez and Maier, 2008). Restoration of this vegetation cover can fulfil the objectives of stabilization, pollution control, visual improvement and removal of threats to human beings (phytostabilization) (Wong, 2003). Also it is very effective in reducing surface erosion; it may return a large proportion of percolating water to the atmosphere through transpiration, thus decreasing the concentration of soluble heavy metals entering watercourses; and, therefore, minimising the visual scars in the landscape, so that successful revegetation may allow recreational use of the land (Tordoff *et al.,* 2000). Several studies about the use of metallophytes for revegetation of metal toxic mine wastes appear in the literature (Peters, 1984; Smith and Bradshaw, 1979; Wong, 2003). According to these studies, combination of metal-tolerant species with proper fertilizer applications and pH adjusters resulted in the successful and rapid revegetation of contaminated soils. However, plant accumulation of heavy metals in above-ground tissues can result in an increase of metal accumulation in topsoil, via leaf deposition, or can create an exposure pathway for metal introduction into the food chain (Mertens *et al.,* 2004; Unterbrunner *et al.,* 2007). Thus, in all reclamation plans, a thorough study of the interaction in the soil-plant system must be developed to be able to reduce environmental risks.

Several researches have carried out pilot experiments in pots or plots under laboratory and field conditions for the reclamation of these areas. In light of the recommendations from those previous studies (Conesa *et al.,* 2007a; Conesa and Faz, 2009; Ottenhof *et al.,* 2007; Zanuzzi *et al.,* 2009a), a large scale experiment was established in 2010 in which different amendments were applied in a bare tailing pond focusing on the heavy metals interactions between soil and indigenous plant cover. The objectives of this study can be summarized as to: 1) evaluate the evolution in vegetation cover, richness and biodiversity; 2) identify the most effective amendment for the reduction of the metal uptake by native plants; 3) identify the most suitable plant species for the reclamation of the study area, in terms of rhizospheric immobilization; and 4) evaluate the relationships between metal concentration in soil and plant tissues.

5. 2. Material and methods

5.2.1. Study area and experimental design

The study was conducted in El Gorguel tailing pond. Since getting the native vegetation growth substantially in El Gorguel tailing pond, investigation was directed and carried out in only El Gorguel pond. The pond was divided in four different field-scale plots (Figure 5.1). The initial characterization of the plots is given in Tables 5.1-5.2.

Two different amendments (pig slurry and marble waste ($CaCO_3$)) were used for reclamation purposes, in order to increase soil organic matter and soil nutrients, decrease heavy metals availability, ameliorate soil structure, and facilitate vegetation colonization. Each plot received a different treatment. The treatments were: marble waste (MW), pig slurry (PS), marble waste + pig slurry (MW+PS), and control (CT) (not receiving amendments). The pig slurry came from a pig farm in Pozo Estrecho (SE of Murcia), while marble waste (formed by particles of 5-10 µm diameters) was collected from quarries at the Cehegín area (NE of Murcia). The characteristics of soil amendments are given in Table 5.3.

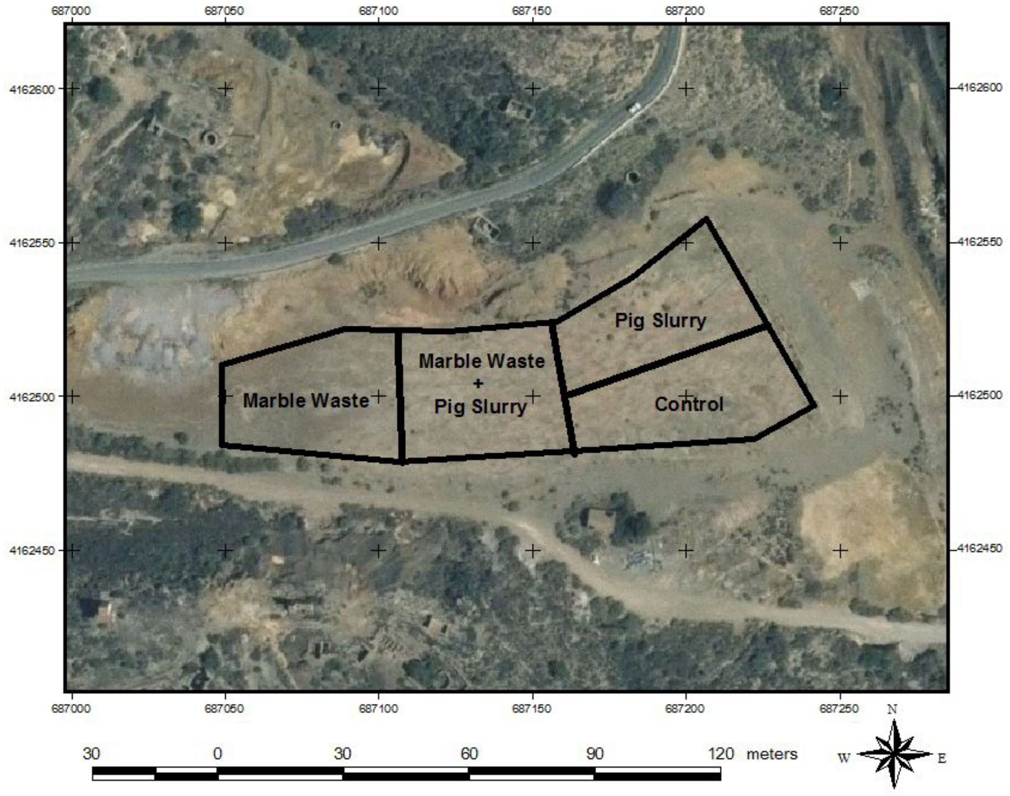


Figure 5.1. The scheme of four field-scale plots with different treatments.

The first activity was tilling the first 50 cm of the surface soil in order to prepare it for the application of the amendments (control plot was also tilled). Amendments were mechanically applied. In the MW+PS plots, first marble waste was added and afterwards it was followed by the application of the pig slurry. After the application of amendments, all materials were mixed in a 0-30 cm depth to incorporate the amendments into the soil. Application of amendments was carried out in September 2010.

Marble waste was applied at a rate of 4 kg m^{-2}. This dose was calculated using the method proposed by Sobek *et al.* (1978), which provides an indication for the quantity of lime required to neutralise all the potential acid according to the percentage of sulphides present in the mine soil. Dose for pig slurry was established by thresholds imposed by legislation regarding the addition of total nitrogen to soil to avoid contamination by nitrates (Council Directive 91/676/EEC). Pig slurry was applied at a rate of 30 m^3 ha^{-1}.

5.2.2. Sampling and analytical methods

Sampling was conducted after one year from the application of amendments. At each plot, five bare soil samples (0-30 cm) were collected. All plants species in the plots were identified (richness) and the vegetation cover was estimated by the percentage of the total plot surface covered by herbs, grasses and shrubs. The biodiversity was calculated with the Shannon-index H (Shannon, 1948):

$$H = -\sum_{i=1}^{R} pi \ln pi,$$

where pi is the relative abundance of each plant species in the total sum, and R is the richness. For the plant survey, a 2x2 m^2 five times randomly placed quadrat was used within each plot. Plant species were sampled according to their abundance and biomass: *Zigophyllum fabago* L. and *Salsola kali* L. in MW+PS, PS and CT plots, and *Atriplex halimus* L. and *Piptatherum miliaceum* (L.) Coss. in MW+PS and PS plots. Colonization was practically null in the MW treatment. Three plants (roots and shoots) of each species were taken along with its corresponding rhizospheric soil for each treatment.

Table 5.1. Main physicochemical characteristics of soils from plots before amendments addition. Values are mean ±standard deviation (n=5).

Treatment[a]	**pH**	**Eh**	**EC**[b]	**OC**[b]	**TN**[b]	**IC**[b]	**TS**[b]	**CEC**[b]	**Clay**	**Silt**	**Sand**
		mV	**dS m^{-1}**	**g kg^{-1}**	**g kg^{-1}**	**g kg^{-1}**	**g kg^{-1}**	**cmol$_c$ kg^{-1}**	**g kg^{-1}**	**g kg^{-1}**	**g kg^{-1}**
MW	7.8(0.2)	188(16)	7.6(0.8)	13.2(2.1)	BDL	3.23(0.14)	29.9(7.8)	16.9(5.3)	150(8)	350(12)	500(15)
MW+PS	7.9(0.1)	173(7)	3.8(0.8)	11.3(3.4)	BDL	3.06(0.06)	28.5(4.6)	8.4(4.6)	90(3)	370(10)	540(8)
PS	7.5(0.4)	193(19)	2.6(0.3)	11.4(3.3)	BDL	0.23(0.03)	26.0(7.3)	15.05(4.3)	70(4)	380(9)	550(12)
CT	7.6(0.3)	175(19)	3.3(0.6)	11.0(3.9)	BDL	0.92(0.08)	32.5(2.4)	4.7(0.6)	70(2)	310(12)	620(6)

[a] MW: marble waste; PS: pig slurry; CT: control

[b] EC: electrical conductivity; OC: organic carbon; TN: total nitrogen; IC: inorganic carbon; TS: total sulphur; CEC: cation exchange capacity

Table 5.2. Total metal, DTPA and water extractable metals concentrations (mg kg^{-}1) in soils from the plots before amendments addition. Values are mean ±standard deviation (n=5).

Treatment[a]	**Total Cd**	**Total Cu**	**Total Pb**	**Total Zn**	**Ext**[b] **Cd**	**Ext Cu**	**Ext Pb**	**Ext Zn**	**W**[c] **Cd**	**W Cu**	**W Pb**	**W Zn**
MW	24(9)	188(39)	5041(1870)	12619(2392)	6.05(2.25)	4.42(0.64)	38(28)	398(3)	0.10(0.01)	0.07(0.02)	0.37(0.13)	1.05(0.52)
MW+PS	32(5)	176(18)	3642(536)	12741(1484)	4.14(0.97)	3.78(0.42)	35(17)	402(10)	0.01(0.02)	0.03(0.01)	0.59(0.43)	1.03(0.31)
PS	26(8)	193(31)	4086(680)	10927(3521)	1.56(1.60)	3.19(1.32)	62(23)	402(27)	0.04(0.08)	0.02(0.02)	0.31(0.24)	1.70(0.05)
CT	33(7)	223(18)	4595(1002)	12405(1028)	3.56(1.23)	4.64(0.91)	52(19)	392(17)	0.07(0.14	0.02(0.0)	0.39(0.34)	1.09(0.23)

[a] MW: marble waste; PS: pig slurry; CT: control; [b] DTPA extractable; [c] Water extractable

Table 5.3. Main characteristics of the pig slurry (PS) and marble waste (MW) used.

Parameters	PS	MW
pH	7.8	8
Electrical conductivity (dS m^{-1})	39.1	2.2
Density (g ml^{-1})	1	-
$CaCO_3$ (%)	-	98
Moisture (%)	96	1
Total Nitrogen (g l^{-1})	5.1	-
NH_4^+-N (g l^{-1})	4.5	-
Total organic carbon (g l^{-1})	18.7	-
Cd (mg l^{-1} / mg kg^{-1})	BDL	0.05
Cu (mg l^{-1} / mg kg^{-1})	19.3	0.36
Zn (mg l^{-1} / mg kg^{-1})	28	0.26
Pb (mg l^{-1} / mg kg^{-1})	BDL	BDL
Chloride (mg l^{-1})	3129	-
Nitrate (mg l^{-1})	22	-
Phosphate (mg l^{-1})	623	-
Sulfate (mg l^{-1})	47.8	-
Calcium (mg l^{-1})	249	-
Magnesium (mg l^{-1})	14.4	-
Sodium (mg l^{-1})	459	-
Potassium (mg l^{1})	1059	-

BDL: below detection limit

The soil samples were taken to the lab, air-dried for seven days, passed through a 2 mm sieve and stored in plastic bags at room temperature before laboratory analysis. A split of each sample was ground using an agate mortar (RetschRM 100). Plant shoots and roots were carefully washed with deionised water, and then, dried at 55 ºC for 72 h. The dried material was ground using a mill (A11 Basic, IKA). For each sample, 0.7 g was incinerated prior to a metal redilution using 6M HNO_3. Plant extracts were stored at 4 ºC until analysed.

Soil pH and Eh were measured in deionised water (1:1 w/v) (Soil Survey Staff, 2004), while electrical conductivity (EC) was measured in deionised water (1:5 w/v) (Andrades, 1996). Total organic carbon (OC), inorganic carbon (IC), total nitrogen (TS) and total sulphur (TS) were determined by an elemental CHNS analyzer (EA-1108, Carlo Erba). The particle size distribution was determined using the Robinson pipette method combined with sieving. Cation exchange capacity (CEC) was measured following the method of Chapman (1965), replacing ammonium acetate by an unbuffered solution of 1M NH_4Cl (Merino *et al.*, 1998). For samples presenting carbonates, CEC was determined using $BaCl_2$ (Roig *et al.*, 1980). For total metals, soil was digested using $HNO_3/HClO_4$ at 210 ºC for 1.5 h (Risser and Baker, 1990). For soil bioavailable metals, DTPA was used in the ratio of 1:2 soil-extractant (Lindsay and Norwell, 1978). The water extractable metal fractions were determined using a 1:5 soil/MilliQ water mixture (Ernst, 1996). Measurements of metal concentrations in soil and plant extraction solutions were carried out using atomic absorption spectrophotometer (AAnalyst 800, Perkin Elmer). The methodology for total metals concentration was referenced using the Certified Reference Material BAM-U110 (Federal Institute for Materials Research and Testing, Germany).

In order to assess the efficiency of plants for phytostabilization, the bioaccumulation factor (BF) was also calculated as $[\text{metal}]_{\text{shoot}}/[\text{extractable metal}]_{\text{soil}}$ (Kumar *et al.*, 1995). Ideally this value would be <1, but it should not exceed a ratio of one, which would indicate that the plant is useful for phytoextraction (accumulation of metals in shoot tissue) but should not be used in phytostabilization (Brooks, 1998).

5.2.3. Statistical treatment

The fitting of the data to a normal distribution for all properties measured was checked with the Kolmogorov-Smirnov test. When necessary, analytical data were transformed using logarithms to assure normal distribution. The data was submitted to one-way ANOVA to assess the differences among treatments and plant species. The separation of means was made according to Tukey's verified significant difference at $P<0.05$. Relationships among properties were studied using Pearson correlations. Statistical analyses were performed with the software SPSS for Windows (Version 17.0).

5.3. Results and discussion

5.3.1. Colonization of spontaneous vegetation

Although the vegetation in the tailing pond was absent, a spontaneous plant colonization belong to the surrounding environment was derived from the application of amendments (Table 5.4).

The MW plot remained practically bare, with the presence of some sparse stems of *S. kali*. The only species able to be grown in the CT plot were *Zigophyllum fabago* and *Salsola kali*, while in the plots receiving the organic amendment a richness of 10 was reached, with higher vegetation cover (25-30 %) and biodiversity (H=1.1-1.3). The understanding of the processes implied in the primary vegetation succession initialized after colonizers establishment is crucial to avoid degradation processes. The fact that two plant species are capable of growing in the CT plot may indicate that these concrete species are resistant to high extractable metals concentrations and, therefore, the previous absence of them may be due to adverse physical conditions for vegetation establishment, as also previously reported by Zornoza *et al.* (2012). The initial tillage contributed to reduce compaction and bulk density, increasing porosity which triggered the germination of seeds and development of seedlings.

Table 5.4. Natural colonization of plant species on the different plots.

Treatment[a]	Richness	Cover (%)	Shannon Index (H)	Plant species
MW	1	0	0	*Salsola kali*
MW+PS	10	25	1.3	*Zigophyllum fabago, Piptatherum miliaceum, Beta vulgaris, Dittrichia viscosa, Atriplex halimus, Salsola kali, Chenopodium album, Sonchus tenerrimus, Chenopodium murale, Diplotaxis lagascana*
PS	10	30	1.1	*Zigophyllum fabago, Dittrichia viscosa, Sonchus tenerrimus, Piptatherum miliaceum, Diplotaxis lagascana, Atriplex halimus, Cakile maritima, Beta vulgaris, Hordeum murinum*
CT	2	5	0.5	*Zigophyllum fabago, Salsola kali*

[a] MW: marble waste; PS: pig slurry; CT: control

The application of pig slurry contributed to the improvement of soil fertility facilitating a higher colonization of natural vegetation. Before and after application of amendments, the development of plants in MW plot, when compared with other plots, was inhibited likely due to the presence of higher contents of salts and clay, as it can be inferred from Tables 5.1 and 5.5.

5.3.2. Effect of treatments and development of vegetation on soil properties and metals

Most of the soil physicochemical properties showed significant differences between bare and rhizospheric soil and among treatments ($P < 0.01$) (Table 5.5). The pH showed the significant lowest value in bare soil of CT plot, while the highest levels of pH were found in the MW amended plots. Eh in rhizospheric soils of MW+PS and PS plots was disposed to decline when compared to the other plots. Electrical conductivity (EC) was significantly highest ($P<0.01$) in the bare soil from MW (5.5 dS m $^{-1}$), while for the rest of samples there were no significant differences. Organic carbon (OC) was significantly higher in rhizospheric soils than in bare soils ($P<0.001$), without significant differences among species. In PS plot, rhizospheric soils showed a significant increment ($P<0.001$) in total nitrogen (TN) compared to the bare soil. Total sulphur (TS) was significantly lower ($P<0.001$) in rhizospheric soils than in bare soils, owing to its utilization by plants, mainly in the form of sulfates. While rhizospheric soils showed a significant increase in CEC in the PS plot, the opposite trend was observed in the MW+PS plot. With regards to particle size distribution, CT showed highest sand content, while MW plot showed the highest clay content, which is a consequence of the formation process of the tailing pond.

Table 5.5. Main physicochemical properties of control and amended plots for bare soil and rhizospheric soils of each sampled species. Values are mean ±standard deviation (*n* = 3).

Treatment[a]	Sample[b]		pH	Eh	EC[c]	OC[c]	TN[c]	IC[c]	TS[c]	CEC[c]	clay	silt	sand
				mV	dS m^{-1}	g kg^{-1}	g kg^{-1}	g kg^{-1}	g kg-^{1}	Cmol$_c$ kg^{-1}	g kg-^{1}	g kg-^{1}	g kg-^{1}
MW	Bare soil		8.2(0.1)c	158(17)c	5.5(0.7)b	13.6(1.4)a	BDL	4.5(1.3)	34.0(3.8)a	17.8(5.1)c	160(60)	370(160)	470(210)a
MW+PS	RS	*A.halimus*	7.5(0.2)b	108(9)a	3.3(1.2)a	15.5(4.3)b	0.06(0.01)abc	0.53(0.29)	25.5(3.5)b	6.8(2.2)ab	-	-	-
		P. miliaceum	7.5(0.3)b	113(10)ab	2.6(0.2)a	13.8(2.5)b	0.09(0.06)abc	0.49(0.21)	25.8(4.8)b	7.1(2.2)ab	-	-	-
		S. kali	7.6(0.1)b	111(26)a	2.6(0.1)a	15.9(0.9)b	0.12(0.06)abc	0.47(0.21)	26.7(3.7)b	6.7(1.4)a	-	-	-
		Z. fabago	7.7(0.2)b	113(15)ab	3.0(0.7)a	13.8(1.5)b	0.23(0.10)abc	0.42(0.16)	29.6(2.3)b	6.6(1.5)a	-	-	-
	Bare soil		8.1(0.1)bc	155(13)c	3.2(0.4)a	12.6(2.1)a	0.21(0.13)ab	4.22(1.49)	33.7(1.1)a	7.4(5.2)ab	80(30)	350(40)	570(10)ab
PS	RS	*A. halimus*	7.8(0.2)b	122(5)abc	3.4(1.1)a	17.7(4.0)b	0.31(0.21)bc	0.80(0.54)	24.4(3.5)b	18.3(4.7)c	-	-	-
		P. miliaceum	7.6(0.1)b	122(4)abc	2.6(0.1)a	14.8(2.4)b	0.30(0.01)bc	0.77(0.39)	25.5(1.4)b	16.2(4.2)bc	-	-	-
		S. kali	7.6(0.2)b	128(4)abc	2.9(0.6)a	22.1(9.1)b	0.34(0.05)bc	0.57(0.27)	23.3(3.7)b	16.7(1.8)bc	-	-	-
		Z. fabago	7.8(0.1)b	122(10)abc	3.6(0.3)a	15.2(6.4)b	0.34(0.08)c	0.63(0.41)	25.7(3.1)b	18.2(4.0)c	-	-	-
	Bare soil		7.6(0.2)b	153(23)bc	2.4(0.3)a	11.8(3.2)a	0.13(0.11)a	0.21(0.12)	28.5(1.9)a	15.2(2.9)bc	80(40)	370(160)	550(110)ab
CT	RS	*S. kali*	7.7(0.1)b	125(4)abc	2.6(0.2)a	23.5(6.2)b	0.06(0.02)ab	1.21(0.55)	25.1(1.9)b	7.6(1.5)ab	-	-	-
		Z. fabago	7.6(0.0)b	125(6)abc	2.6(0.3)a	19.4(5.1)b	0.08(0.04)abc	1.08(0.53)	24.7(2.5)b	6.7(0.3)a	-	-	-
	Bare soil		6.8(0.1)a	134(14)abc	2.5(0.5)a	16.6(3.4)a	0.17(0.09)ab	0.86(0.56)	31.1(5.5)a	7.0(4.2)ab	60(10)	290(160)	830(50)b
F-value[d]			14.45***	3.47**	6.71***	97.85***	22.5***	1.77 ns	222***	6.80***	1.44 ns	0.13 ns	4.83*

[a] MW: marble waste; PS: pig slurry; CT: control

[b] RS: rhizospheric soil

[c] EC: electrical conductivity; OC: organic carbon; TN: total nitrogen; IC: inorganic carbon; TS: total sulphur; CEC: cation exchange capacity

[d] Significant at: ***P*<0.01, ****P*<0.001; ns: not significant (*P*>0.05). Different letters indicate significant differences (*P*<0.05) among means in same column.

BDL= below detection limit

Thus, the application of marble mud led to an increase in soil pH. The additions of organic substances to soils which are poor in organic matter and the release of root exudates usually provoke decreases in Eh (Sudhalakhsmi *et al.,* 2007). Generally, the effect of organic amendments on soil OC is less clear. In the study area, despite the application of pig slurry, no increments were observed in OC because the organic carbon applied with the amendment was too low to be significantly detected (Tables 5.1and 5.5).

Contrary to what it is often observed for solid animal manure, application of liquid pig manure does not always increase soil C content (Angers *et al.,* 2010). The organic matter fraction of liquid pig manure is largely composed of rapidly decomposable organic C which may not significantly contribute to stabilize organic matter. Moreover, its high content in labile C and in available N and P could accelerate the decomposition of native soil C (Peu *et al.,* 2007; Rochette *et al.,* 2000). Nonetheless, it is important to highlight that increment in OC (and TN in PS plots) in rhizospheric soils owing to the release of root exudates can ameliorate soil structure and provide nutrients for microbial populations, being the base to guarantee the recovery of the ecosystem. An increment in soil organic matter content favours also an increase in soil CEC, a factor which may affect both soluble and exchangeable metal levels (Bulluck III *et al.,* 2002; Walker *et al.,* 2004). In the present study CEC was not affected by the plant species of each plot since bare soils and rhizospheric soils have similar values.

The total metals concentrations in the entire tailing pond before the application of the amendments were high, mainly for Pb and Zn (Table 5.2). One year after the application of the amendments the average concentrations of total metals did not change (30, 195, 4341 and 12173 mg kg^{-1} for Cd, Cu, Pb and Zn, respectively), as it was expected. The purpose of application of amendments and promotion of vegetation development is not to decontaminate the area, but to immobilize and retain soil metals, so that they are less available, and transfer by erosion or leaching is minimized.

Among treatments, in DTPA-extractable Cu and Pb, no significant shifts were detected owing to the high variability of data (Table 5.6). Nonetheless, the development of vegetation led to a slight decrease of DTPA-extractable Cd in rhizospheric soils compared to bare soils from all plots, although differences were not significant (Table 5.6). Oppositely, the concentration of DTPA-extractable Zn was slightly higher in rhizospheric soils in all treatments, being significant only in the rhizospheric soil of *S. kali* in PS plot (Table 5.6). Several studies have reported that plant presence can increase Zn mobility by forming soluble complexes with root exudates (Jacob and Otte, 2004; Wright and Otte, 1999), especially at neutral pH (Yin *et al.*, 2002).

Both the effects of amendments and development of vegetation significantly reduced the water extractable fraction of Cd, which was significantly highest in the bare soil from CT (Table 5.6). The development of vegetation also significantly reduced the concentration of water extractable Cu and Pb in the rhizospheric soils in all treatments ($P<0.001$). This reduction in metals availability was probably achieved by the effects of complexation by organic matter from pig slurry and the formation of insoluble carbonates from marble waste (Alvarenga *et al.*, 2008; Liu *et al.*, 2009). Walker *et al.* (2004) observed that the soil available concentrations of Cu and Zn decreased permitting the growth of *Chenopodium album* after the application of manure on contaminated soils. It is important to highlight that the effect of the presence of vegetation itself was higher on the reduction of Cd, Cu, and Pb availability than the direct effect of the application of PS and PS+MW. Vangronsveld *et al.* (1995), by reporting more than 85% of reduction in the amount of percolating Zn and Cd by the effect of vegetation in semi-field simulations of lixiviation, strengthens the idea of vegetation essentiality of contaminated soils to guarantee the stabilization of heavy metals in soils.

5.3.3. Metals accumulation in plant tissues

Cadmium, Pb, Cu, and Zn concentrations in shoots and roots of the dominant plant species in the different plots are shown in Table 5.7. Plants growing in MW+PS plot showed no accumulation of Cd, while some accumulation of this chemical element was observed only in shoots in PS and CT plots.

According to De la Rosa *et al.* (2004), *S. kali* is considered as a Cd hyperaccumulator species, contrary to the findings observed in this study where this species show low Cd accumulation. *Atriplex halimus* accumulated higher levels of Pb in shoots than in roots. The highest accumulation of Pb occurred in *P. miliaceum* roots, suggesting that below-ground parts of this species may accumulate great quantities of soil Pb (Garcia *et al.*, 2004). In this study, *P. miliaceum* accumulated 350 mg kg^{-1} of Pb in roots, being almost 18 times higher than Pb content in shoots in MW+PS plot, similar to values reported by Conesa *et al.* (2006) and Melendo *et al.* (2002) in mine soils from SE Spain. Thus, *P. miliaceum* seems to be a suitable species for the objectives of Pb phytostabilization.

Copper concentrations in *A. halimus* and *S.kali* were higher in shoots than in roots, being statistically significant in the amended plots ($P<0.001$). As a general trend, the highest accumulation of Cu was found in *A. halimus* and *Z. fabago* shoots, while the lowest accumulation was observed in *S. kali* roots. Regarding Zn, in PS plot shoot concentrations in *A. halimus*, *S.kali* and *Z. fabago* were significantly higher ($P<0.001$) than their concentration in roots, as previously reported by Conesa *et al.* (2007b). The highest accumulation of Zn occurred in *A. halimus* and *S. kali* shoots, while the lowest concentration was observed in *Z. fabago* roots. *Atriplex halimus* was able to accumulate up to 720 mg kg^{-1} of Zn in shoots when PS was applied. These values are higher than those reported by Lutts *et al.* (2004) in a hydroponic greenhouse study (440 mg kg^{-1}). Nonetheless, despite the high accumulation of Zn in the studied species, these levels are considered too low for making efficient phytoextraction according to the criteria proposed by Brooks (1998), who indicates that a plant is an efficient phytoextracter if it concentrates 100 times higher than in normal plants for each metal of interest.

Table 5.6. DTPA and water extractable metals in control and amended plots. Values are mean ±standard deviation (*n* = 3).

Treatment[a]	Sample[b]	Ext[c] Cd	Ext Cu	Ext Pb	Ext Zn	W[d] Cd	W Cu	W Pb	W Zn
		mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}
MW	Bare soil	7.38(2.34)b	3.16(1.04)	19.4(6.5)	543(18)a	0.06(0.02)a	0.10(0.05)a	1.19(0.42)	1.59(0.27)
MW+PS	RS *A.halimus*	3.09(1.57)a	4.16(1.66)	91.0(48.6)	619(145)ab	0.05(0.04)a	0.23(0.12)ab	BDL	1.37(1.04)
	P. miliaceum	3.02(0.64)a	3.54(0.53)	89.9(20.2)	676(89)ab	0.06(0.02)a	0.17(0.01)a	BDL	1.54(0.61)
	S. kali	2.48(0.72)a	3.51(1.14)	90.2(26.6)	630(102)ab	0.05(0.02)a	0.23(0.08)ab	BDL	1.63(0.80)
	Z. fabago	2.52(1.03)a	3.85(1.09)	72.8(56.9)	604(162)ab	0.05(0.02)a	0.21(0.06)ab	BDL	1.30(0.60)
	Bare soil	4.99(0.91)ab	2.12(0.55)	13.5(6.2)	574(24)ab	0.10(0.02)ab	0.39(0.02)bc	1.21(0.69)	1.83(0.24)
PS	RS *A. halimus*	3.24(0.46)a	4.36(0.13)	53.6(34.7)	704(100)ab	0.08(0.03)ab	0.21(0.04)ab	BDL	1.16(0.67)
	P. miliaceum	2.73(0.25)a	3.78(0.27)	56.5(21.1)	619(39)ab	0.08(0.01)ab	0.20(0.03)ab	BDL	1.50(0.44)
	S. kali	2.78(0.99)a	3.66(0.75)	48.2(39.4)	762(29)b	0.08(0.03)ab	0.20(0.03)a	BDL	1.40(0.21)
	Z. fabago	3.43(1.24)a	4.28(0.86)	38.5(3.9)	696(91)ab	0.10(0.02)ab	0.23(0.04)ab	BDL	1.24(0.36)
	Bare soil	3.93(1.60)ab	4.23(0.77)	48.5(39.8)	544(68)a	0.12(0.06)ab	0.42(0.03)c	1.00(0.46)	2.74(1.87)
CT	RS *S. kali*	2.78(0.85)a	4.47(1.03)	103.5(87.0)	677(42)ab	0.06(0.03)a	0.17(0.02)a	BDL	1.58(1.20)
	Z. fabago	2.41(0.59)a	4.02(0.60)	120.2(83.2)	666(76)ab	0.05(0.02)a	0.19(0.03)a	BDL	0.95(0.19)
	Bare soil	3.98(1.81)ab	4.33(0.88)	41.5(30.0)	502(56)a	0.15(0.03)b	0.44(0.01)c	0.64(0.45)	1.71(0.63)
F-value[e]		2.10*	1.76 ns	1.31 ns	2.55*	3.8**	16.21***	-	0.95 ns

[a] MW: marble waste; PS: pig slurry; CT: control

[b] RS: rhizospheric soil

[c] DTPA extractable

[d] Water extractable

[e] Significant at: **P*<0.05, ***P*<0.01, ****P*<0.001; ns: not significant (*P*>0.05). Different letters indicate significant differences (*P*<0.05) among means in same column.

BDL: below detection limit

Table 5.7. Metal concentrations in shoots and roots for the most dominant plant species in the different plots. Values are mean ± Standard Deviation (n=3).

Treatment[a]	Species		Cd	Pb	Cu	Zn
			mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}
MW+PS	*A. halimus*	Roots	BDL	22.6(3.9)ab	13.9(2.4)a	198 (13)ab
		Shoots	BDL	143.8(17.1)c	31.4 (1.9)c	520(84)bc
	P. miliaceum	Roots	BDL	350.4(48.7)c	16.1(6.0)ab	662(333)c
		Shoots	BDL	20.4(6.4)ab	19.7(1.3)abc	520(84)abc
	S. kali	Roots	BDL	43.7(17.9)bc	10,9(2.5)a	202(20)ab
		Shoots	BDL	51.5(9.0)bc	28.7(3.7)bc	507(50)bc
	Z. fabago	Roots	BDL	20.6(10.0)ab	11.8(0.26)a	116(18)a
		Shoots	BDL	BDL	24.1(2.5)abc	224(113)ab
PS	*A. halimus*	Roots	BDL	17.1(9.2)ab	19.4(1.3)ab	191(32)ab
		Shoots	2.83(2.51)	127.3(40.3)bc	36.3(2.9)c	720(153)c
	P. miliaceum	Roots	BDL	299.6(136.1)c	19.2(2.8)ab	381(102)bc
		Shoots	0.91(0.85)	BDL	22.2(4.8)bc	261(32)abc
	S. kali	Roots	BDL	18.3(11.1)ab	17.1(2.4)ab	178(25)a
		Shoots	3.75(2.31)	9.97(2.05)ab	32.5(2.2)c	792(316)c
	Z. fabago	Roots	BDL	23.1(21.4)ab	19.3(0.9)ab	136(30)a
		Shoots	1.34(1.07)	38.8(7.2)bc	31.1(5.8)c	490(98)bc
CT	*S. kali*	Roots	BDL	18.3(7.7)ab	14.9(6.5)ab	182(69)a
		Shoots	0.78(0.31)	10.0(7.1)a	22.2(2.7)abc	210(53)ab
	Z. fabago	Roots	BDL	23.8(3.7)ab	17.3(3.7)ab	105(19)a
		Shoots	3.89(2.80)	25.6(14.0)ab	29.9(7.3)bc	422(351)abc
F-value[b]			-	23.64***	12.39***	10.8***

[a] MW: marble waste; PS: pig slurry; CT: control

[b] Significant at ****P*<0.001. Different letters indicate significant differences (*P*<0.05) among means in same column.

BDL: below detection limit

The mobility of the heavy metals from the polluted substrate into the plant shoots was evaluated by means of the bioaccumulation factor (BF) (Figure 5.2). *Salsola kali* in PS plot was the unique species with BF > 1 (1.40) for Cd. Regarding Cu, all species showed BF > 1 (5.19-9.11), showing *A. halimus* and *S. kali* in MW+PS and PS plots the highest values. With regards to Pb, BF was < 1 in all cases except for *A. halimus* and *Z. fabago* in PS plot. No bioaccumulation was observed for Zn in any species. No correlation between soil properties (including total, DTPA-extractable and water extractable metals) and metals in any tested species was found. Thus, these concrete species show a range of different mechanisms for protecting themselves against uptake of toxic elements and for restricting their transport within the plant.

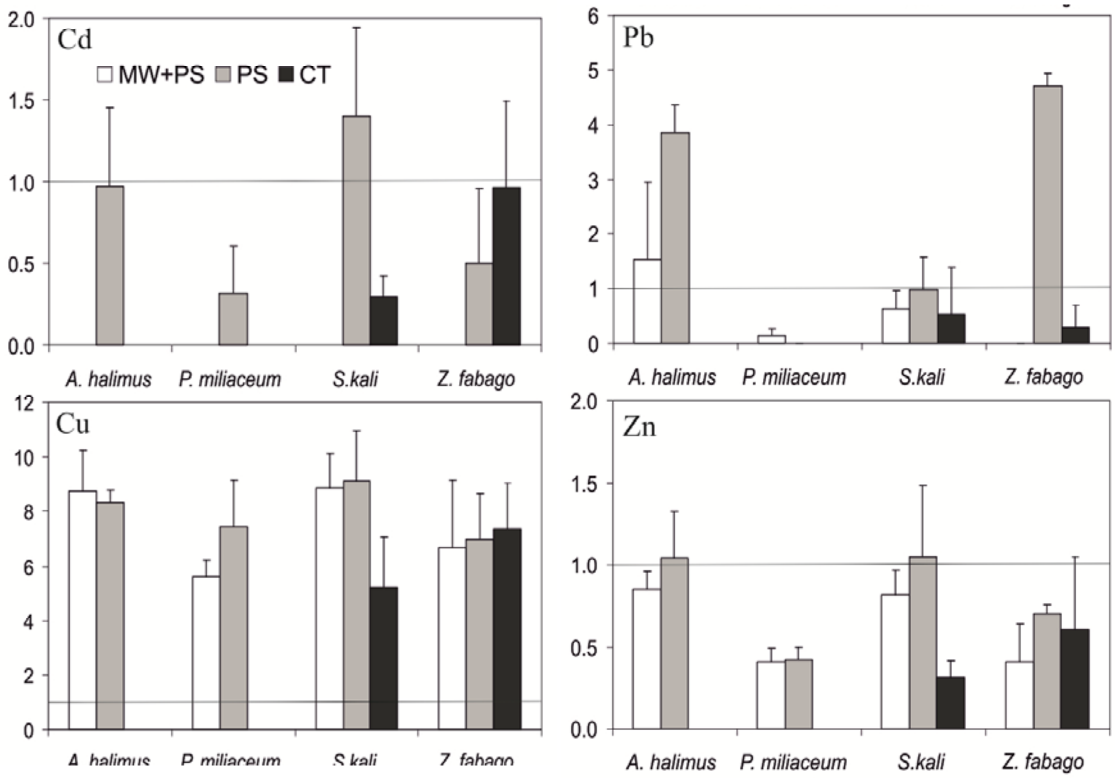


Figure 5.2. Bioaccumulation factor (BF = $[\text{metal}]_{\text{shoot}}/[\text{extractable metal}]_{\text{soil}}$) for the different studied plant species in each treatment. Error bars indicate standard deviation. Horizontal line indicates BF =1 (MW+PS: Marble Waste and Pig Slurry; PS: Pig Slurry; CT: Control).

In some cases, the application of PS increased the accumulation of metals in shoots, mainly for Pb, and Cd and Cu in *S. kali*. This may be due to the formation of soluble organic ligands with root exudates which would increase the uptake of these trace elements (Almas *et al.,* 1999). As a general pattern, the application of MW reduced the accumulation of metals in plant shoots. This may indicate that the formation of metal carbonates hinders the absorption of metals by plants.

Chemical elements shoot accumulation of candidate phytostabilization species should meet the US Domestic Animal Metal Toxicity Limits (10, 40, 100, and 500 mg kg^{-1}; for Cd, Cu, Pb, and Zn, respectively (Kabata Pendias and Pendias, 2001)) to prevent exposure to foraging animals (Mendez and Maier, 2008). In this respect, Pb shoot concentration in *A. halimus* (> 100 mg kg^{-1}) and Zn shoot concentrations in *A. halimus, P. miliaceum* and *S. kali* (> 500 mg kg^{-1}) stand out and have to be handled carefully in the toxicity context, avoiding the entrance of foraging animals while the reclamation techniques are still under process. In addition, *S. kali* shows a peculiarity in the dispersion of seeds, since when the plant has concluded its biological cycle, shoots come off with wind, rolling on the soil and releasing the seeds. This means that there is a direct transfer of metal-enriched biomass from the contaminated area to the surroundings. Thus, actions should be carried out to remove the plants before their dispersion.

5.4. Conclusions

The applications of marble waste + pig slurry (MW+PS) and pig slurry (PS) were effective in the growth of native vegetation, increment of vegetation cover, richness and biodiversity, and in the reduction of heavy metals mobility in the tailing pond. Triggered plant growth by the effect of amendments improved soil conditions, particularly by the help of the medium created by their rhizosphere systems. Increments in OC and TN content, and decreases in the available metals fraction concentration were observed in rhizospheric soils when compared to the bare soils.

As a general trend, in some cases, the application of PS increased the accumulation of metals in shoots, whereas the application of PS together with MW reduced this accumulation. According to the collected data, *P. miliaceum* showed the characteristics of Pb phytostabilizer species. Even though *A. halimus* and *Z. fabago* made phytoextraction of Cu-Pb, they did not show the characteristics of hyperaccumulator species. Nonetheless, a monitoring of the evolution of plants with time and the heavy metal dynamics is needed to establish a better selection of the most adequate species to develop a phytostabilization program.

CHAPTER 6

Syrian Bean-caper (*Zygophyllum fabago* L.) Improves Organic Matter and Other Properties of Mine Wastes Deposits

Abstract

The omni-presence of *Zygophyllum fabago* L. (Syrian bean-caper) natural colonies in post mining areas prompted us to investigate its contributions to reclamation of mine wastes deposits in southeast Spain. Select plant-related (edaphic) characteristics and bio- and water soluble-Cd, Cu, Pb and Zn in rhizosphere of *Z. fabago* were compared to deposits one year since application of pig slurry and marble waste. Total N in rhizosphere increased up to a factor of 20X (339 vs 17 mg N kg^{-1}) in El Gorguel and 27X (85 vs 3.1 mg N kg^{-1}) in El Lirio sites. Organic matter accumulation in rhizosphere from litter and roots of *Z. fabago* increased organic C from 6.6 to 19.5 g kg^{-1} in El Gorguel and from 2.1 to 5.7 g kg^{-1} in El Lirio in one year. Dissolution of inorganic C takes place due to organic acids from root exudates of *Z. fabago*. Reduction in bio-available Cd, Cu, Pb and Zn in rhizosphere of *Z. fabago* at El Lirio is attributed to increase in pH from 5.3 to 7.7 through marble waste addition, although increased cation exchange capacity may also have played a role. Addition of marble waste to encourage colonization by *Z. fabago* in acidic mine wastes deposits was recommended.

6.1. Introduction

Syrian bean-caper (*Zygophyllum fabago* L.) is a perennial plant species with long thin stems, ovate succulent 2 to 3 cm waxy green leaflets and is a member of the *Zygophyllaceae* family, many of which are adapted to dry and salt-affected environments in tropical and sub-tropical areas in central Asia, Africa, Australia, Middle East, South America, Mexico, and USA (Heywood, 1993; Beier *et al.*, 2003). *Z. fabago* is resistant to drought because of its waxy leaves (Roche, 1991) and can tolerate high concentrations of Cd (up to 10 µmol·Cd L^{-1}), due to its ability to regulate translocation of Cd from roots to shoots (Lefèvre *et al.,* 2005). Xylem loading and transpiration rate control the amount of metals in the leaf cell regardless of the ability of cells to cope with high concentrations of metals (Lefèvre *et al.,* 2010).

The adaptability to limited water supply and high metal contents may explain the colonization and survival of *Z. fabago* in several mine sites in highly saline semi-arid areas in southeast Spain (Conesa *et al.,* 2006; Conesa *et al.*, 2007b; Zanuzzi *et al.*, 2009a; Lefèvre *et al.,* 2010; Martínez-Sánchez *et al.*, 2012). Resistance to drought is also implicated as one possible mechanism to high tolerance for Cd by *Z. fabago* (Lefèvre *et al.*, 2005). Similarly, arid lands with neutral pH around previous Pb and Zn mine sites in Iran are naturally-colonized by *Z. fabago* containing higher Pb, Zn and without any symptoms of metal toxicity than other plant species in the area (Boorjar and Tavakkoli, 2011). The high tolerance for metals and survival under the conditions of low water amount makes *Z. fabago* a good candidate species for the reclamation of mine wastes sites (Lefèvre *et al.,* 2005; Conesa *et al.,* 2007b; Boorjar and Tavakkoli, 2011).

Z. fabago has always been one of the pioneer species that is observed in several mine sites in SE Spain. Isolated patches of *Z. fabago* along the edges of acidic (pH ~ 2.8) mine wastes was reported by Zanuzzi *et al.* (2009a) while natural colonization by *Z. fabago* in all mine wastes plots with slightly alkaline pH (pH 7-8) subjected additions of pig manure and marble wastes was reported by Zornoza *et al.* (2012) . In other mine areas in SE Spain, *Z. fabago* was the only vegetation observed in sites with neutral pH as well as in mine areas with acidic pH (Conesa *et al.,* 2007c). The omni-presence of *Z. fabago* in many areas affected by mining activities in SE Spain prompted us to evaluate the contribution of this pioneer plant species to the improvement of mine tailing properties for both vegetation (or edaphic) and environmental purposes (e.g., metal retention and leaching). Although the latter has been the subject of previous studies (e.g. Conesa *et al.,* 2006; 2007b; b; Lefevre *et al.,* 2010), the influence of *Z. fabago* on the edaphic (or establishment of vegetation) properties such as pH, total nitrogen, cation exchange capacity of tailing deposits is hardly ever discussed until now.

The objective of this study was to make contribution to the knowledge related to the role of *Z. fabago* to understand the challenges associated with vegetation establishment in unproductive deposits of mine wastes. The improvement was quantified to select edaphic characteristics by comparison of properties in mine wastes deposits to rhizosphere materials influenced by the growth of *Z. fabago* in experimental plots subjected to pig manure and marble wastes amendments in SE Spain. Changes to bio-available and water-soluble metals were also investigated. The results will be useful for the establishment of ecosystem functions in otherwise unproductive deposits of mine wastes using aggressive endemic pioneer plant species such as *Z. fabago*.

6.2. Materials and Methods

6.2.1. Field experiments

A field experiment comprising plots amended with marble wastes (MW) and pig slurry (PS) were conducted in El Gorguel (pH 7.7) and El Lirio (pH 5.3) mine wastes deposits. The 5-10 µm-sized MW was acquired from Cehegín area (NE Murcia) quarry and contains 98% $CaCO_3$ while the PS came from a pig farm in Pozo Estrecho (SE Murcia) with a pH of 7.8 and is a good source of SOM with 5.1 g total N L^{-1} and 18.7 g organic C L^{-1}.

The experimental treatments were Control (0 MW+0 PS), MW (4 kg MW m^{-2}), PS (30 m^3 PS ha^{-1}) and MW+PS (4 kg MW m^{-2} + 30 m^3 PS ha^{-1}) and randomly assigned to experimental plots ranging between 1,300 and 2,300 m^2 at El Gorguel and from 3,500 to 3,750 m^2 at El Lirio sites. The amount of PS addition was calculated based on maximum N addition to avoid nitrate leaching to groundwater (Council Directive 91/676/EEC). The MW added was the amount of $CaCO_3$ needed to neutralise acidity based on sulphide contents of mine wastes deposits (Sobek *et al.,* 1978). Experimental plots were left un-vegetated to encourage natural colonization by *Z. fabago* and other pioneer plant species. Other details of the experiments are reported elsewhere (Kabas *et al.*, 2012).

6.2.2. Collection and analyses of waste deposits and rhizosphere materials

After one year since the applications of amendments, samples of bare waste and rhizosphere (or waste materials influenced by root growth) soils were collected solely from experimental plots colonized by *Z. fabago* to estimate the changes to properties of waste materials. We also collected samples from control plots.

Five samples from 0-30 cm depth were randomly collected from every experimental plots colonized by *Z. fabago*. A rhizosphere sample constitutes any materials that were clinging to the roots of *Z. fabago*. In El Lirio site, samples were only collected from MW, MW+PS and control plots because *Z, fabago* did not grow in the PS plot; while MW+PS, PS and control treatments were sampled in El Gorguel tailing pond, because of *Z. fabago* was not able to grow in MW plot. Control treatment in El Gorguel recruited *Z. fabago* but not the Control plot in El Lirio. Samples of waste and rhizosphere materials were air-dried, sieved through a 2-mm sieve and stored in plastic bags at room temperature for laboratory analyses.

Eh and pH were determined using de-ionised water at 1:1 w/v following Soil Survey Staff (2004), electrical conductivity (EC) in de-ionised water at 1:5 w/v (Andrades, 1996), total organic C, inorganic C, total nitrogen (TN) and total sulphur (TS) using a Carlo Erba model EA-1108 CHNS elemental analyzer. The cation exchange capacity (CEC) of waste materials with no carbonates was determined using unbuffered solution of 1M NH_4Cl (Merino *et al.*, 1998) while CEC of samples with carbonates was estimated using the $BaCl_2$ method (Roig *et al.*, 1980).

Total metal contents were estimated from digest obtained from $HNO_3/HClO_4$ mixture at 210 ºC for 1.5 h (Risser and Baker, 1990). We estimated the amounts of bio-available metals using the diethylene triamine pentaacetic acid (DTPA) method (Lindsay and Norwell, 1978) while the water soluble metals were determined in a 1:5 materials to MilliQ water mixture (Ernst, 1996). Metal concentrations in extracts and digests were estimated using a Perkin Elmer AAnalyst 800 atomic absorption spectrophotometer. The QA/QC materials used throughout the analysis was the

Certified Reference Material BAM-U110 (Federal Institute for Materials Research and Testing, Germany).

6.2.3. Statistical analyses

The changes in properties of mine wastes due to natural colonization by *Z. fabago* were separately evaluated for El Gorguel and El Lirio sites, because of differences in pH (i.e., pH 7.7 and 5.3 for El Gorguel and El Lirio sites, respectively). We used two techniques of analysis of variance (ANOVA) to analyze data set. A two-factor (i.e., amendments – Control, MW, PS amendments, and types of materials – rhizosphere, bare soil and waste materials) ANOVA was conducted to determine any interactions between amendments and types of materials to alter the properties of mine wastes (Tables 6.2, 6.4 and 6.6). For variables with no interaction effects, a one-way ANOVA was used to compare the properties of bare soil, rhizosphere soil and waste materials from control plots one year after the applications of PS and MW amendments (Tables 6.3, 6.5, 6.7 and 6.8). We used the Fisher LSD test to compare means of significantly different treatments. All statistical analyses were conducted using Statistica version 10 (StatSoft Inc., 2011).

6.3. Results

6.3.1. Natural colonization by *Z. fabago*

Mine wastes amended with MW and PS recruited a total of 13 pioneer plant species in El Gorguel and El Lirio sites (Table 6.1). El Gorguel site (12 species) had more diversity of plant species than El Lirio (3 species).

In El Gorguel, 2 plant species were observed at the control plots and 10 pioneer species in both the PS and MW+PS plots. *Z. fabago* was present in all plots colonized by pioneer species and had the largest area colonized with estimated area coverage (%) as follows: Control – 4.2 % (8-15 plants per plot), PS – 20 % (9-36 plants per plot) and MW+PS – 10.1 % (1-19 plants per plot).

In El Lirio site, the three pioneer species observed were *Z. fabago, Piptatherum miliaceum* and *Pinus halepensis* (Table 6.1). At least one *Z. fabago* plant was reported in plots colonized by pioneer species and the largest area covered was estimated at 14.6 % (15-45 plants per plot) in the MW+PS plots in El Lirio site.

Table 6.1. Species, number of plants per plot and mean area coverage for pioneer plants that colonized the experimental plots at El Gorguel and El Lirio tailing ponds amended with pig slurry (**PS**) and marble wastes (**MW**), number in parenthesis represents standard deviation.

EL GORGUEL	**MW+PS**		**PS**		**Control**	
	Plants per Plot	Coverage (SD)	Plants per Plot	Coverage (SD)	Plants per Plot	Coverage (SD)
	(number)	(% Area)	(number)	(% Area)	(number)	(% Area)
Atriplex halimus	1-4	2.0 (2.8)	0-2	0.9 (1.5)	0	0
Zygophyllum fabago	**1-19**	**10.1 (10.3)**	**9-36**	**20 (10.4)**	**8-15**	**4.2 (3.8)**
Salsola kali	0-5	1.2 (1.2)	1-2	0.9 (0.9)	1-6	1.1 (0.9)
Chenopodium album	1-3	1.5 (1.1)	0	0	0	0
Beta vulgaris	0-20	3.1 (5.4)	0-2	0.6 (1.0)	0	0
Diplotaxis lagascana	0-1	0.2 (0.3)	0-2	1.5 (1.4)	0	0
Piptatherum miliaceum	0-27	4.2 (7.3)	0-4	1.6 (1.8)	0	0
Dittrichia viscose	0-8	1.6 (1.7)	0-17	5 (8.7)	0	0
Sonchus tenerrimus	0-5	0.9 (1.3)	0-5	1.8 (2.3)	0	0
Chenopodium murale	0-1	0.2 (0.3)	0	0	0	0
Cakile maritima	0	0	0-1	0.7 (0.7)	0	0
Hordeum murinum	0	0	0-1	0.3 (0.5)	0	0
EL LIRIO	**MW+PS**		**MW**		**Control**	
	Plants per Plot	Coverage (SD)	Plants per Plot	Coverage (SD)	Plants per Plot	Coverage (SD)
	(number)	(% Area)	(number)	(% Area)	(number)	(% Area)
Zygophyllum fabago	**15-45**	**14.6 (6.9)**	**0-112**	**3.3 (2.9)**	**0-1**	**0 (0)**
Piptatherum miliaceum	3-17	5.0 (3.3)	0-4	1.6 (1.8)	0	0
Pinus halepensis	0-1	0.2 (0.4)	0-1	0.7 (0.7)	0	0

6.3.2. Plant-related properties of mine wastes

In El Gorguel site, total nitrogen (TN), total carbon (TC) and organic carbon (OC) were affected by interactions between treatments and types of materials (Table 6.2). Rhizosphere soils under PS treatment recorded the highest total N (339 mg N kg^{-1} soil) with bare wastes in Control plots containing the least total N (17 mg N kg^{-1} soil). Only the bare wastes and rhizopshere soils in control plot were significantly different with respect to TN and OC contents.

Properties that were not affected by the interactions between treatments and materials in El Gorguel site include pH, EC, Eh and total S and showed no significant differences between rhizosphere, bare wastes and control (Table 6.3). Inorganic C at 3.5 g C kg^{-1} in bare waste was the highest amount compared to rhizosphere soil and Control. Control had the least CEC (7.0 $cmol_+$ kg^{-1}). In El Lirio site, the CEC is the only property influenced by the interaction between treatments and types of materials (Table 6.4). Estimates of CEC in the rhizosphere and bare wastes in MW and PS amended plots ranged approximately for more than double compared to the control plot and recorded as 7.6 $cmol_+$ kg^{-1}.

Table 6.2. Mean and (standard error) of plant-related properties affected by significant interaction between treatments and rhizosphere of *Z. fabago* and bare mine wastes one year since the applications of pig slurry (PS) and marble wastes (MW) in the El Gorguel site, n = number of observations.

Treatment	Materials	n	Total Nitrogen (mg kg^{-1})	Total Carbon (g kg^{-1})	Organic Carbon (g kg^{-1})
MW+PS	Bare wastes	5	210 (13) a†	16.8 (1.82) ab	12.6 (2.10) b
MW+PS	Rhizosphere	3	230 (10) a	15.2 (2.35) ab	13.8 (1.51) ab
PS	Bare wastes	5	130 (8) a	12.0 (1.82) b	11.8 (3.22) b
PS	Rhizosphere	3	339 (42) c	15.8 (2.35) ab	15.2 (2.02) ab
Control	Bare wastes	5	17 (9) b	7.46 (1.82) b	6.6 (3.43) c
Control	Rhizosphere	3	81 (41) ab	20.5 (2.35) a	19.5 (2.02) a

† - within each column, means followed by similar letter are not significantly different ($p > 0.05$) using the Fisher LSD test

Plant-related properties not affected by the interactions were pH, EC, Eh, organic C, total N, total S, total C and inorganic C (Table 6.5). pH in bare wastes and rhizosphere soil were significantly higher that pH (5.3) observed in the control materials, while EC and total S did not significantly vary among types of materials. Eh was significantly lower in rhizosphere soils at 136 mV compared to bare wastes and control materials.

Table 6.3. Mean and (standard error) of plant-related properties in rhizosphere of *Z. fabago* and bare mine wastes one year since the applications of pig slurry (PS) and marble wastes (MW) in the El Gorguel site, n = number of observations.

Materials	n	pH	EC ($dS\ m^{-1}$)	Eh (mV)	Total Sulfur ($g\ kg^{-1}$)	Inorganic C ($g\ kg^{-1}$)	CEC ($cmol_{+}\ kg^{-1}$)
Bare wastes	10	7.8	3.5	130	24.5	3.50 a[†]	13.0 b
		(0.1)	(0.4)	(5)	(1.5)	(0.33)	(1.5)
Rhizosphere	9	7.7	3.1	120	27.1	0.71 b	10.5 ab
		(0.1)	(0.4)	(5)	(1.6)	(0.35)	(1.6)
Control	5	6.8	2.5	134	31.1	0.86 b	7.0 a
		(0.1)	(0.5)	(14)	(5.5)	(0.56)	(4.2)

[†] - within each column, means followed by similar letter are not significantly different ($p > 0.05$) using the Fisher LSD test

Table 6.4. Mean and (standard error) of cation exchange capacity as affected by significant interaction between treatments and rhizosphere of *Z. fabago* and bare mine wastes one year since the applications of pig slurry (PS) and marble wastes (MW) in the El Lirio site, n = number of observations.

Treatment	Materials	n	Cation Exchange Capacity ($cmol_{+}\ kg^{-1}$)
MW+PS	Bare wastes	5	13.0 (1.03) ab[†]
MW+PS	Rhizosphere	3	17.8 (1.33) a
MW	Bare wastes	4	14.2 (1.16) a
MW	Rhizosphere	3	11.4 (1.34) b
Control	Bare wastes	5	7.6 (1.03) c

[†] - means followed by similar letter are not significantly different ($p > 0.05$) using the Fisher LSD test

Table 6.5. Mean and (standard error) of plant-related properties in rhizosphere of *Z. fabago* and bare mine wastes one year since the applications of pig slurry (PS) and marble wastes (MW) in the El Lirio site, *n* = number of observations

Materials	*n*	pH	EC (dS m^{-1})	Eh (mV)	Organic Carbon (g kg^{-1})	Total Nitrogen (mg kg^{-1})	Total Sulfur (g kg^{-1})	Total Carbon (g kg^{-1})	Inorganic Carbon (g kg^{-1})
Bare wastes	*10*	7.2a[†] (0.14)	3.3 (0.28)	192b (9.9)	2.5a (0.25)	14a (6.8)	20.8 (1.45)	4.8b (0.38)	2.2b (0.23)
Rhizosphere	*6*	7.9a (0.18)	2.7 (0.36)	136a (12.8)	5.7b (0.32)	85b (8.8)	14.6 (1.87)	6.1c (0.49)	0.36a (0.30)
Control	*5*	5.3b (0.20)	3.9 (0.40)	234c (14.0)	2.1a (0.35)	3.1a (9.7)	19.8 (2.04)	2.6a (0.54)	0.57a (0.32)

[†] - within each column, means followed by similar letter are not significantly different ($p > 0.05$) using the Fisher LSD test

Organic C, total N and total C in rhizosphere soils were significantly higher among materials at 5.7 g organic C kg^{-1}, 85 mg N kg^{-1} and 6.1 g total C kg^{1}, respectively (Table 6.5). Inorganic C in bare wastes was higher at 2.2 g C kg^{-1} compared to rhizosphere and control materials.

6.3.3. Bio-available and water-soluble metals in mine wastes

In El Gorguel site, DTPA-Cd and water soluble-Cd were affected by the interactions between treatments and types of materials (Table 6.6). DTPA-Cd in bare waste in amended and control plots were not statistically different, with values ranging between 3.9 and 4.9 mg Cd kg^{-1}. However, water soluble-Cd was significantly higher in bare wastes in MW+PS compared with bare wastes from control and PS plots. In addition, water soluble-Cd was the highest in rhizosphere in PS treatment estimated at 20 μg Cd L^{-1} solution. DTPA- and water soluble-Cu, Pb and Zn were not affected by the interactions between treatments and types of materials (Table 6.7).

Both DTPA-Cu and Pb were not significantly different among materials but DTPA-Zn content was highest in rhizosphere soils at 656 mg Zn kg^{-1}. Water soluble-Cu was the highest at 41 μg Cu L^{-1}, while water soluble-Pb was the lowest at non-detectable amount in the rhizosphere soils. Water soluble Zn was the highest in bare wastes at 293 μg Zn L^{-1}.

None of the DTPA- and water soluble metals in El Lirio site was influenced by the interactions between treatments and types of materials. DTPA-Cd (5.9 mg Cd kg^{-1}), Cu (2.1 mg Cu kg^{-1}), Pb (129 mg Pb kg^{-1}) and Zn (592 mg Zn kg^{-1}) were significantly lower in the rhizosphere soils compared to Control, but similar compared to bare wastes (Table 6.8). Similarly, water soluble Cd (30 μg Cd L^{-1}), Pb (not-detectable) and Zn (431 μg Zn L^{-1}) were the lowest while water soluble-Cu (31 μg Cu L^{-1}) was the highest in rhizosphere soils (Table 6.8).

Table 6.6. Mean and (standard error) of DTPA- and water soluble-Cd affected by significant interaction between amendments and rhizosphere of *Z. fabago* and bare mine wastes one year since the applications of pig slurry (PS) and marble wastes (MW) in the El Gorguel site, n = number of observations.

Treatment	Materials	n	DTPA-Cd (mg kg^{-1})	Water Soluble Cd (µg L^{-1})
MW+PS	Bare wastes	5	4.9 (0.91) a[†]	11 (1.8) a
MW+PS	Rhizosphere	3	2.5 (0.52) b	10 (2.3) a
PS	Bare wastes	5	3.9 (1.6) a	3.0 (1.8) b
PS	Rhizosphere	3	3.4 (0.53) a	20 (2.3) c
Control	Bare wastes	5	3.9 (1.81) a	2.7 (1.8) b
Control	Rhizosphere	3	2.4 (0.53) b	10 (2.3) a

[†] - within each column, means followed by similar letter are not significantly different (p > 0.05) using the Fisher LSD test

Table 6.7. Mean and (standard error) of bio-available and water soluble metals in rhizosphere of *Z. fabago* and bare mine wastes one year since the application of pig slurry (PS) and marble wastes (MW) amendments in the El Gorguel site, *n* = number of observations. Drinking water guidelines are appended in the table.

Materials	*n*	DTPA Cu	DTPA Pb (mg kg^{-1})	DTPA Zn	W S Cu	W S Pb (µg L^{-1})	W S Zn
Bare wastes	*10*	4.3 (0.22)	112 (16)	519a[†](23)	4.1a (1.6)	69b (9.7)	293b (19)
Rhizosphere	*9*	4.1 (0.23)	77 (17)	656b (24)	41b (1.8)	nd a	232b (20)
Control	*5*	4.3 (0.88)	41 (30)	502a (56)	2.3a (2.2)	123c (14)	170a (27)
Drinking water threshold guidelines (µg L^{-1})							
United States of America (US EPA 2007)					1300	15	5000
World Health Organization (WHO 2011)					2000	10	3000
European Community (Council Directive 98/83/EC 2008)					2000	10	-----

[†] - within each column, means followed by similar letter are not significantly different (p > 0.05) using the Fisher LSD test

WS: water soluble

nd: non-detectable

Table 6.8. Mean and (standard error) of bio-available and water soluble metals in rhizosphere of *Z. fabago* and bare mine wastes one year since the application of pig slurry (PS) and marble wastes (MW) amendments in the El Lirio site, *n* = number of observations.

Materials	*n*	DTPA Cd	DTPA Cu	DTPA Pb	DTPA Zn	W S Cd	W S Cu	W S Pb	W S Zn
		(mg kg^{-1})				(µg L^{-1})			
Bare wastes	*10*	10ab[†] (1.5)	1.6a (0.35)	62a (34)	583a (44)	108a (66)	7.7a (1.5)	103a (50)	6852a (5620)
Rhizosphere	*6*	5.9a (2.0)	2.1a (0.46)	129a (43)	592a (56)	30a (85)	31c (1.9)	nda	431a (7255)
Control	*5*	12b (2.1)	4.3b (0.50)	657b (48)	3906b (62)	1183b (94)	22b (63)	1050b (71)	234568b (7948)

[†] - within each column, means followed by similar letter are not significantly different (p > 0.05) using the Fisher LSD test

6.4. Discussion

6.4.1. *Z. fabago* naturally colonizes in unproductive mine wastes deposits

Our results confirm earlier reports (Conesa *et al.*, 2006; 2007b; Zanuzzi *et al.*, 2009a; Lefèvre *et al.*, 2010; Martínez-Sánchez *et al.*, 2012) on the the ability of *Z. fabago* to colonize harsh environments such as unproductive mine wastes deposits in dry conditions in SE Spain. *Z. fabago* occupies the largest area covered by plant species in both El Goguel and El Lirio sites (Table 6.1). However, the acidic nature (pH 5.3) of materials in El Lirio restricted the establishment of *Z. fabago* in plots amended with MW and may indicate its sensitivity to slightly acid environments.

Only one *Z. fabago* plant was observed in Control plot where pH is 5.3 in El Lirio while 8-15 *Z. fabago* plants colonized the Control plot in El Gorguel where pH measured was pH 7.7 (Table 6.1). The increased pH from the MW addition in El Lirio wastes materials allowed the growth of *Z. fabago* in these uncolonizable materials. The differential colonization by *Z. fabago* of mine wastes based on pH suggests the need for remedial action to raise the acidic pH to neutrality to support the natural colonization by *Z. fabago.*

6.4.2. Improvements of plant-related properties due to the growth of *Z. fabago*

The most significant improvement to plant-related (or edaphic) properties of mine wastes from *Z. fabago* colonization is associated with increased soil organic matter (SOM) in rhizosphere soils. This observation is especially true for total N where colonization by *Z. fabago* increased the total N in rhizosphere soils (85 mg kg^{-1}) by about 27X compared to control (3.1 mg kg^{-1}) and 6X compared to bare waste (14 mg kg^{-1}) in El Lirio (Table 6.5). Similarly, 13-20X enrichments are observed in El Gorguel site comparing rhizosphere soils from the MW+PS (230 mg kg^{-1}) and PS (339 mg kg^{-1}) plots to bare waste in control plot (17 mg kg^{-1}), respectively (Table 6.2).

Pig slurry applications can certainly add N, however the increment in total N in rhizosphere of the control plot in El Gorguel site is due solely to growth of *Z. fabago*, because no PS materials were added to this plot, where N increased by 5X (Table 6.2). Increment in total N might be related to biomass deposited by the above-ground and rooting materials as well as to the microorganisms thriving in the rhizosphere of *Z. fabago.* Zornoza *et al.* (2012) reported positive relationships between plant cover, including *Z. fabago*, and enzymes such as β-glucosidase, phospho-diesterase and arylsulfatase in mine wastes deposits with similar properties to our study sites in SE Spain. Soil micro-organisms in rhizosphere of *Z. fabago* are likely the producers of the above-mentioned enzymes.

Rhizosphere is the most reactive sites in soil, as it contents of many low molecular organic acids are much higher than in bulk soil (Tuason and Arocena, 2009). Although any reference related to mycorrhizal associations in *Z. fabago* could not be found, it is thought that fungi are active in the rhizosphere of *Z. fabago* considering that the root systems of 95% of plant species are colonized by symbiotic mycorrhizal fungal–root associations (Sylvia, 1998). In addition, OC is another edaphic property that was significantly improved by the growth of *Z. fabago* in mine wastes deposits. At least 3X higher OC in rhizosphere soils influenced by the growth of *Z. fabago* is most likely due to increased SOM from litter and roots (Table 6.2).

Organic matter contains plenty of functional groups such as -COOH and –OH that can undergo de-protonation reactions to generate negative charges – the site of cation exchange reactions in soils, especially when the pH is increased (pH dependent). As much as 200 $\text{cmol}^+ \text{ kg}^{-1}$ is commonly attributed to SOM (Stevenson, 1994; Sollins *et al.*, 2006). Inorganic C (IC) is also affected by the rhizosphere of *Z. fabago*, dissolution of IC by organic acids from root exudates can be the responsible to the decrease of IC in the rhizosphere by 5-6X compared to bare wastes in El Gorguel and El Lirio (Table 6.3 and 6.5).

6.4.3. Bio- and water soluble-metals in rhizosphere of *Z. fabago*

The bio-available (or the DTPA-extractable) metals in rhizosphere of *Z. fabago* seems to be controlled by the pH of the wastes materials. In El Gorguel site (pH 7.7), bio-available Cu and Pb in rhizosphere are similar to those in bare wastes and control (Table 6.7) while consistently lower bio-available Pb, Cu, Cd and Zn are observed in rhizosphere of *Z. fabago* and bare waste compared to control plot in El Lirio site (pH 5.3) (Table 6.8). The low pH in the control site at El Lirio is responsible for the higher bio-available metals because at pH 5.3 (Table 6.5), metals such as Cd, Cu, Pb and Zn remains in solution while free metals such Cd and Cu decrease with increasing pH (e.g., pH 7.7 in El Gorguel) (McBride, 1994).

The significant decreased in bio-available Cd, Cu, Pb and Zn in El Lirio site is likely due to increased pH (up to pH 7.9) resulting from MW amendments. Degryse *et al.* (2009) stated that more Zn ions are mobile at low compared to high pH environments. In addition, the increased in CEC may also contribute to the reduction in bio-available metals in rhizosphere. De-protonation of the carboxyl and hydroxyl groups in organic matter generates negative charges available to absorb free Cd, Cu, Pb and Zn.

The water soluble Cd content in rhizosphere of *Z. fabago* in both El Gorguel and El Lirio sites may pose environmental problem, because the amounts are above drinking water guidelines established by the USA-Environmental Protection Agency (US EPA, 2007), World Health Organization (WHO, 2011) and the European Community (Council Directive 98/83/EC 1998) set at 5, 3 and 5 µg Cd L^{-1}, respectively (Table 6.6 and 6.8).

Water soluble Cu and Pb contents in rhizosphere of *Z. fabago* in two sites are below drinking water quality guidelines in the US, WHO and Europe. In El Gorguel site, the increase in water soluble Cd, Cu and Zn in rhizosphere compared to bare wastes in the control plots (Table 6.6 and 6.7) might be due to increase chelation reactions between free Cd, Cu and Zn and organic matter. However, water soluble Pb in rhizosphere is significantly reduced below any drinking water quality guidelines. In El Lirio site, the significant reduction in water soluble Cd, Pb and Zn (Table 6.8) might be mainly due to high pH after the addition of marble wastes, and likely, partly on the increased accumulations of OM in the rhizosphere. Contents of water soluble Pb and Zn in the rhizosphere of *Z. fabago* in El Lirio are greatly reduced to values below the water quality guidelines established by the USA, WHO and the European Union.

6.5. Conclusions

The natural colonization by *Zygophyllum fabago* of mine wastes subjected to marble wastes and pig slurry applications improves edaphic and environmental properties of mine wastes materials. Total N in rhizosphere of *Z. fabago* increased from 17 to 339 mg N kg^{-1} in El Gorguel and from 3.1 to 85 mg N kg^{-1} in El Lirio sites. Organic matter accumulation in rhizosphere from litter and roots of *Z. fabago* increased soil organic carbon from 6.6 to 19.5 g kg^{-1} in El Gorguel and from 2.1 to 5.7 g kg^{-1} in El

Lirio. As expected, inorganic C in rhizosphere decreased and this was due to organic acids from the exudates of *Z. fabago*. Other plant-related properties such as water holding capacity are also expected to improve with continuous accumulations of organic matter from above and below ground biomass of *Z. fabago*. The initial colonization by *Z. fabago* likely will lead to secondary plant successions.

Major reduction in bio-available Cd, Cu, Pb and Zn in El Lirio site is not due to colonization of *Z. fabago* but the direct result of increased pH from the addition of marble wastes. The amounts of water soluble Cu, Pb and Zn in rhizosphere of *Z. fabago* are below the environmental guidelines set by EPA in the USA, World Health Organization and the European Community.

CHAPTER 7

A conceptual landscape design approach for the sustainable reclamation activities of a post-mining area in Cartagena-La Unión, SE Spain

Abstract

Utilization of Cartagena-La Unión Mining District (SE Spain) for more than 2500 years created deleterious effects on the environment and human health because of its chemical and physical characteristics. These effects can be ameliorated by the help of sustainable reclamation activities which can be seen as a required solution in order to return the mining area to an acceptable environmental condition. Sustainable reclamation activities, which require an extensive ecological knowledge, have to consider landscape values and functionality of the area, with the attention to the historical, socioeconomic and cultural aspects.

7.1. Introduction

Throughout the world, mining has created landscapes of both wasteland and wonder, profoundly altering the earth's surface. The necessity to reclaim these post-mined landscapes rises as an important issue of ecology, society, and aesthetics. Planning for ecological processes or new land uses were absent in the process of mining reclamation, but today, however, with new regulations and heightened environmental concern for post-industrial and mined lands, designers are beginning to play a vital role in the design of reclaimed mines. Consequently, new challenges for both scientists and designers include rethinking reclamation strategies across disciplines, and designing for evolving social and ecological landscapes that confront our perception of mining and its reclamation (Fisher, 2006).

Owing to the mentioned environmental impacts of these areas remediation is required. Recently the use of plants for removing heavy metals from soil has received increased attention which is generally called phytoremediation (García *et al.*, 2003). But some soils are so heavily contaminated, like in Cartagena-La Unión, that removal of metals using plants would take an unrealistic amount of time, so that an alternative phytoremediation technique phytostabilization has been emerged.

Phytostabilization is the use of metal tolerant plant species to immobilize heavy metals through absorption and accumulation by roots, adsorption onto roots, or precipitation within the rhizosphere, creates a new ecological condition in the area, prevents erosion and spreading of pollution, reduces metal mobility and bioavailability for entry into the food chain. Using metal-tolerant species for stabilizing mine spoils also could provide improved conditions for natural attenuation (Wong, 2003). Phytostabilization needs to use the native plant species in which the mine tailings are found, appropriate to the harsh climate of semiarid environments and native plants also avoid introduction of nonnative and potentially invasive species that may result in decresing regional plant diversity (Mendez and Maier, 2008). Utilization of natural plant species, especially in post-mining areas, is also necessary for landscape design for creating a self-sustainable system. There is a growing evidence that phytostabilization can facilitate the restoration of mining degraded land (Li, 2006). Several phytostabilization experiments held in the area showed successful results such as recuperation of some soil properties. In Zanuzzi *et al.* (2009b) and Carmona *et al.*

(2010), it is possible to see the information related to phytostabilization trials in the area and their results. Though the objective of the phytostabilization studies on the area mostly relies on the achievement of recuperation of soil properties, the final object is to create a new land use. By considering this in our aspect we tried to combine landscape design with solutions or solution processes of environmental risks. Based on this knowledge; our purpose is to try to provide a general approach related to the integration of landscape design and reclamation techniques.

7.2. Mine reclamation and sustainability

Within the mining concept, reclamation refers to the general process whereby the mined wasteland is returned to some forms of beneficial use. Other similar concepts, which are used as synonyms of reclamation, are restoration and rehabilitation; in the abstract have different meanings.

While restoration refers to reinstatement of the pre-mining ecosystem in all its structural and functional aspects**;** rehabilitation means the progression towards the reinstatement of the original ecosystem. In fact; restoration and rehabilitation are impossible to realize in abandoned mining areas, because turning back to their historical trajectory, especially in an area such as Cartagena-La Unión Mining District, very old and full of human prints, can only be an imaginary way of thinking (Mchaina, 2001; Fisher, 2006). According to Schulz and Wiegleb (2000), a pre-mining situation does not exist and even if it did, it could never be restored. However reclamation does not attempt to restore the landscape to its historical trajectory; rather it converts the land to a new land-use and creates new ecological conditions. So that the concept of “reclamation” combines all measures needed to make surface-mined landscapes productive and visually attractive again (Mchaina, 2001; Fisher, 2006).

Mine reclamation has to be formed an integral part of the planning process which includes feasibility studies and environmental impact assessment for new mines. Following objectives have to be provided by the help of reclamation (Mchaina, 2001):

1. To allow a productive and sustainable post-mining use of the site which is acceptable to all stakeholders
2. To protect public health and safety

3. To alleviate or eliminate environmental damage and as a result encourage environmental sustainability
4. To conserve valuable attributes, and
5. To minimize adverse socio-economic impacts.

Accomplishment of these objectives by mine reclamation is directly related to the sustainable character of mining reclamation activities.

The definition of sustainability, approved by FAO in 1998, is the handling and conservation of natural resources and the orientation of technological and institutional change so as to ensure the continuous satisfaction of human needs for present and future generations (Leitão and Ahern, 2002).

IUCN (1992) states; sustainable development is widely accepted as a strategic framework for decisions on the future use of land. The principles of sustainable development imply that in developing land, ecological, social and economical functions are balanced in space and time to maintain their potential to deliver goods and services to future generations (Termorshuizen *et al.*, 2007).

In this context, decision making is, in the first place, on attributing targets for nature conservation, quality of life or economic welfare to the landscape region. Secondly, it includes the assessment of ecological, social and economic values and their interactions. Thirdly, decisions are made on the allocation of land use functions (Termorshuizen *et al.*, 2007).

7.3. Landscape value and function

To evaluate a specific form of resource management, for example, the maintenance of valuable cultural landscapes, the contributions of many different viewpoints related to history, inhabitants, legislations and etc. must be considered (Gómez-Sal *et al.*, 2003). Landscape reclamation and design is also the subject of resource management and requires the consideration of landscape values such as natural value, historical value, productive value, socio-economic value.

The natural components of the landscape form the basis of all resources and ecological functioning of the landscape. Increasing fragmentation and losing their connectivity causes malfunctioning and, consequently, restructuring of the environment.

Many natural values remain as isolated relicts lost in the superimposed landscape structured by man in a different way. For example, industrial changes deform the structures, and thus their functioning, of the existing landscapes. In some places, the landscape was even wiped away entirely to create a completely new landscape. Economical rationalization controls it and all regional diversity and the identity of landscapes become unrecognizable. The spirit or the character of the place is lost. Conservation of biological and geological/geomorphologic remains is a first value to protect. This can be achieved by creating buffer zones and connected isolated units by corridors in order to keep their functioning going. Landscape reclamation and creation are, therefore, additional instruments (Antrop, 2000). Sklenicka *et al.* (2004) also supports the value of natural components by asserting biological diversity (at all levels) and speed (success) of revitalization are the two key criteria for post-mining landscape reclamation.

Many abandoned mines, despite their altered natural characteristics, have significant historical value and should be protected from destruction, vandalism, and theft. The U.S. National Historic Preservation Act established the National Register of Historic Places (NRHP) as a federal listing of cultural resources worthy of preservation. The NHRP is maintained by the National Park Service, and to be eligible for listing, abandoned mine lands must be demonstrated to have significance to history, architecture, engineering, or culture. The NHRP nomination process uses additional criteria in order to determine the historic significance of sites, buildings, structures, and objects. Besides meeting one or more of the NHRP criteria, a mine site generally must also be at least 50 years old, and have integrity of location, design, setting, materials, workmanship, feeling, and association in order to be eligible for inclusion. If a site has been compromised by significant alterations, it may not be eligible (CAM, 2000). According to Antrop (2000) landscapes that are made by society reflect the changing society and attitude towards the environment. Landscapes reflect the superposition of all attempts man makes to adapt the environment to improve living conditions. The landscape is full of past memories, which still have a strong symbolic value. This can be seen clearly when they are exploited as tourist attractions.

Related to the historical-cultural value of Cartagena-La Unión Mining District several authors asserted different ideas. Manteca and Berrocal (1997) related the mining elements with archaeological and geological value in order to justify the creation of a geo-mining and archaeological park in the region. According to those authors the mining heritage elements in the Mining District have two components regarding to their value: 1) an educational value to raise public awareness about cultural, natural and historic resources and to a didactic tool for researchers and 2) their socio-economic value, since they can constitute an important tourist attraction because of their geographic situation near an important tourist focus. Rodríguez-Estrella *et al.* (2003) proposed the use of mine tailings in didactic works because in these structures it is possible to identify sedimentary structures very similar to old rocks although the age of the tailing is less than hundred years. As a consequence, these authors consider these tailings like “natural laboratories with high didactic and scientific interest”. The most important proposal, mentioned in La Verdad de Cartagena (2005) and has already been made real, is based on the creation of a thematic park about mining, that is considered the local mining heritage site with highest historic interest (Conesa *et al.*, 2008a).

Aesthetics and ecological sustainability are also two highly regarded landscape values (Gobster, 1999). In developed societies aesthetics plays a relevant role in public acceptance of landscape interventions. The understanding of aesthetic aspects of landscape and clarification of its relation to sustainable principles in a reclamation project presents itself as a useful tool, resolving potential conflicts between ecology and sustainability principles and public perceptions and expectations (Rodrigues-Ramos and Panagopoulos, 2007).While the sense for beauty is universal, the expression of beauty may differ between regions, cultures and periods. Aesthetics are also found in the way society organized the landscape during history. The most striking examples are found in gardening; landscapes that are considered having ‘outstanding beauty’ are appreciated, receive a special legal status and are sometimes protected. Cleanness and a well-maintained appearance of the landscape, the durability which is expressed in its old age (represented by monuments) and its naturalness (as a symbol for the slow evolution and growth) are positive landscape characteristics and generally appreciated by people. For example, degraded and derelict land is without order, is not clean and not well maintained, so it receives only a poor value and ‘attracts’ spontaneous waste dumping of any kind and, thus, reinforces the degraded character (Antrop, 2000). Positive landscape characteristics can provide an easier adoption of the local people to the new land use. Once adoption is provided, protection and maintenance can be realized by the pleasure of local people.

High level ecosystems have a multifunctional feature which often serves more than one function. But generally, there are one or two functions outstanding. Biological production function includes cultivation, forestry, stock raising, fisheries and other agricultural production-oriented uses of land. Cultural support function includes urban constructional purposes, such housing and infrastructure uses. Environmental service function includes greening and tourist areas. Though such activities are generally not part of pre-mining land uses, they are an important part of holistic land-use plans and serve to implement the environmental service function of the landscape system. This function is applied to degraded areas where agriculture cannot be developed, like in our case. Green area development and rehabilitation supports the implementation of the environmental service function, whose fundamental aim is to eliminate pollution in the mining area. Owing to the special status given to green areas, special technology guarantees and meticulous care are needed at each stage of development from feasibility analysis to land levelling, species selection, planting and managing. If tourism function can be concentrated in those areas, it can also be possible to supply local industry (Wang *et al.,* 2001).

In order to create a successful and sustainable reclamation design it is important to recognize and interpret the historic and cultural significance of the landscape, collaboration of different ecological disciplines and to understand how “landscape ecology and design can invent alternative forms of relationships between people, place, and cosmos, so that landscape design projects become more about invention and programs rather merely corrective measures of restoration”. Without ecological knowledge, new sustainable landscapes cannot be achieved (Hüttl and Gerwin, 2005; Loures and Panagopoulos, 2007).

7.4. Design strategy

Derelict and degraded industrial areas can be filled with a new spirit and can be made worth living by keeping visible the spirit of existing site, by applying design strategies that contribute to economic prosperity, social cohesion and environmental quality (Loures and Panagopoulos, 2007). Punter (2002) draws the limits with five fundamental principles that have to be integrated by landscape reclamation design: protect and conserve the quality of landscapes; develop a clear vision and strategy for an area; apply collaborative design principles; allow resources for long-term aftercare of new landscapes; enhance biodiversity, social stability and economic development (Loures *et al.,* 2006). While these principles aim to preserve the innate medium by giving a new vision to the area, also they present the necessity of sustainability.

At this point also it is important to indicate that planning of land use cannot be restricted to the determination of the uses of each field or land parcel. Landscape is not something to be used only by the landowners, but also by temporary visitors: recreants, tourists, and neighbors. Landscape is multifunctional and the design must be taken into account as a whole as well, because each element only gets its meaning, significance or value according to its position and relationship with the surrounding elements. It should not be forgotten that changing one element always means changing the whole in some way (Antrop, 2000).

Leitão and Ahern (2002) after their comparison related to several ecology based plannings, collapsed the stages included by each method into five basic phases: (1) setting goals and objectives, (2) analysis, (3) diagnosis, (4) prognosis, and (5) syntheresis, or implementation. Some included more recent planning methods and tools such as spatial modeling and GIS, alternative scenarios and simulation techniques, monitoring, and the participation of stakeholders and public in general into the planning process were found fundamental components of sustainable landscape planning.

Design strategy in our case (Figure 7.1) has a similar mechanism with the ecology based plannings that are mentioned above. But in our approach determination of objectives takes place after the step of diagnosis instead of being in the beginning, because objectives are wanted to be established related to the characterization of the area. This consideration can be explained with an approach which can be applied in a situation of illness. Priorities should be directed to the recovery of the person or living organism. On the other hand determination of the objectives without knowing the characterization of the area can hinder the emerging of optimal potential land use. Giving a function to the area according to its present situation is the base idea. Determination of landscape values by examining landscape components is one of the step leads us to the function, but also solution ways for environmental risks can canalize us to the same point. This feature can come forward in problematic areas, like in Cartagena-La Unión, and can be formed according to the feature of the problem.

The problematic features of the area can be transformed to a functional stage by providing their association with landscape components. With a controlled usage such as tampon zones, fences etc., physical character of tailing ponds or color of acid mine drainage pools can be seen aesthetic and can provide a touristic attraction centre in the region. Solutions for environmental risks can be combined with the main landscape value or specifically with one of the landscape components.

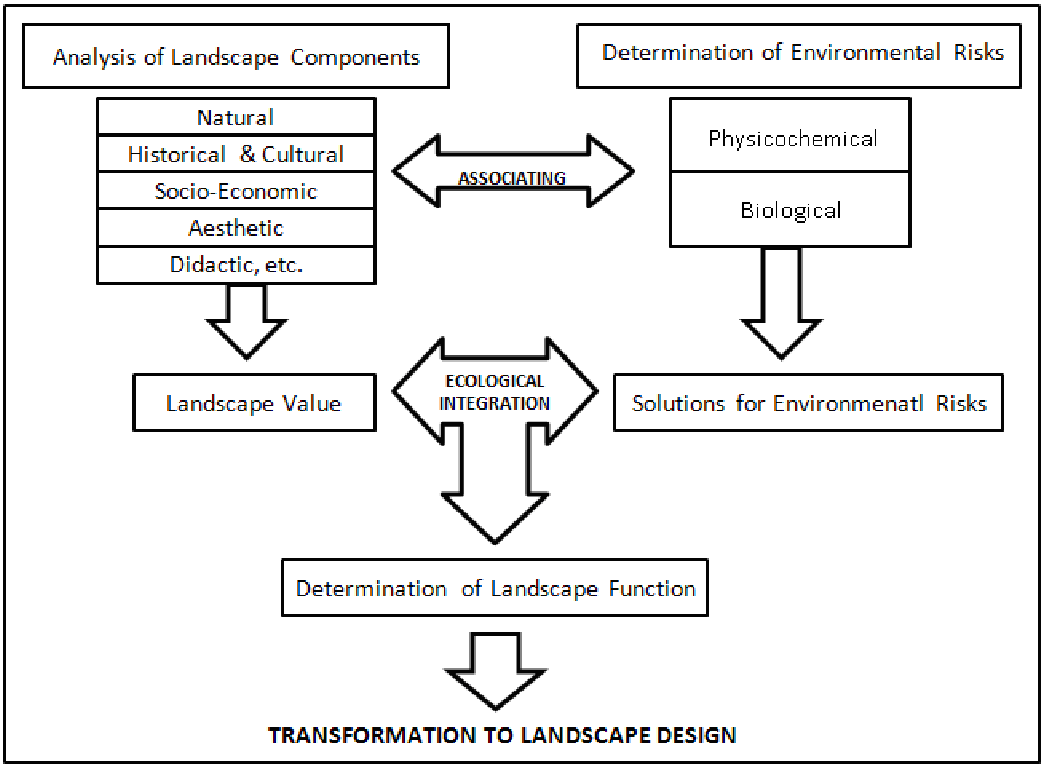


Figure 7.1. Scheme of the landscape design approach in problematic areas.

For example in our case phytostabilization can be seen the way of solution for various environmental problems of the area, which can immobilize the heavy metals, thus prevent spreading of pollutants to the surroundings and while the new vegetation cover creates a new ecological condition also it can get erosion and participation of heavy metals to the food chain under control. Phytostabilization process itself has a didactic value which can be utilized in a thematic park in order to improve the knowledge of visitors. Also mining elements (tools, shafts, etc.) can be represented by providing their safety; their educative and museum effect can be helpful in the reforming of the area. In this situation didactic value can be the main value of the area which is prominent in all, or a sub-value which is auxiliary for the main value.

Transformation of the ultimate decision of function to the landscape design has to be realized delicately by professions from different disciplines.

7.5. Conclusions

Cartagena-La Unión Mining District because of its fragmented land form has a potential for different kinds of land use. But related to the physical and chemical hazards in the tailing ponds while agriculture cannot be developed, environmental service function which includes recreational and tourist areas emerges as an alternative land use for these ponds. With these alternative land uses it is possible to carry out the elimination of pollution in the area simultaneously. Regarding to phytostabilization which is planned to use in our case in order to eliminate pollution and achieve self sustainable revegetation, it is thought to make a combination between potential land values and resolution advisories for environmental risks. According to the values and solutions, recreational area can serve for different aims such as thematic park or geo-mining and archaeological park etc. Each tailing pond can have its own characteristics and has to be investigated in order to determine the potential abilities.

Beside the considerations such as recovery of environmental conditions, generation economic opportunities, maintenance of historic and cultural values, development of aesthetic values; landscape design and planning has to establish relationships between people, place, and cosmos. Study areas have to be taken into account with their surroundings regarding to the holism principle.

Landscape design approach, which is emerged related to phytostabilization studies in Cartagena-La Union Mining District, required associations between landscape values and solutions. By considering this association a general approach was tried to explain in order to light the way for similar cases.

CHAPTER 8

Integration of landscape reclamation and design in the mine tailings of Cartagena-La Unión Post-Mining District, SE Spain

Abstract

Mine waste hills, in other words mine tailings, especially heavy metal accumulated ones are the subject of environmental problems and pending questions for local communities and administrations. In order to find sustainable solution for these problems and gain these problematic areas back, new functions have to be brought out for them, but initially their environmental risks have to be reduced or eliminated. Traditional solutions used in mining areas such as excavation and backfilling works are not feasible and appropriate in Cartagena-La Unión Mining District because of the high amount of pollutants and the big volume of polluted soil of mine tailings. Therefore minimization of some negative effects of former mining activities can be provided by creating a native vegetation cover which can also serve in the process of metal immobilization, called phytostabilization. This study explores how an optimal landscape design can be developed for a mine tailing by considering the process of phytostabilization as a reclamation technique, and how reclamation efforts can be integrated in the landscape design by taking into account not only the scientific considerations and also cultural and human aspects.

8.1. Introduction

One of the most significant issues that arise from the length of mining operations is the inability to fill the metal mine pits back in, if it takes a hundred years to dig the ore out, it ought to take about the same amount of time to fill it back in, assuming the use of similarly sized equipment (Micsak, 2008). Mining activities had been under operation for more than 2500 years in southeast Spain and have generated high amounts of sterile materials accumulated in pyramidal structures called mine tailings or tailing ponds, characterized by strong acidification processes, high salinity, scarce or null vegetation and accumulation of heavy metals (Zornoza *et al.*, 2010). Heavy metals are natural components of the soil and they cannot be decomposed in simpler forms nor be destroyed. They are not always toxic pollutants but all heavy metals are potentially toxic if their concentration exceeds upper limits (Souflias *et al.,* 2008). Reintroduction of a vegetation cover can achieve immobilization of metals, stabilization, pollution control, visual improvement and removal of threats to human beings (Wong, 2003). In the initializing of plant colonization, incorporation of organic amendments into contaminated mine soils has also been proposed as feasible, inexpensive and environmentally solution practice, as generally such wastes can improve soil properties (Barker, 1997). Besides, spontaneous vegetation itself may contribute to metal immobilization processes through biological activities in the production of organic matter (Bouwman and Vangronsveld, 2004), which is seen an emerging technology called phytostabilization. Phytostabilization is a phytoremediation technique. Phytoremediation is used to remove, stabilize, or detoxify hazardous pollutants in soil which is also known as green remediation, botanical remediation or eco-remediation (Sung-Hyun *et al.,* 2008).

Remediation of polluted sediments and soils is possible by means of eco-remediation which is due to its lasting operation, sustainability, efficiency, affordability and landscape attractiveness (Tjasa *et al.,* 2007). At sites contaminated with metals, plants are used to either stabilize or remove the metals from the soil and ground water through different mechanisms. Phytostabilization is one of those mechanisms used for the stabilization of metals, and defines as the use of metal tolerant plant species to immobilize heavy metals through absorption and accumulation by roots, adsorption onto roots, or precipitation within the rhizosphere, but not in plant tissues, thus reduces the mobility of the contaminant and prevents migration to the ground water or air, and it reduces bioavailability for entry into the food chain, prevents erosion and spreading of pollution, creates a new ecological condition in the area. Using metal-tolerant species for stabilizing mine spoils also could provide improved conditions for natural attenuation (Wong, 2003; Uemura and Menezes, 2007).

There is a growing evidence that phytostabilization can facilitate the restoration of mining degraded land (Li, 2006). Because in so heavily contaminated soils, like in Cartagena-La Unión Mining District, removal of metals using plants would take an unrealistic amount of time, so that phytostabilization can change metals to a less bioavailable form; exposure of livestock, wildlife and human can be reduced (Cunningham *et al.,* 1995). Phytostabilization needs to use native plant species which are found in the tailings, appropriate to the specific conditions of the areas. Also these native plant species can prevent the introduction of non-native and potentially invasive species that may result in decreasing regional plant diversity (Mendez and Maier, 2008). For creating a self-sustainable landscape in post-mining areas, utilization of natural plant species is also important.

Thus, new ecological conditions can be created in the area. However, finding solutions for environmental problems is not only a technical problem; also it requires an understanding of the environment as a social, economic and natural system, among people (Toorn, 2007). According to Comp (2008) when one works for a very long time in environmental issues, particularly in reclamation, one begins to realize that environmental problems are created and defined not only by science, but also by our culture. We immediately set about measuring the problem and the potential of its fix, somehow leaping from a culturally defined problem to a scientifically defined fix. While all this measurement, this science is necessary, it is not sufficient to fully address the real landscape in which we live. We need to address the underlying culture as much as the science, particularly in the places with significant public access or visibility. We inherit the sum of all the previous cultural decisions made about this landscape, and we address those we choose to address. That decision can be a cultural decision, but too often we neglect the cultural side of the solutions: the arts. Comp (2008) suggests that the vast array of environmental-reclamation science and technology is not sufficient, that the degraded environments we address are cultural artifacts as much as they are problems for science, and that we must address these with the full range of the arts and humanities, as well as the sciences, if we are to be effective. It also should not be forgotten as Fisher (2006) highlights in the key concepts of design strategies which belong to AMD&ART "arts can be found in the process not just in the form". While this study explores the problems related to the reclamation and new land use functions of two mine tailings, on the other hand integration of several components (solutions or solution processes for reclamation efforts and the new identity or the new recreational potential of the area) in a recreational area is trying to be achieved in a landscape conceptual design.

8.2. Material and methods

8.2.1. Case study description

The study was conducted in El Lirio and El Gorguel tailing ponds (Figure 8.1). El Lirio is located next to newly emerging resorts in a scenery location, while El Gorguel offers interesting post-mining views from an easily accessible location covering 1.5 ha and 1 ha respectively.

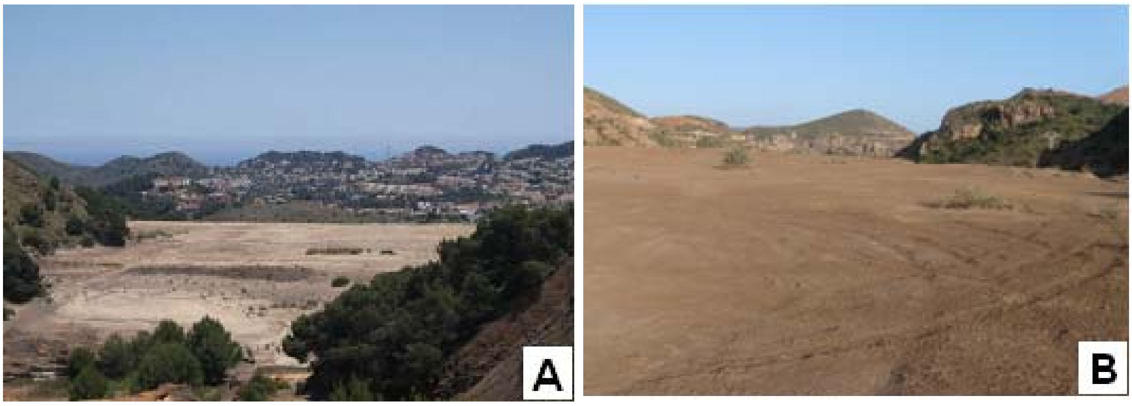


Figure 8.1. El Lirio (A) and El Gorguel (B) mine tailings.

Mentioned environmental problems resulting from the unvegetated structure of the tailings, and public safety concerns especially due to the proximity of El Lirio mining tailing to the settlements and on the other hand potential appropriateness of both tailings for being recreational areas such as topography, location and views, made these tailings suitable examples for a conceptual integration of landscape design and reclamation activities on them.

8.2.2. Procedure

Natural, cultural, geophysical, biological, and geochemical characteristics of the landscape were analyzed in the previous chapters. These characteristics are all important for the reclamation process, for the new function of the area and for being able to see the interactions between the reclamation process and the new function of the area which are wanted to be integrated in the landscape design of the mine tailing ponds.

According to the field experiments in El Lirio and El Gorguel mentioned in the previous chapters, the effects of different amendments on the plant colonization and their successful results on the recuperation of some soil properties were reported. By the help of these previous and ongoing studies; application of marble mud and pig slurry and development of phytostabilization and vegetation techniques were suggested in order to realize the landscape reclamation of the area. Especially because of the soil reclamation priority, the phytostabilization plantation design was aimed to be determined. In a metal-mining area, in order to be able to get phytostabilization plant species, available heavy metal distributions have to be known, because available heavy metals constitute one of the most important factors which directly effects growth of the plants, since they are the fraction of metals that can be uptaken by plants.

In the measurement of available metals, diethylentriamene pentaacetate (DTPA) was used in the ratio of 1:2 soilextractant (Lindsay and Norvell, 1978), and measurements were carried out using atomic absorption spectrophotometer (AAnalyst 800, Perkin Elmer). Analyzing the heavy metal distribution maps, in other words distribution of pollution, can help in the determination of land uses such as places which need phytostabilization measures, which can be used as an experimental area, which can be used for public requirement, etc. The land use decisions were given after the assessments of heavy metal distribution maps. Due to the priority of plantation because of the soil reclamation efforts, after choosing the contaminated areas for phytostabilization objectives, landscape design suggestions have been made for the rest of the area in the context of conservation and incorporation of the history and culture. Distribution maps (Figure 8.2) were prepared using Arcview 3.1 in which metal concentrations were used as input data. Figures 8.4, 8.5, 8.7, and 8.8 were made in Autocad 2008.

8.3. Results and discussion

Figure 8.2 shows the distribution of available heavy metals in both tailings. In this distribution it is possible to see 9 different level polluted areas according to their context for each element (Zn, Pb, Cd). With respect to the soil plant toxicity thresholds showed in Table 8.1 (Kabata-Pendias and Pendias, 2001), in El Lirio; Zn is not toxic in the 1. level of the area and is partially acceptable in 2. level, but in the rest of the mine tailing, Zn is approximately from 1.8 to 19 times higher than the toxicity threshold. Pb is not toxic in the 1., 2., 3., 4., and 5. levels of the area. However, Pb toxicity from 6. to 9. levels of the area reaches until 3 times more than the threshold. With respect to Cd amount, it is not toxic in 1., 2. and 3. levels of the area, is partially acceptable in 4. level, whereas in the rest Cd toxicity threshold is ranging from 2.5 to 8.3 times more for the plants. In El Gorguel; Zn is not toxic in 1. and 2. level, partially acceptable in 3. level, and in the rest almost 14 times toxic for plants. Pb is not toxic until 7. level, partially acceptable in 8., and in the last level 2 times toxic. Cadmium is not toxic in 1., partially acceptable in 2. level, and in the rest until 4 times it seems toxic for plants. With regards to these gradual changes in the distribution of available heavy metals, density of phytostabilizion measures can be separated into graded ranks.

In Figure 8.3 toxic amount distribution of metals and the zones under toxic limits are shown. In some zones only one element is toxic, whereas in some two or all three elements are. In the plot experiment which is previously mentioned related to effects of different amendments on plant colonization, marble mud (CaCO3) was used for immobilizing metals, removing them in a mineral form such as carbonates or indirectly oxi-hydroxides as a consequence of increasing soil pH, and for creating better conditions for plant development.

Table 8.1. Metal toxicity threshold (mg/kg) (Kabata-Pendias and Pendias, 2001).

Metal	Zn	Pb	Cd
Soil plant toxicity threshold	400	500	3

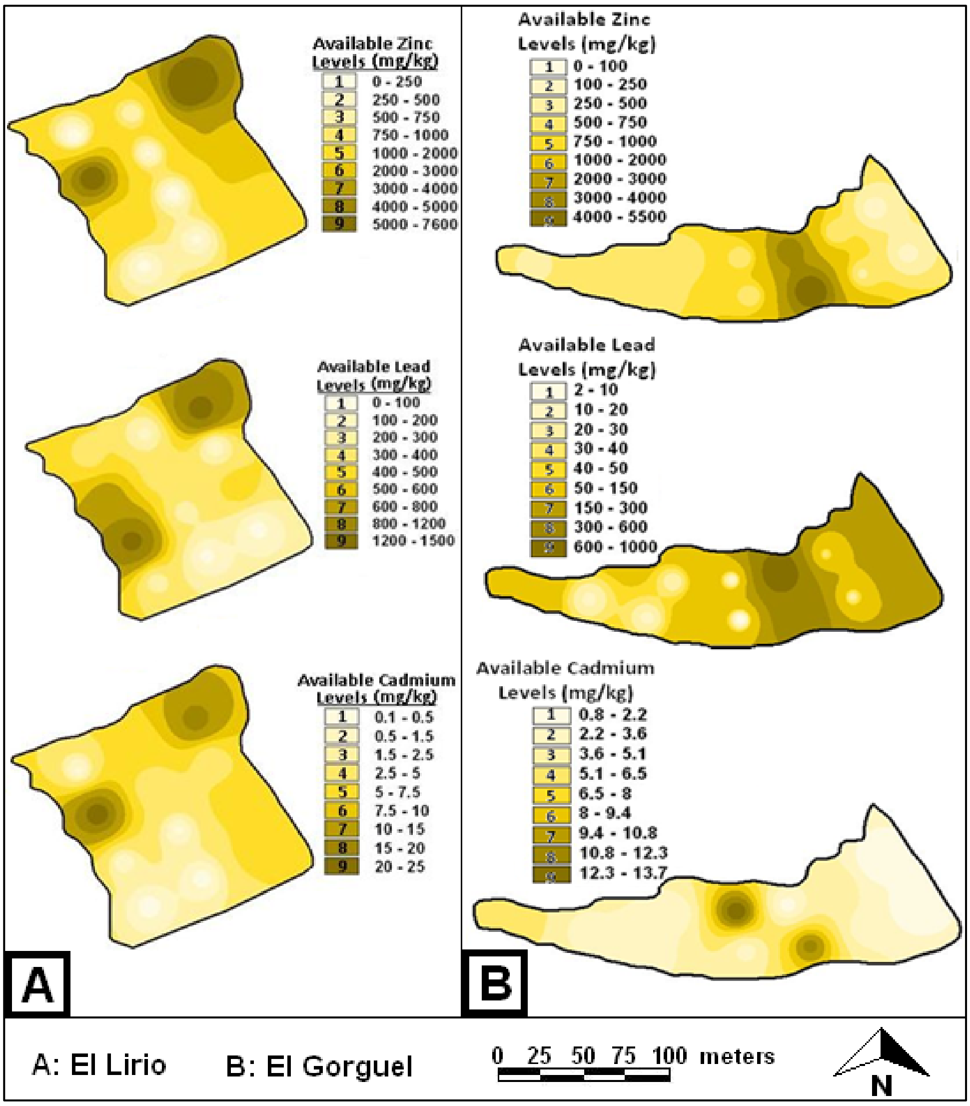


Figure 8.2. Spatial distributions of available metals (Arcview 3.2).

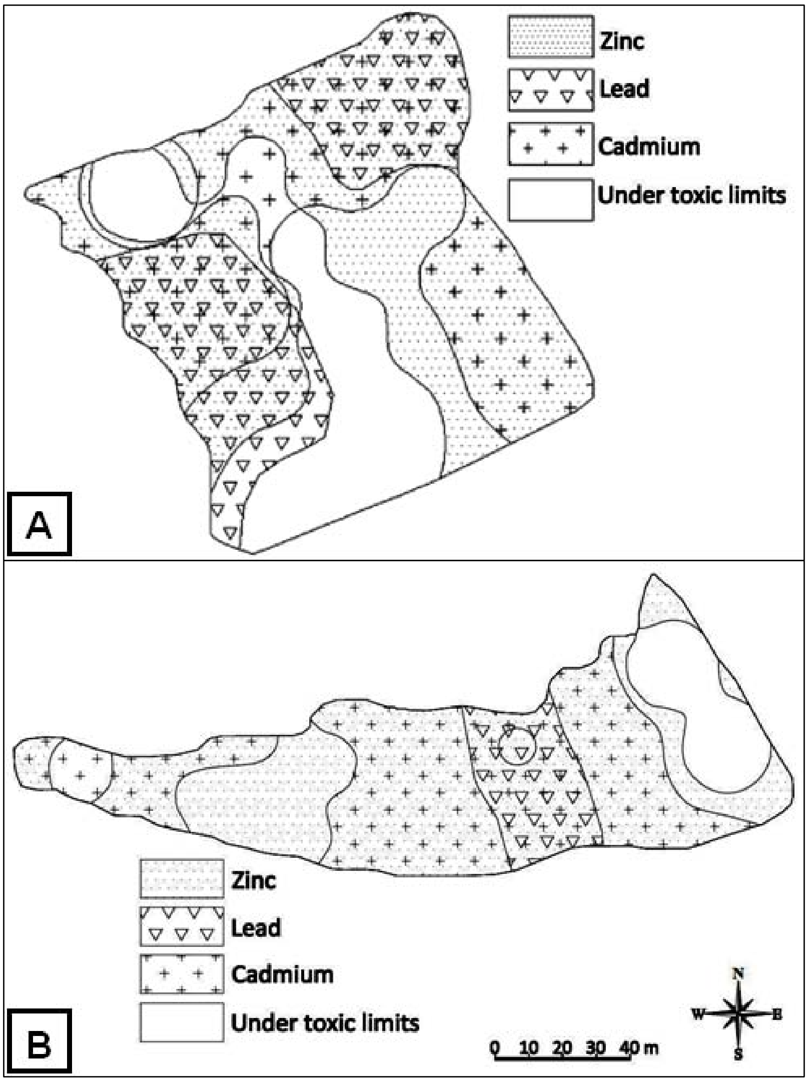


Figure 8.3. Distribution of metals above toxicity thresholds in El Lirio (A) and El Gorguel (B) tailing ponds (Autocad 2008).

In order to add nutrients and organic matter; pig manure and sewage sludge were applied and according to the results of the experiment the better conditions were obtained from the pig manure amended soils. This initial incorporation of amendments has promoted the microbial activity and establishment of vegetation, which remains after 5 years of application. This vegetation cover includes some native species of the area: *Zigophyllum fabago, Piptatherum miliaceum, Dittrichia viscosa, Phragmites australis, Helichrysum decumbens, Sonchus tenerrimus.* Eventhough after the application of amendments these spontaneous plant species colonized in the plots without seeding, some plant species are suitable for phytostabilization process. In order to continue to observe their effects in the most polluted and therefore more problematic soil conditions, we suggest establishing experimental areas in these most polluted parts of the mine tailings. Figure 8.4 shows a proposed design of the experimental area which is inspired from Mel Chin's Revival Field (Collins, 2000; Felson and Pickett, 2005).

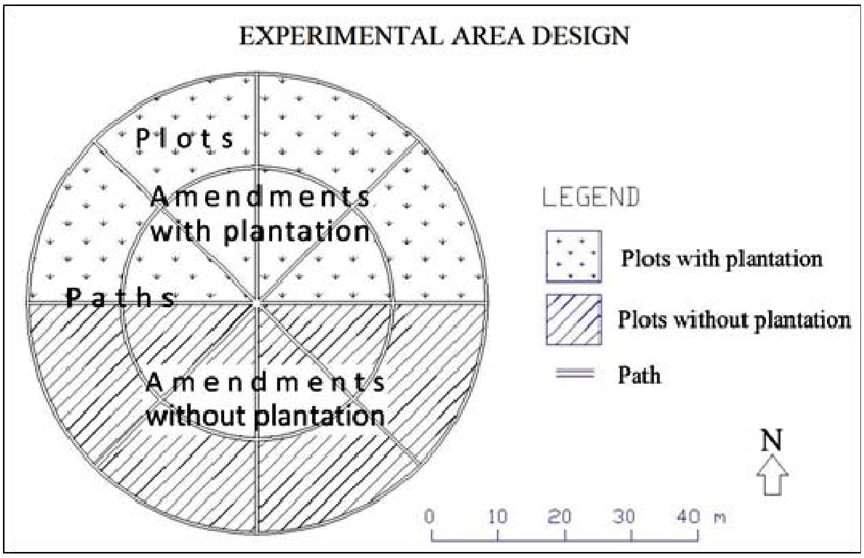


Figure 8.4. Proposed design of experimental areas (Autocad 2008).

Revival Field (Figure 8.5) is an example which shows that public art can also serve as a venue for experimental installations. It is possible to see the collaboration between artist and scientist in Mel Chin's Revival Field. He developed the project proposal in collaboration with USDA agronomist Rufus L. Chaney, an 18.2 x 18.2 m remediation project built on a landfill in St Paul, Minnesota. It was an art-science work that explores how plants can safely remove compounds from contaminated soils and was the first replicated field test conducted as an art installation in the US. Chin selected plants to remove toxins from degraded land and arranged them into a bulls-eye shape, surrounded by industrial fencing. At the time, little was known about the effectiveness of phytoremediation, and both research efforts and money were scarce. The project helped to confirm the effectiveness of the technique Thus, in addition to showing the role art can play in generating research with cultural meaning; his efforts also represent an alternative route to funding urban ecological experiments. Chin sees his work in two forms: as a formal planting on the landscape and as a complex series of 'systemic sculptures' that occur as the plants and roots act on the contaminants in the soil (Collins, 2000; Felson and Pickett, 2005).

Figure 8.5. Mel Chin’s Revival Field.

In the mine tailings, these experimental areas can be diversified according to the aim of the phytostabilization technique such as sections with amendments without seeding, or sections with amendments and with seeding, plantation of different plant species, etc. The aim is to minimize the negative effects of the mine tailings by creating a landscape design which brings a new sustainable function to the tailings as shown in the Figure 8.6, 8.7 presents the ideal concept designs of the tailings.

According to these designs it is suggested to use for the public only the area under the toxicity thresholds. Visitors are not allowed to enter to the phytostabilization areas because of the maintenance requirement of phytostabilization process. They can see the phytostabilization areas through the walk way and they can enter to the surrounding circulation of the experimental areas in order to see the experimental plots. Surroundings of the no-entry areas were closed by using fences and in several places with native naturally grown ornamental plants, by allocating spaces which allow seeing inside sufficiently. Through on the both sides of the walk way and in the surrounding way of experimental areas, design process of the mine tailing and phytoreclamation explanation panels (Figure 8.8) are recommended. Several antique mining tools or their sculptures can also be organized among the both sides of the walk way. Their information panels should be included too.

Plant species	Picture	Life Period	Blooming Period											
Z. fabago		Perennial*	1	2	3	**4**	**5**	**6**	**7**	**8**	9	10	11	12
H. decumbens		Perennial*	1	2	3	4	5	6	**7**	**8**	**9**	**10**	11	12
D. viscosa		Perennial*	1	2	3	4	5	6	**7**	**8**	**9**	**10**	**11**	**12**
P. miliaceum		Perennial*	1	**2**	**3**	**4**	**5**	**6**	**7**	8	9	10	11	12
S. tenerrimus		Annual/Perennial*	1	2	**3**	**4**	**5**	**6**	7	8	9	10	11	12
P. australis		Perennial*	1	2	3	4	5	**6**	**7**	**8**	9	10	11	12

Perennial* A perennial plant is a plant that lives for more than **two years**.

Figure 8.6. Proposed design of El Lirio mine tailing (Autocad 2008).


EL GORGUEL TAILING POND LANDSCAPE DESIGN
Zigophyllum fabago
Salsola kali
Chenopodium murale
Sonchus tenerrimus
Diplotaxis lagascana
Conyza bonariensis
Atriplex halimus
Dittrichia viscosa
Malva sylvestris
Carduus tenuiflorus
Piptatherum miliaceum
(Lead (Pb) Phytostabilizer)
Viewpoint &
Bench-Canopy
Resting area & viewpoint
Different phytostabilization plant species
Piptatherum miliaceum garden
Different phytostabilization plant species
Experimental area
Entrance
Pedestrian & bicycle path
Ancient engine house & headframe
N
W
E
S
0 10 20 30 40 m
Experimental area
a
b
Entrance &
Information Panels
Wooden Way
& Bicycle Path
Restoration of the ancient engine house & headframe

Figure 8.7. Proposed design of El Gorguel mine tailing (Autocad 2008).

Figure 8.8. Phytoreclamation explanation panels.

Besides phytostabilization plantation, the use of native ornamental plant species was suggested in non contaminated areas for several aims such as increasing attraction, redirecting of visitors, creating a barrier between the places for visitors and no-entry places. Parallel to the walk way, a bidirectional bicycle path was proposed which is separated from the pedestrians´ with a plant cover border in order to provide the safety of both pedestrian and cyclist. At the end of both ways (walk way and bicycle path), in the south of El Lirio and in the east of El Gorguel which is the most scenic place, sitting areas are planned. In sitting area pergolas and/or gazebos were designed. All the material to be used in the tailings should be resistant to water and semi-arid climatic conditions. In order to ensure the security of both public and the reclamation processes, throughout the implementation, precautions should be provided by several methods such as employments of watchmen.

8.4. Conclusions

The present work shows that if the environmental risks can be minimized, recreational activities can be developed in a mine tailing. Integration of reclamation efforts and recreational activities, based on the safety of both environment and public, can be realized by the help of appropriate landscape design suggestions.

Use of amendments and phytostabilization plant species can reduce the environmental risks of the area, by immobilizing heavy metals, their spread to the surroundings and by preventing erosion. Once these conditions are obtained, prominent value of the area can be featured by landscape design, in our case the didactic and educative value of the phytostabilization, experimental areas and mining culture can be used as a prominent value in the recreation area in order to increase public awareness and knowledge about environmental issues and challenges, this educative value should enable people to gain an understanding of how their individual actions affect the environment (Toorn, 2007). Also educational and academic institutions can use these new investigation opportunities as environmental education tools.

Conceptual design of El Lirio mine tailing can help to develop a theorical design approach for the rest of the tailings in Cartagena-La Unión Mining District. As noted by Swaffield (2002) in Loures *et al.* (2010) “theory can also evolve from practical experience”. Although this design is not an implementation yet, it is an approach for implementation and creation of more approaches would be useful for the creation of the practical design.

Instead of creating new recreational areas, instead of destroying natural or virgin lands more and more, if we can give a value to the ones which we have already started to destroy, we can discard the potential problems of today and the future by transforming a waste land to a new functional and sustainable area which can serve for the requirements of the public.

CHAPTER 9

Multifunctional greenway approach for landscape planning and reclamation of a post-mining district: Cartagena-La Unión, SE Spain

Abstract

It is vital to create a sustainable manner for healing the landscape wounds of post-mining activities in Sierra Minera Cartagena-La Unión, SE Spain. When the reclamation requirement of the post-mining district considered in the context of its critical location nested in the conflicting land uses around, creating practical solutions for bringing the ecological and cultural functions back comes out as a landscape planning challenge. Greenway approach shows the main veins which sustain the mentioned functions of the area are crucial to keep alive. With this study, it is aimed at developing a local greenway network for conserving the significant resources and values of the area and thus triggering the reclamation activities. Conservation areas, cultural-educational resources of post-mining activities, riverbeds and the agricultural areas are the main building stones for the proposed greenway corridor.

In the light of greenway approach, planners and land managers can make their decisions more delicately by considering the priority zones. Protect, benefit and reclaim of significant resources can be provided through a multifunctional greenway approach as seen in the case of Cartagena-La Unión Mining District.

9.1. Introduction

Habitat loss, alterations of ecological and cultural processes due to the fragmented structures of landscape and in this way generated metaphorical wounds are the most important leading threats to biodiversity worldwide, and have become a significant subject of ecological research (Penrod *et al.,* 2006; Serrano *et al.,* 2002).

Greenways concept as an increasingly accepted planning-design approach has become popular in Europe for almost two decades. It is a suitable tool for developing the ecological quality of natural processes, and for the conservation of biodiversity and cultural-historical heritage (Hepcan *et al.,* 2009). At the same time greenways provide multiple opportunities, being within the framework of sustainability concept, such as recreation, education, cultural and aesthetic benefits (Yokohari *et al.,* 2006). Fabos (1995) defines greenways as linear network systems of land that serve for various purposes including connection and protection of ecological, recreational-touristic and/or historical-cultural purposes compatible with the sustainable land use concept. Delineation of greenways is provided by the application of worldwide recognized landscape planning principles (Ribeiro and Barao, 2006).

Spain with its 1,800 km of greenways operated in 80 routes is one of the most important greenway promoter countries in Europe (Colorado *et al.,* 2011; European greenways info 15, 2012). Even so, abandoned mining areas distributed almost to the entire country come up as an unsolvable landscape planning issue (Fernandez-Caliani *et al.,* 2009; Martínez-Coronado *et al.,* 2011; Ordoñez *et al.,* 2011).

As a part of the Seventh Framework Programme Project "Integrated European Industrial Risk Reduction System (IRIS)" carried out between 2008 and 2012 in different European countries (Poland, Romania, Spain, Sweden and UK), two mine tailing ponds in Cartagena-La Unión Mining District, southeast Spain, were handled to reduce their environmental risks by making soil and landscape reclamation. The project aimed to 1) ameliorate the soil conditions of the tailing ponds for obtaining a vegetative cover, and therefore to minimize their adverse effects of past metal mining practices for the protection of public health, safety and general welfare; 2) create landscape designs on the mine tailing ponds to give them certain land use functions as a contribution to the local land-use planning, and gain back them in the context of ecologic and social benefits providing their environmental, historical and cultural sustainability and connectivity.

Cartagena-La Unión Mining District despite having a significant socio-economic dynamism potential (tourism, agriculture, exploitation of salt marshes, fishing, aquaculture and post-mining related activities) around it (Brugarolas-Molina, 2003), the lack of an integrated land planning system related to the conflicted surrounding land uses (natural protected areas, industrial areas, urban zones, touristic areas, commercial ports, leisure harbors, agricultural fields) created difficulties in the decision making process of mine tailings´ (~ 1 ha and 1.5 ha) landscape designs (Kabas *et al.*, 2011), when they are considered in a larger-scale unplanned piece of land (Cartagena-La Unión Mining District ~ 50 km^2). Based on the deficiency of spatial and functional connections between the fragments and the whole, a prudential integrated land planning system which is able to provide supportive outcomes for people-nature and promotes sustainable solutions for landscape alterations came into question as an important landscape planning requirement. In this study it is aimed to 1) develop an integrated local greenway network preserving the significant resources and values of the district, 2) develop the greenway network as a part of a reclamation process for degraded areas, 3) give a contribution to the dissemination of the greenway concept.

9.2. Material and methods

9.2.1. Delimitation of the study area

Cartagena La Unión Mining District was addressed with its surrounding representative land uses (conservation, industrial, urban, agriculture, and natural areas) and the study area was limited by the highways of CT-32 and MU-312 in the north and by the Mediterranean Sea in the south (Figure 9.1). In the north, fertile arable lands; in the east, urban areas and one of the most important lagoons of the Mediterranean Area, Mar Menor Lagoon; in the south, protected areas and Mediterranean Sea; and in the west, industrial areas are located.

9.2.2. Methods

The main supporting theorem of the greenways concept is the co-occurrence of the most valuable landscape resources (historical-cultural, ecological, natural, recreational) in common spatial distribution patterns in the landscape especially in corridor-like areas such as natural streams, ridges, steep slopes, and coastal areas (Lewis, 1964; Ribeiro and Barao, 2006). Professor Philip J. Lewis indicated that, when guarded, these landscape patterns could act form determinants to conduct progression of growth. These patterns were classified as greenways and were utilized as guides to create priority zones for future researches (Land Information Bulletin, 1998).

It has been remarked in many studies (Jongman *et al.,* 2004; Miller *et al.,* 1998) that when the most valuable landscape resources (environmentally sensitive areas) such as wetlands, fauna habitats, steep slopes, cultural-historical resources and significant agricultural areas, are connected they could form greenway networks providing ecological, cultural and recreational advantages to a society. Also Luymes and Tamminga (1995) indicate that such an interconnected landscape brings the public safety together.

Abandoned areas rationally have two conflicting land use opportunities; development and nature protection. Anyhow appropriate abandoned areas should be reclaimed by greenway planners incorporating them into a greenway network (Fabos, 1995). In this study, nature protection concept is considered as a series of strategies focused on preserving natural and cultural resources, as well as reclaiming and improving degraded land. Greenways can be seen as landscape restoration frameworks because of their connection creating characteristic in fragmented landscapes (Frischenbruder and Pellegrino, 2006). In this sense, in Cartagena-La Unión Mining District, reclamation of mine tailing ponds, using amendments, marble waste and native vegetation, have been reported in several studies (Acosta *et al.,* 2011; Kabas *et al.,* 2011; Kabas *et al.,* 2012). Also some of these tailing ponds can serve for recreational activities (Zornoza *et al.,* 2012b). Besides mine tailing ponds, some other mining forms such as mining pits and tunnels, and mining heritage can be utilized for several recreational activities (Conesa *et al.,* 2008a).

As a consequence IRIS project brought to the agenda focusing not only on the landscape designs of the mentioned mine tailings but also making a comprehensive planning in the entire Cartagena-La Unión Mining District in order to be able to suggest rational and practical land use designs for the tailing ponds and to highlight the requirement of a local planning system.

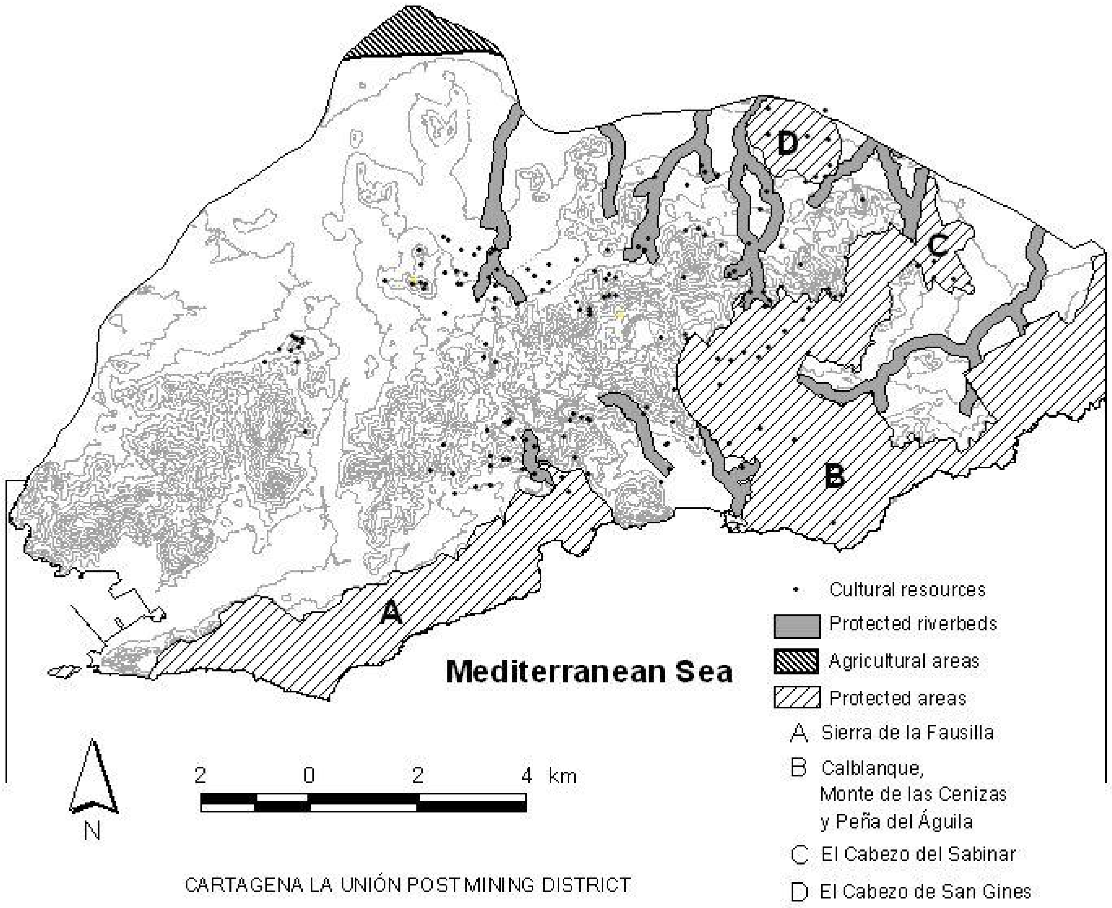
For greenway planning; landscape planning methods based on landscape analysis and assessment, planning proposals and evaluation are commonly used since they have been related to the identification and assessment of valuable resources (Ribeiro and Barao, 2006; Toccolini *et al.*, 2006).

9.2.3. Data collection

Topographical and land use maps, and aerial images were obtained from the "Servicio de Cartografía, Consejería de Obras Públicas y Ordenación del Territorio" (Murcia) and used as data base of this study.

The map of most significant areas (Figure 9.1) was created by the usage of data layers of land use map and the patrimonial resources were assigned on it using a satellite image with a grid size of 0.5 m, topographical maps, and the plan data of patrimonial resources from Martos-Miralles (2007).

Figure 9.1. Most significant areas of the Cartagena-La Unión Mining District.



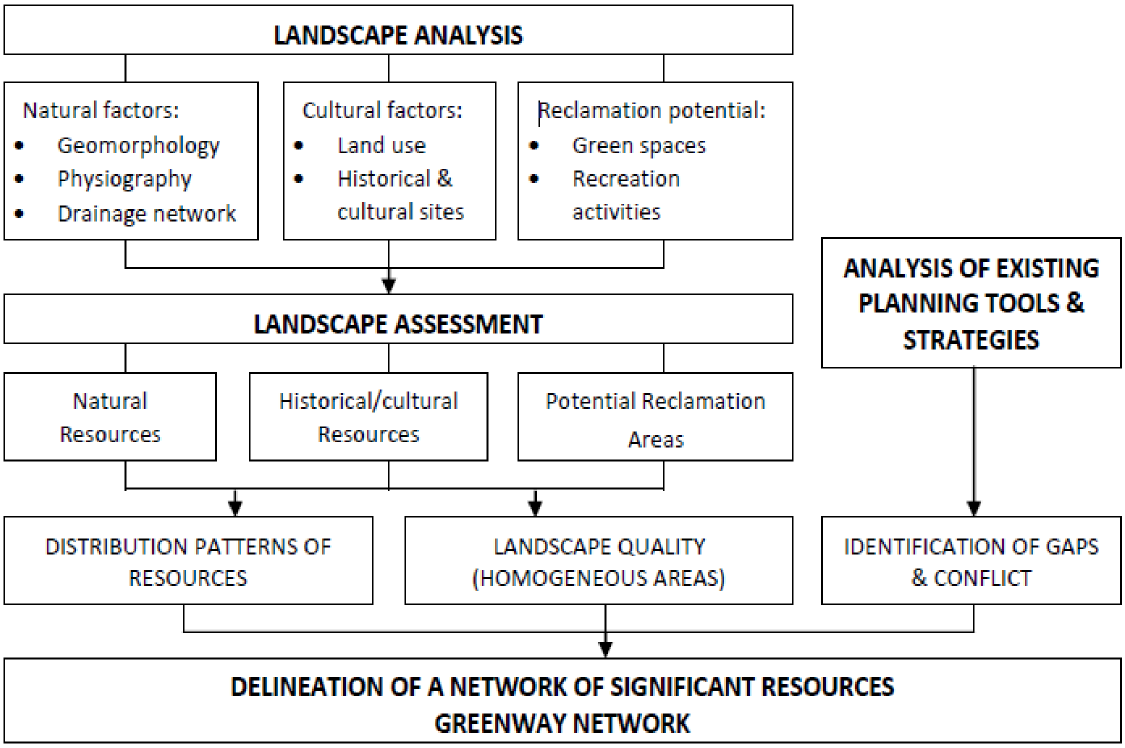
Overlapped layers of the most significant resources and assigned patrimonial resources were supported with the interpretation of satellite images, field checks and expert opinions.

Additionally related literature and interviews with local people and experts were used as data sources. The data for the identification and evaluation of the greenway system were stored and treated using ArcView GIS 3.1 (ESRI, 2005). Spatial links for significant recourses were delineated by the assessment of homogenous areas.

9.2.4. Procedure

Standard methodology of landscape planning which includes the steps of analysis, assessment and identification of valuable resources was employed (Flowchart of the procedure is shown in Figure 9.2) (Ribeiro and Barao, 2006).

Figure 9.2. Flowchart of the procedure for greenway corridor planning in Cartagena-La Unión Mining District (Modified from Ribeiro and Barao (2006)).

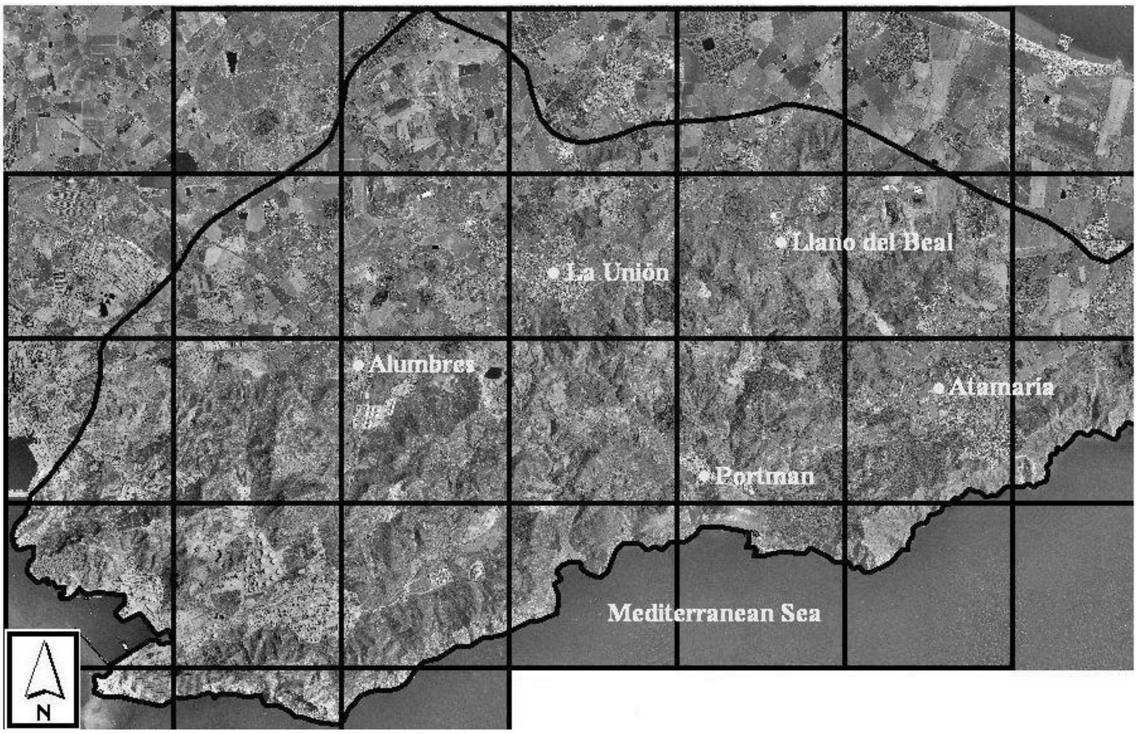


Natural and cultural factors such as geomorphology, physiography, natural drainage network, land use, historic/cultural sites were analyzed to identify the most valuable resources of the area including the potential connectivity resources that might be used to create linkages (Conine *et al.*, 2004). Assessments of the resources were made in terms of biodiversity, ecological functions, water-soil conservation, reclamation potential, and natural/historical characteristics.

The methodology was modified for reclamation planning purposes. Besides natural and cultural factors, the reclamation potential areas of the Cartagena-La Unión Mining District which could be included to the greenway network by reclamation efforts were assessed.

In order to conduct a throughout survey of all areas within the Cartagena-La Unión Mining District, the area was underwent a 28 parts grill sectorization using 1:20 000 scale topographic map, and the national and the digital orthophotos of 2002 (Figure 9.3).

Figure 9.3. Sectorization of Cartagena-La Unión Mining District for the survey of the significant resources (Scale: 1/125000, Size of each division ≈ 8 km^2).



Following these steps the distribution patterns of homogeneous zones were analyzed by using the overlapped distribution of potential reclamation points (Figure 9.4). Following the assessment of the most valuable and potential connectivity resources and distribution patterns of homogeneous areas, the greenway corridors are determined (Figure 9.5). Utilization of the most valuable resources and areas making connections with the highest demand centers ideally meets the goals and objectives of greenways, and serves for their multiple purposes (Conine *et al.,* 2004).

Figure 9.4. Distribution patterns of homogeneous areas.

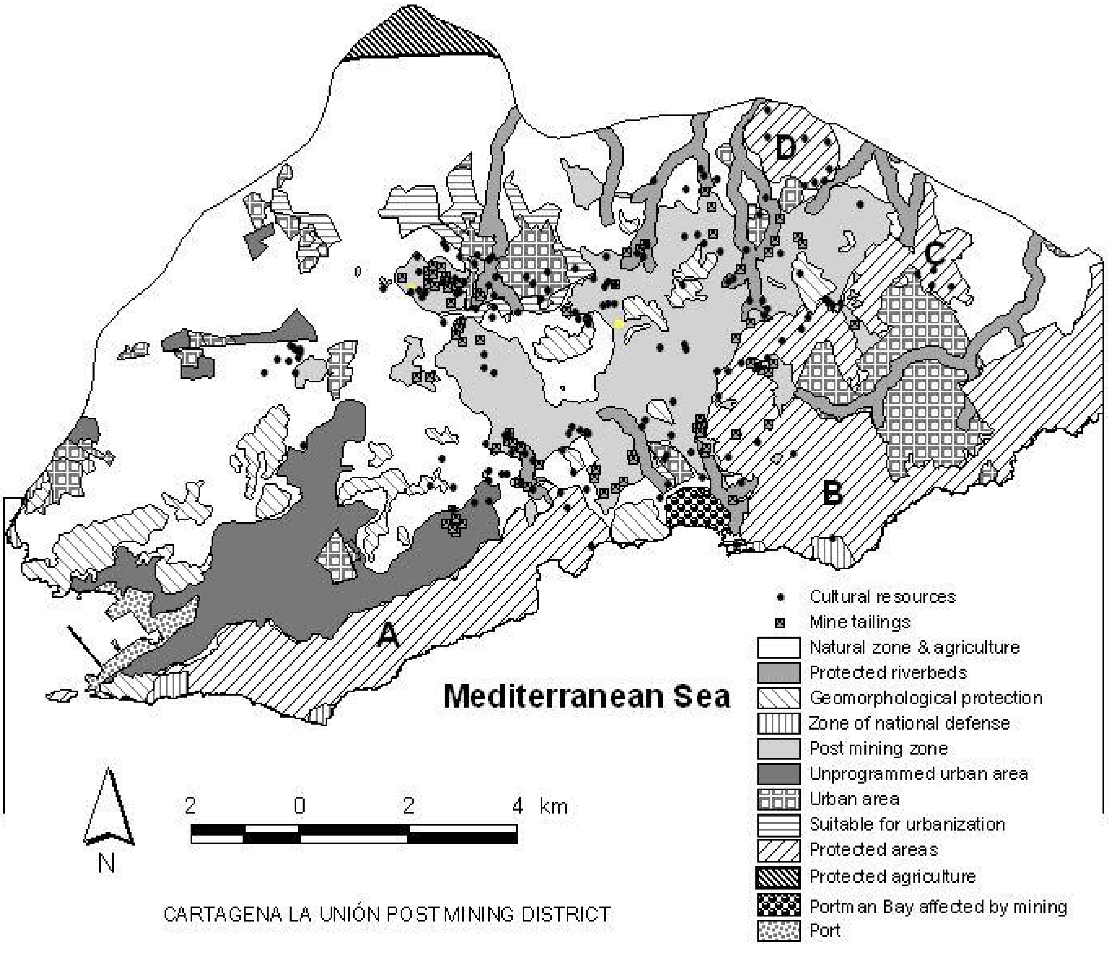
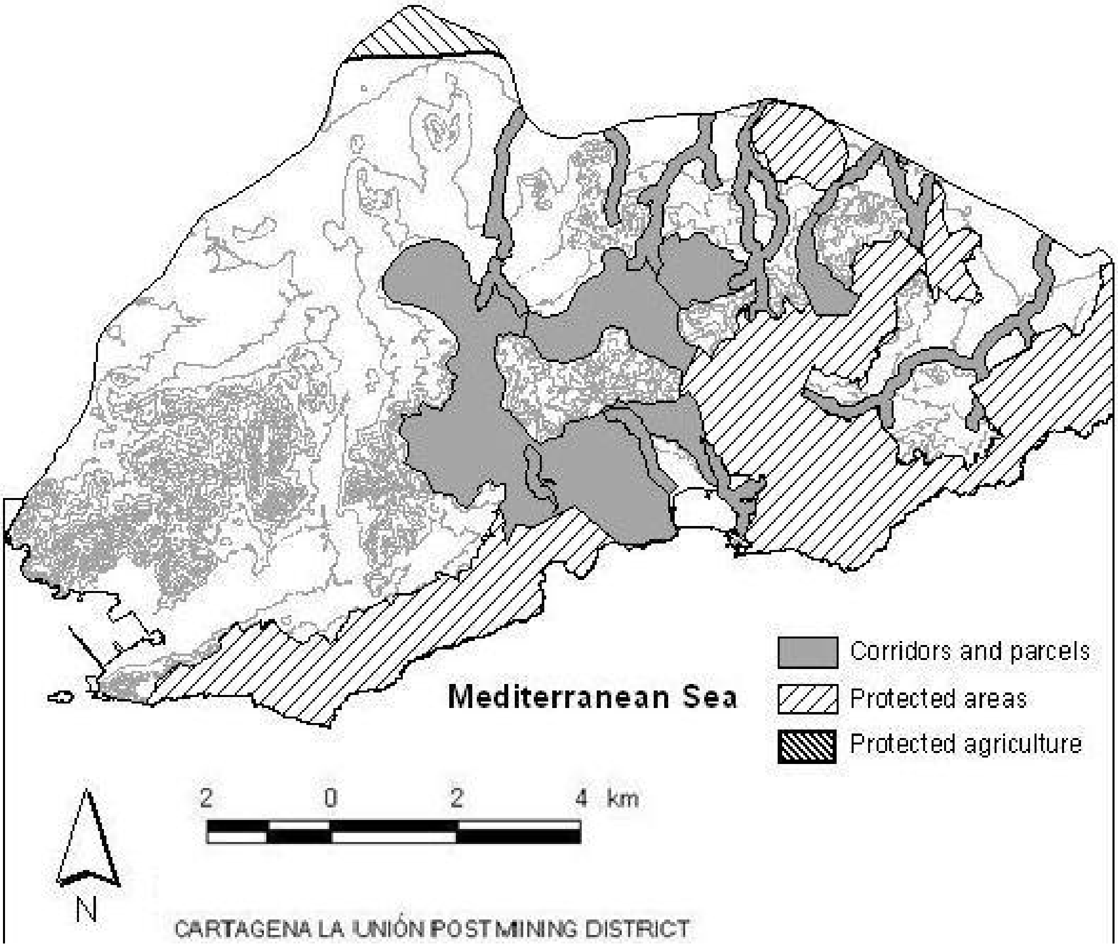


Figure 9.5. Cartagena-La Unión Mining District Greenway network.



9.3. Results

9.3.1. The most valuable resources

Using the related literature (Conesa *et al.,* 2008a; Jongman *et al.,* 2004; Hepcan *et al.,* 2009; Steward *et al.,* 2012) four most valuable resources were determined in Cartagena-La Unión Mining District. These clustering and linear resource patterns include natural drainage network, nature conservation areas, agricultural areas and cultural resources (mining heritage) (Figure 9.1):

1) Natural drainage network

The coastline of the Region of Murcia, and thereby the study area, is characterized by the absence of permanent hydrologic resources. Natural drainage network even consists solely of wadis subject to certain periodicity to flood risks in

Cartagena-La Unión Mining District, has a connectivity potential between different resources (D.P.O.L., 2004; Zornoza *et al.,* 2011).

2) Nature conservation areas

According to the Council Directive (92/43/EEC) "Calblanque, Monte de las Cenizas y Peña del Águila" (2822 ha); "Sierra de la Fausilla" (791 ha); "El Cabezo de San Gines" (160 ha) and "El Cabezo del Sabinar" (105 ha) are under the protection of Natura 2000 since 1992 and Site of Community Importance **(**SCI) since 2000. In accordance with the Council Directive (79/409/EEC) "Sierra de la Fausilla", due to its importance of reserving bird habitats, has been taken under the conservation of Special Protection Area (SPA) since 1979; while "Calblanque, Monte de las Cenizas y Peña del Águila" was also declared as a regional natural park by the act 4/1992 of land management and protection of the Region of Murcia in 1992 (Brugarolas-Molina, 2003; ESRI, 2005). These protected areas are characterized by a vegetation of xerophytic Mediterranean shrub communities, which highlights the presence of a large number of endemic and Iberian-African plant species, some of which constitute endangered species such as *Caralluma europaea* Guss., *Sideritis marminorensis* Obón & D.Rivera, *Limonium carthaginense* (Rouy) C.E. Hubb. & Sandwith, *Teucrium carthaginense* Lange, *Anthemis chrysantha* J. Gay, and *Teucrium freynii* Reverchon ex Willk.

3) Agricultural areas

Agricultural areas include the most productive and fertile agricultural soils having sufficient infrastructure and an appropriate management (Decreto 57/2004).

4) Mining heritage

2500 years memory of mining heritage, mining structures and forms shown in Table 9.1 were marked in Figure 9.1 as 160 points. Among the listed cultural resources, only a few come from the military and urban heritage. The assessment of these cultural/historical resources showed concentration patterns along streambed corridors, ridgelines, in the surroundings of urban areas, and inside of the protected areas.

9.3.2. Reclamation potential

The mining heritage being one of the most characteristic valuable resources of the area should be considered in the context of restoration possibilities (Conesa *et al.,* 2008a).

The mine tailings, because of their environmental threats to the environment and human health (D.P.O.L., 2004); and their transformation possibilities to the recreational and educational areas (Kabas *et al.,* 2011; Zornoza *et al.,* 2012b); are considered as primarily important reclamation points.

Table 9.1. Cultural-historical resources in Cartagena La Unión Mining District (developed using Martos-Miralles (2007))

Cultural resources	**Quantity**
Headframe	64
Chimneys of fabricas, storages, foundries and galleries	19
Mining stove	18
Mine galleries and various remnants	14
Flotation plant	11
Quarry	7
Explosive storage	4
Battery	2
Caves	2
Ancient settlement	2
House for managers	2
Tunnel	2
Roman way	1
Cemetery	1
Education house of miners	1
Market building	1
Hermit	1
Foundry	1
Hospital	1
Church	1
Factory of mining machines	1
Monastery	1
Museum	1
Passage	1
Villa	1
Total	160

9.3.3. Homogenous zones

Homogenous zones of landscape quality were examined by considering the land use classification of “Servicio de Cartografía, Consejería de Obras Públicas y Ordenación del Territorio” (Murcia) to clarify the interrelations between different land uses. Twelve different homogenous zones (Figure 9.4 and Table 9.2) are as follows:

1) Riverbeds

Dry riverbeds are located in the north of the area between protected areas and cultural resources.

2) Protected areas

Cover the largest areas among the classified categories being located generally in the coastline of the entire zone.

3) Protected agriculture

Although in the study area agricultural areas seem relatively independent from the other land uses, in a larger scale continuation of riverbeds towards the north provide a significant connection with them.

4) Geomorphological protection

The slopes greater than 50% are considered in geomorphologic protection (Decreto 57/2004). They are completely distributed to the entire zone.

5) Abandoned zones of national defense

These three areas are not directly connected with the post mining district but they are nested in the surrounding land uses. In the south two of them are inside of the environmental protection areas and one, in the west, is surrounded by industrial and natural areas.

Table 9.2. Areas covered by homogenous zones (ESRI, 2005).

Homogenous zones	**Area (km2)**	**Area (%)**
Riverbeds	1.7	5.6
Protected areas	6.6	21.6
Protected agriculture	0.3	1.0
Geomorphological protection	1.6	5.2
Zone of national defense	0.4	1.3
Post mining zone	4.9	16.1
Urban area	2.6	8.5
Suitable area for urbanization	0.7	2.3
Unprogrammed urban area	2.6	8.5
Portman Bay	0.1	0.3
Port	0.3	1.0
Natural zone	8.7	28.5

6) Post mining zone

The high visual impact generated by opencast mining in Cartagena-La Unión Mining District affects broad areas with the occupation of mining pits, sterile materials resulting from the mineral washing and the deteriorations of the land form (Decreto 57/2004). The environmental impacts of the long term mining activities include large areas of soils characterized by strong acidification processes, high salinity, accumulation of metals, deficiency of organic matter, and scare or null vegetation. High amounts of mine wastes, containing materials of high Fe-oxyhydroxides, sulphates, and potentially leachable elevated contents of heavy metals and metalloids (mainly Zn, Pb, Cd and As) due to extreme acidic conditions, were accumulated in almost 80 mine tailing ponds (Zornoza *et al.,* 2010). The government prohibited the dumping of the mining wastes to dry streambed and to the sea in 1955, and then the mining wastes were dumped to the terrain to create the mine tailing ponds until 1991. Nevertheless, these mine residues have been transported downstream during periods of high rainfall and runoff, while at the same time these unvegetated tailings have been exposed to eolian dispersion especially due to the semiarid climate conditions of the region (Garcia-Fernández and Romero-Díaz, 2009). As a consequence an excessive amount of toxic metals continue to relocate in the surrounding ecosystems. Especially in periods of high rainfall, streambeds have an important role in the transportation of these materials to the Mediterranean Sea coasts. Studies have reported 500 mg kg^{-1} As and 12,000 mg kg^{-1} Pb concentrations in the sediments of streambeds and in alluviums of nearby coastal marshes. Beside sediments and alluviums, also agricultural fields are negatively affected (Conesa and Schulin, 2010). With respect to the soil plant toxicity thresholds of Kabata-Pendias and Pendias (1992), typical crop phytotoxicity starts when As in shoots reaches 5-20 mg kg^{-1} and Pb upper toxic levels range from 100 to 500 mg kg^{-1}.

Stability of the tailings constitutes another risk factor for the public safety. In 1972 after strong rainfalls collapsing of a mine tailing caused the loss of one life. The high heavy metal concentration context of the tailings is an undesirable condition especially for nearby settlements (Conesa *et al.,* 2008a).

The mine tailings show a similar distribution to the mining heritage, being close to the streambed corridors and valleys especially resulting from the nature of mining process mechanism.

7) Urban area

The study area includes four population nuclei, La Unión mining town, and villages of Alumbres, Portman and Llano del Beal, with a population of 16745, 3371, 1044 and 2273, respectively (CREM, 2011). Atamaria resorts with its golf courses and wide green open spaces also take place as a newly emerging settlement.

8) Suitable area for urbanization

Several areas in the surroundings of the La Union Town are shown as suitable areas for future urban development (Decreto 57/2004).

9) Unprogrammed urban area

This area is occupied by a large part of significantly important industrial settlements. Its nearby location to the nature conservation areas takes attention.

10) Portman Bay

Approximately 57 million tons of wastes were dumped into the Mediterranean Sea over the operation period from 1957 to 1990. Almost 30 million of these wastes completely filled the Portman Bay getting 10 m depth at its center. The bay is considered one of the most contaminated spot in the entire Mediterranean (Conesa *et al.,* 2008a).

11) Port

This port is one of the major bulk ports of Spain having 3850 m of quays; especially it is important in liquid bulk, petroleum and gas. It has a clean traffic way which passes along the edge of the Cartagena City (Decreto 57/2004).

12) Natural zone

Apart from the classified categories above, the rest of the area was considered as natural zone. Even this zone presents a high vegetation biodiversity, negative effects of post-mining activities are also seen in some of these natural areas (Martinez-Martinez *et al.,* 2012).

9.4. Discussion

This study was realized to delineate the multifunctional greenway corridor by considering the preservation of the most significant resources and the reclamation potential of the Cartagena-La Unión Mining District. The first assessment was the determination of the significant resources (Figure 9.1). Among the significant resources related to the hydrologic network of the district, despite being a dry ecosystem, their numerous ecological values and important roles among humans were subjected to different researchs. For example; in Australia, Todd River is known with its cultural significance, while Mitchell River with its vehicle transport route characteristic, and some dry riverbeds serve as habitats for terrestrial biota; In Italy, Tagliamento River is used as wildlife corridors; and in Spain storage sites for organic matter . For safeguarding the many valuable aspects of dry riverbeds, protection of them should be incorporated into biodiversity and conservation planning studies (Steward *et al.,* 2012).

Greenway development supports nature protection, while realizing touristic and recreational achievements (Yu *et al.,* 2006). Hepcan *et al.,* (2009) explains the importance of the creation of ecological network, especially for fauna, between the key biodiversity areas in Izmir, Turkey and indicates the significance of other human dynamics for maintaining the viability of the networks. In this study proposed linkages between protected areas also would support the transportation of fauna, but a detailed inventory of the fauna is needed for further research. In terms of recreation it should be restated that nature conservation areas of the region especially in summer season are exposed to population increases due to the mass tourism purposes (Brugarolas-Molina, 2003). It is important to preserve these tourism activities as a part of ecotourism concept. The mentioned tourism attraction occurs in a totally isolated manner from the adjacent settlements and the post-mining district. The cultural-historical potential of the Cartagena-La Unión Mining District cannot participate to this tourism mobility even located on an important tourism route. Development of a greenway corridor would improve ecotourism activities in the region while triggering the reclamation activities.

The location of the protected agricultural fields in the north, inside and outside of the study area strengthens the idea of riverbed reclamation since they are the potential hydrological connectivity resources between the post mining district and the agricultural fields themselves (Bocchi *et al.,* 2012; Hoctor *et al.,* 2000). As indicated in Jongman *et al.,* (2004) on the contrary of the West European networks where it is mostly avoided to disturb the private ownership and the agricultural or forestry development, greenways with a nature conservation strategy should include the integration of agriculture and forestry.

Mining heritage was one of the most important driving forces for the creation of this greenway approach. It is the prominent historical-cultural, educational and recreational feature of the district. Greenways development without recreational elements is almost impossible (Erickson, 2004). Despite nationally recognition of this value, a legal conservation status in the context of mining heritage was not realized because of the lack of reclamation plans. This planning deficiency also affects the surrounding natural and protected areas negatively. Restoration of the mining heritage by valuating its recreational potential and its cooperation is fundamental for the creation of a greenway system in the district (Conesa *et al.,* 2008a). In the context of restoration and reclamation concept beside mining heritage, the reclamation of adequate mine tailings should be provided by evaluating their recreational, educational, and didactic potentials (Kabas *et al.,* 2011).

The interrelations between different land uses types were assessed by using distribution patterns of homogenous zones (Figure 9.4). Among these homogenous zones, riverbeds even if consist of wadis subjected to certain periodicity to flood risks; their incorporation into the conservation plannings were suggested (Steward *et al.,* 2012). In the distrcit they show a potential connectivity characteristic with their critical location between protected areas and cultural resources.

Preservation of nature conservation areas and providing connectivity through spatial connected landscapes between them are being very important in many countries (Hepcan *et al.,* 2009). By greenway approach this connectivity will be provided between separated parts of nature conservation areas in the district.

Geomorphologic protection areas are suitable only for hiking and nature protection (Decreto 57/2004). Because of their high visual fragility they have to take place in the greenway system by providing precautions for erosion risks (Beatriz Pena *et al.,* 2010). Spatially clustering character of these resources gives them a gap completing character between riverbeds, protected areas and cultural resources.

Abandoned zones of national defense generally take place in the coastline and have a touristic and cultural attraction in the region. Because of their location, they are suitable for being an end or start point of an excursion or hiking activity. The west one, surrounded by industrial and natural areas, is located next to the motorway, to city center and some popular beaches. Instead of realization its restoration, it has been included to a demolition project. Within the framework of this study their restoration and inclusion to the greenway corridor would be remarkable such the rest of cultural heritages.

Aforementioned environmental problems come from the past mining activities isolate the unique cultural-historical importance of Cartagena-La Unión Mining District and also protected areas nested in the study area are affected negatively under the press of serious environmental threats especially because of the construction of mine tailing ponds. It is obvious that the development of a reclamation plan is an urgent need for the region. Small initiatives of local administrations such as foundation of a mining park, restoration of several mining structures and plantation efforts should be supported with larger scale projects. Many surface mining artificial landscape forms can serve to recreational utilities such as green areas, golf courses, sculptural uses, or lakes as done in Anaconda copper smelter, Montana zinc mine tunnel or Utah gold mine (Berger, 2002). Furthermore the tourism mobility around the district can be canalized to the post mining district by the qualification of the mining heritage with ecotourism mobility as mentioned in the example of Australian open-cut coal mining landscapes (Satherley, 2006).

Creation of a greenway network makes contributions to ecotourism and socio-cultural mobility in the region, and thus the socio-economic requirements of the region can be supported once again. This socio-economic development would be particularly important for the La Unión mining town citizens who suffered because of its past mining-dependent socio-economic monocultural situation (Conesa *et al.,* 2008a).

Inclusion of some urbanizable areas to the greenway system was found to be suitable because of their location between riverbeds and cultural resources. Urban development in these areas is not recommendable.

The spontaneous distribution of the unprogrammed urban area causes landscape fragmentation. As indicated in Decreto 57/2004 it is obvious that the area cannot support more industrial developments. Its location creates quite negative effects on the city center and the protected areas. The area should be isolated from the surroundings by providing a buffer system. In the example of Michigan's Ramsar Wetland an industrial brownfield was transformed into an ecological buffer (Hartig *et al.,* 2012), but in the case of CLPMP because of the foreseeing land use planning deficiencies creation of a buffer system is more complicated.

Portman Bay is currently handled within the framework of an environmental reclamation project (Decreto 57/2004). The project proposes to construct a 45m wide and 250m length shoreline by transporting the contaminated sediments to a mining pit (BOE, 2011). Its critical location between protected areas and its negative effects to the marine ecosystem (Martinez-Coronado *et al.,* 2011) are the driving forces for its reclamation. In the case of reclamation its cooperation to the greenway system would be recommendable.

The port is mostly surrounded by the unprogrammed urban area, while only in the south surrounded by the protected areas. Separation of the port from the neighbor protected areas and thereby from the greenway corridor is recommendable. In this way, the negative effects arise from the contiguity of these conflicting land uses (commercial port and nature protected areas) can be minimized.

The natural zones are suitable to serve as buffer zones for the protection of greenway corridors and protected areas. Furthermore, their reclamation should be realized in the points that complete the gaps of the corridor system.

In the light of the considerations of the most significant areas, reclamation potential and distribution pattern of homogenous zones, greenway corridors were delineated as in Figure 9.5. In the corridor system interconnection of legally protected areas was suggested through the reclamation potential of the post mining district. This interconnection provides transference of the varieties from fauna, but a deeper investigation of the varieties is needed for any especial zoning in required places.

Landscape planning and reclamation in Cartagena-La Unión Mining District is an urgent regional requirement. In the study it is aimed to create a multifunctional greenway system to overcome this requirement minimizing the environmental risks originated from the past mining activities. Minimization of the environmental risks in the entire district is not totally feasible or economic. Development of a greenway corridor system would help to run the ecologic functions and social-economic processes in priority zones. For the subsequently ongoing self-reclamation process of the post-mining zone, improvements of these functions are vital. For the reclamation works that are not taking into account the natural processes with an integral approach, it is not possible to produce sustainable landscape reclamation and planning solutions.

9.5. Conclusion

Uses and potentials of greenways and the protection of ecologically significant corridors show that the greenways are appropriate means to integrate single purpose ideas and plans with a more comprehensive planning vision and that is greenways (Fabos, 1995). In this respect creating spatially and functionally interconnected landscapes create mutual advantages for both society and nature.

The urgent landscape reclamation and planning requirement of Cartagena La Union Mining District in an integrated manner has been hardly mentioned in Spain up to now. This study introduces the multifunctional greenway approach based on spatial interrelations of the most valuable resources, reclamation potentials and land uses. This multifunctional greenway approach can serve as landscape reclamation and planning tool in degraded areas by determining the priority zones of reclamation. In these vital veins of the area landscape planners have to be more decent with their land use decisions. Protection of the corridors has to be provided through a combination of land ownership, land use regulation and policies to avoid inappropriate land use developments in the corridors.

It is important to highlight that spatial and functional opportunities for social, cultural and economic demands have to be considered in an ecological context for the sustainability and viability of the proposed greenways.

CHAPTER 10

Scientific inferences of the thesis

In this chapter the main conclusions of the research are given as a summary:

- Total Pb, Zn, and Cd concentrations were markedly higher than the threshold values in both tailing ponds (El Lirio and El Gorguel). That means a reclamation program should be carried out in both ponds. High extractable concentrations of metals suggest high risk of mobility via plant uptake with the subsequent risk for the food chain, while high soluble concentrations are subject of transportation by runoff water that may reach streams or contaminate soils and even groundwater under the ponds and surrounding areas.

- Most of the waste properties of the studied ponds were similar, except the pH (pH 7.41 in El Lirio, pH 5.39 in El Gorguel). The spatial distribution of metals in the ponds is affected by the physicochemical properties and topography of ponds surface.

- For the purpose of reclamation, addition of marble waste and pig slurry in one year showed that initial pH of tailing materials determines the improvement to the environmental properties in tailing ponds (significant reductions to the DTPA- and water-soluble Zn, Pb are limited to the El Lirio site only. Unlike in the El Gorguel site, water-extractable Cd and Cu and DPTA-Cu did not vary with treatment and times in the El Lirio site). However, pH seems to have a minor regulatory role with respect to changes to key plant-related properties of tailings, because most of the studied edaphic properties are affected by the treatment and time, except (TS and CEC), in both tailing ponds. Addition of used amendments is beneficial to enhance the environmental and edaphic properties of tailing deposits.

- The applications of marble waste + pig slurry (MW+PS) and pig slurry (PS) were effective in the growth of native vegetation, increment of vegetation cover, richness and biodiversity, and in the reduction of heavy metals mobility in the tailing pond. Triggered plant growth by the effect of amendments improved soil conditions, particularly by the help of the medium created by their rhizosphere systems.

- According to the realized vegetation study, collected information showed that *P. miliaceum* plant species has the characteristics of phytostabilizer species. Even though *A. halimus* and *Z. fabago* made phytoextraction of Cu-Pb, they did not show the characteristics of hyperaccumulator species. Nonetheless, a monitoring of the evolution of plants with time and the heavy metal dynamics is needed to establish a better selection of the most adequate species to develop a phytostabilization program.

- The omni-presence of *Zygophyllum fabago* L. (Syrian bean-caper) natural colonies in post mining areas prompted us to investigate its contributions to reclamation of mine wastes deposits. The natural colonization by *Zygophyllum fabago* of mine wastes subjected to marble wastes and pig slurry applications improves edaphic and environmental properties of mine wastes materials. The initial colonization by *Z. fabago* likely will lead to secondary plant successions.

- The first of two major focuses in surface mine reclamation is the technical aspects concerning revegatation of the landscape and the science of reclamation. The second focus is in the planning and design arena addressing the creation of usable post-mining land. Cartagena-La Unión Mining District because of its fragmented land form has a potential for various kinds of land uses. But its inherent characteristics come from the mining activities and consequently essential reclamation processes reveal a higher land use potential which can integrate the reclamation with the landscape design. This integration can be realized by the installation of thematic parks. Additionally maintenance of historical and cultural values and generation of economic opportunities are significant to be considered in a landscape design that establishes connections between people and the place.

- In the mine tailing landscape design in which the revegetation reclamation techniques are used, it is important to know the heavy metal surface distribution in order to be able to realize the plantation design and to take the land use decisions.

- Landscape design has to be developed in a holistic manner. Pieces cannot be separated from the whole. For this reason in Cartagena La Unión Mining District while realizing the landscape designs of mine tailings, connections with the whole area should be provided. But providing these connections in Cartagena La Unión Mining District is not feasible, due to the landscape planning requirement of the whole area itself. Development of a greenway corridor would facilitate the landscape planning process.

- Instead of destroying natural or virgin lands to create new land uses, if it can be taken the advantage of the degraded areas, the potential land use problems of today and the future can be discarded.

CHAPTER 11

References

Acosta, J.A., Faz, A., Martinez-Martinez, S., 2009. Identification of heavy metal sources by multivariable analysis in a typical Mediterranean city (SE Spain). Environmental Monitoring and Assessment 169: 519-530.

Acosta, J.A., Faz, A., Martínez-Martínez, S., Zornoza, R., Carmona, D.M., Kabas, S., 2011. Multivariate statistical and GIS-based approach to evaluate heavy metals behavior in mine sites for future reclamation. Journal of Geochemical Exploration 109: 8-17.

Adriano, D.C., 2001. Trace Elements in Terrestrial Environments: Biogeochemistry, Bioavailability and Risks of Metals, second ed. Springer-Verlang, New York.

Almas, A., Singh, B.R., Salbu, B., 1999. Mobility of cadmium-109 and zinc-65 in soil influenced by equilibration time, temperature, and organic matter. Journal of Environmental Quality 28: 1742-1750.

Alvarenga, P., Gonçalves, A.P., Fernandes, R.M., de Varennes, A., Vallini, G., Duarte, E., 2008. Evaluation of composts and liming materials in the phytostabilization of a mine soil using perennial ryegrass. Science of the Total Environment 406: 43-56.

Alvarenga, P., Gonçalves, A.P., Fernandes, R.M., de Varennes, A., Vallini, G., Duarte, E., Cunha-Queda, A.C., 2009. Organic residues as immobilizing agents in aided phytostabilization: (I) Effects on soil chemical characteristics. Chemosphere 74: 1292-1300.

Alvim, M., Ferraz, C.M., Lourenco, J.C.N., 2000. The influence of organic matter content of contaminated soils on the leaching rate of heavy metals. Environmental Progress 19: 53-58.

Andrades, M., 1996. Prácticas de Edafología y Climatología. Universidad de la Rioja (Ed.). Logroño, La Rioja, España.

Angers, D.A., Chantigny, M.H., MacDonald, J.D., Rochette, P., Cote, D., 2010. Differential retention of carbon, nitrogen and phosphorus in grassland soil profiles with long-term manure application. Nutrient Cycling in Agroecosystems 86: 225-229.

Antrop, M., 2000. Background concepts for integrated landscape analysis. Agriculture, Ecosystems and Environment 77: 17-28.

Arocena, J.M., van Mourik, J.M., Faz Cano, Á., 2012. Granular soil structure indicates reclamation of degraded to productive soils: A case study in Southeast Spain. Canadian J Soil Science 92: 243-251.

Autier, V., White, D., 2004. Examination of cadmium sorption characteristics for a boreal soil near Fairbanks, Alaska. Journal of Hazardous Materials 106: 149-155.

Barker, A.V., 1997. Composition and uses of compost. In Agricultural uses of by-products and wastes. ACS Symposium Series No. 668, Vol 10, Rechling JE, Mackimon HC (eds). American Chemical Society, Washington DC, 140-162.

Beatriz Pena, S., Manuela Abreu, M., Teles, R., Espirito-Santo, M. D. (2010). A methodology for creating greenways through multidisciplinary sustainable landscape planning. Journal of Environmental Management 91: 970-983.

Beier, B.A., Chase, M.W., Thulin, M., 2003. Phylogenetic relationships and taxonomy of subfamily Zygophylloideae (Zygophyllaceae) based on molecular and morphological data. Plant Syst. Evol. 240: 11-39.

Berger, A., (Ed.) 2002. Reclaiming the American West. New York.

Bhagat, R.M., Verma, T.S., 1991. Impact of rice straw management on soil physical properties and wheat yield. Soil Science 152: 108-115.

Bocchi, S., La Rosa, D., Pileri, P., 2012. Agro-ecological analysis for the EU water framework directive: An applied case study for the river contract of the Seveso Basin (Italy). Environmental Management 50: 514-529.

BOE, 2011. Boletín Oficial del Estado (Government Official Bulletin). Núm. 45, Martes 22 de Febrero de 2011, Sec. III, pág. 20530-20560. ISSN: 0212-033X.

Boorjar, M.M., Tavakkoli, Z., 2011. Antioxidative responses and metal accumulation in invasive plant species growing on mine tailings in Zanjan, Iran. Pedosphere 21(6): 802-812.

Bouwman, L.A., Vangronsveld, J., 2004. Rehabilitation of the nematode fauna in a phytostabilized heavily zinc-contaminated, sandy soil. Journal of Soils and Sediments 4: 17-23.

Bowman, W.S., Faye, G.H., Sutarno, R., McKeague, J.A. and Kodama, H., 1979. Soil Samples SO-1, SO-2, SO-3 and SO-4. Certified Reference Materials. CANMET Report 79-3. CANMET Mining and Mineral Sciences Laboratories, Ottawa, ON. 34 pp.

Brady, N.C., Weil, R.R., 2001. The Nature and Properties of Soils (13th edition). Englewood, NJ: Prentice Hall. 960 pp.

Brady, N.C., Weil, R., 2007. Nature and properties of soil. 14th ed., Prentice Hall, New York.

Brallier, S., Harrison, R.B., Henry, C.L., Dongsen, X., 1996. Liming effects on availability of Cd, Cu, Ni and Zn in soil amended with sewage sludge 16 years previously. Water, Air and Soil Pollution 86: 195-206.

Brooks, R.R., 1998. Plant that hyperaccumulate heavy metals: their role in phytoremediation, microbiology, archaeology, mineral exploration and phytomining. Cab International, Wallingford, UK.

Brown, S.L., Sprenger M., Maxemchuk, A., Compton, H., 2005. Ecosystem function in alluvial tailings after biosolids and lime application. Journal of Environmental Quality 34: 1-6.

Brugarolas-Molina, C., 2003. El patrimonio natural de la región de Murcia (The natural heritage of the Murcia Region). Cuadernos de Biodiversidad 13: 11-17.

Bulluck III, L.R., Brosius, M., Evanylo, G.K., Ristaino, J.B., 2002. Organic and synthetic fertility amendments influence soil microbial, physical and chemical properties on organic and conventional farms. Applied Soil Ecology 19: 147-160.

Burgos, P., Madejon, E., Perez-de-Mora, A., Cabrera, F., 2006. Spatial variability of the chemical characteristics of a trace-element-contaminated soil before and after remediation. Geoderma 130: 157-175.

Burgos, P., Madejon, E., Perez-de-Mora, A., Cabrera, F., 2008. Horizontal and vertical variability of soil properties in a trace element contaminated area. International Journal of Applied Earth Observation and Geoinformation 10: 11-25.

Burley, J.B., 2001. Post mining land use reclamation: an introduction from a planning and design perspective. In: Environmental Design for Reclaiming Surface Mines. Burley, J.B. (ed.), ISBN 0-7734-7478-1, The Edwin Mellen Press, Lewiston, New York, USA. 1-25.

Burrough, P.A, McDonnell, R.A., 1998. Creating continuous surfaces from point data. In: Burrough, P.A., Goodchild, M.F., McDonnell, R.A., Switzer, P., Worboys, M. (Eds.), Principles of Geographic Information Systems. Oxford University Press, Oxford, UK.

CAM, 2000. California's Abandoned Mines. A Report on the Magnitude and Scope of the Issue in the State, Volume I, US Department of Conservation Office of Mine Reclamation Abandoned Mine Lands Unit.

CAAMA, 1999. Consejería de Agricultura Agua y Medio Ambiente de la Comunidad Autónoma de la Región de Murcia. Guía ambiental de minería en la Región de Murcia. 279 pp.

Carmona, D.M., Faz, Á., Zornoza, R., Büyükkiliç, A., Kabas, S., Acosta J.A., Martínez-Martínez, S., 2010. Influence of inorganic and organic amendments for mine soils reclamation on spontaneous vegetation colonization and metal plant bioaccumulation. 19th World Congress of Soil Science, Soil Solutions for a Changing World. 1-6 August 2010, Brisbane, Australia.

CDMG, 2002. Colorado Division of Minerals and Geology. Best Practices in Abandoned Mine Land Reclamation: The remediation of past mining activities. Published by the state of Colorado Department of Natural Resources Division of Minerals and Geology 2002.

This manual is also available as a Printable Document Format (PDF) file on the Internet at www.mining.state.co.us/bmp.pdf

Celine, S.L., Xiangdong, L., Wenzhong, S., Sharon, C., Iain, T., 2006. Metal contamination in urban, suburban, and country park soils of Hong Kong: A study based on GIS and multivariate statistics. Science of the Total Environment 356: 45-61.

Chambers, J., Sidle, R., 1991. Fate of heavy metals in an abandoned lead-zinc tailings pond: I. Vegetation. Journal of Environmental Quality 20(4): 745-751.

Chapman, H.D., 1965. Cation Exchange Capacity. In C. A. Black (ed). Methods of Soil Analysis. American Society of Agronomy. Madison, Wisconsin, U.S.A. 2, 891-900.

Cobertera, E., 1993. Edafología aplicada. Ediciones Cátedra S.A. Madrid. 326p.

Collins, G., 2001. The Principles of Mining. In: Environmental Design for Reclaiming Surface Mines. Burley, J.B. (ed.), ISBN 0-7734-7478-1, The Edwin Mellen Press, Lewiston, New York, USA. 27-47.

Collins, T., 2000. “Interventions in the rust belt: the art and ecology of postindustrial public space,” in Ecumene-A Journal of Cultural Geographies 7(4): 461-467.

Colorado, A.H., Giráldez, N.A., Luengo, C.A., 2011. Desarrollo sostenible y empleo en las vías verdes (Sustainable development and employment in the greenways). Printed by Gráficas La Paz. http://www.viasverdes.com/pdf/libro_emplea_verde_indices.pdf

Comp, T.A., 2008. Science, art, and environment reclamation: three projects and a few thoughts. In Designing the reclaimed landscape, A. Berger, Ed. New York, 63-76.

Conesa, H.M., 2005. Restauración/estabilización de suelos contaminados por metales pesados como consecuencia de actividades mineras en la zona de Cartagena y La Unión (in Spanish). PhD Dissertation. Universidad Politécnica de Cartagena.

Conesa, H.M., 2006. Restauración/estabilización de suelos contaminados por metales pesados como consecuencia de actividades mineras en la zona de Cartagena y la Unión. PhD Thesis, Technical University of Cartagena, Spain. 398 pp.

Conesa, H.M., Faz, A., 2009. Metal uptake by naturally occurring vegetation in a metal polluted salt marsh in southeast Spain, in: Faz, A., Mermut, A.R., Arocena, J.M., Ortiz, R. (Eds.), Land Degradation and Rehabilitation. CATENA VERLAG GMBH, 35447 Reiskirchen, Germany, 287-294.

Conesa, H.M., Faz Cano, A., Arnaldos, R., 2006. Heavy metal accumulation and tolerance in plants from mine tailings of the semiarid Cartagena-La Unión mining district (SE Spain). Science of the Total Environment 366: 1-11.

Conesa, H.M., Faz Cano, A., Arnaldos, R., 2007. Initial studies for the phytostabilization of a mine tailing from the Cartagena-La Union Mining District (SE Spain). Chemosphere, 66: 38-44.

Conesa, H.M., Faz, A., Arnaldos, R., 2007b. Initial studies for the phytostabilization of a mine tailing from the Cartagena-La Union Mining District (SE Spain). Chemosphere 66: 38-44.

Conesa, H.M., Garcia, G., Faz A., Arnaldos, R., 2007c. Dynamics of metal tolerant plant communities’ development in mine tailings from the Cartagena-La Unión Mining District (SE Spain) and their interest for further revegetation purposes. Chemosphere 68: 1180-1185.

Conesa, H.M., Moradia, A.B., Robinson, B.H., Kühneb, G., Lehmannb, E., Schulin, R., 2009. Response of native grasses and Cicer arietinum to soil polluted with mining wastes: Implications for the management of land adjacent to mine sites. Environmental and Experimental Botany 65: 198-204.

Conesa, H.M., Robinson, B.H., Schulin, R., Nowack, B., 2007a. Growth of Lygeum spartum in acid mine tailings: response of plants developed from seedlings, rhizomes and at field conditions. Environmental Pollution 145: 700-707.

Conesa, H.M., Robinson, B.H., Schulin, R., Nowack, B., 2008b. Metal extractability in acidic and neutral mine tailings from the Cartagena-La Union Mining District (SE Spain). Applied Geochemistry 23: 1232-1240.

Conesa, H.M., Schulin, R., Nowack, B., 2008a. Mining landscape: A cultural tourist opportunity or an environmental problem? The study case of the Cartagena-La Unión mining district (SE Spain), Ecological Economics 64: 690-700.

Conesa, H.M., Schulin, R., 2010. The Cartagena-La Unión mining district (SE Spain): a review of environmental problems and emerging phytoremediation solutions after fifteen years research. Journal of Environmental Monitoring 12(6): 1225-33.

Conine, A., Xiang, W.N., Young, J., Whitley, D., 2004. Planning for multi-purpose greenways in Concord, North Carolina. Landscape and Urban Planning 68: 271-287.

Council Directive 79/409/EEC, 1979. Conservation of wild birds.

Council Directive 91/676/EEC, 1991. Protection of waters against pollution caused by nitrates from agricultural sources. Official Journal L 375, pp 1-8, 31-12-1991.

Council Directive 92/43/EEC, 1992. Conservation of natural habitats and of wild fauna and flora.

Council Directive 98/83/EC, 1998. Quality of water intended for human consumption. Adopted by the Council on 3 November 1998.

CREM, 2011. Centro Regional de Estadística de Murcia (Regional Centre of Statistics of Murcia).

Cunningham, S.D., Berti, W.R., Huang, J.W.W., 1995. Phytoremediation of contaminated soils. Trends in Biotechnology 13: 393-397.

De la Rosa, G., Peralta-Videa, J.R., Montes, M., Parsons, J.G., Cano-Aguilera, I., Gardea-Torresdey, J.L., 2004. Cadmium uptake and translocation in tumbleweed (*Salsola kali*), a potential Cd-hyperaccumulator desert plant species: ICP/OES and XAS studies. Chemosphere 55, 1159-1168.

De Sousa, C.A., 2003. Turning brownfields into green space in the City of Toronto. Landscape and Urban Planning 62: 181-198.

Decreto 57/2004, de 18 de junio, por el que se aprueban las Directrices y Plan de Ordenación Territorial del Litoral de la Región de Murcia (Decree 57/2004, 18 of june, by approving the Guidelines and Spatial Plan for the Coastal Region of Murcia).

Degryse, F., Smolders, E., Parker, R.D., 2009. Partitioning of metals (Cd, Co, Cu, Ni, Pb, Zn) in soils: concepts, methodologies, prediction and applications - a review. European Journal of Soil Science 60: 590-612.

Dilts, T.E., 2007. Morphometric characterization of artificial post-mining landforms and natural landforms using a Geographic Information System. Master Thesis in Geography, University of Nevada, Reno, U.S.A. 71 pp.

Doumett, S., Lamperi, L., Checchini, L., Azzarello, E., Mugnai, S., Mancuso, S., Petruzzelli, G., Del Bubba, M., 2008. Heavy metal distribution between contaminated soil and *Paulownia tomentosa*, in a pilot-scale assisted phytoremediation study: Influence of different complexing agents. Chemosphere 72, 1481-1490.

D.P.O.L., 2004. Directrices y plan de ordenación territorial del litoral de la región de Murcia (Guidelines and land use plan for the coastal region of Murcia). Memoria. Consejería de Turismo y Ordenación del Territorio. Dirección General de Ordenación del Territorio y Costas, 80 pp.

Duchaufour, P., 1970. Précis de Pedologie. In Masson y Cie (Ed.). París.

Dudka, S., Adriano, D.C., 1997. Environmental impacts of metal ore mining and processing: A review. J. Environmental Quality 26: 590- 602.

EPA, 1997. U.S. Environmental Protection Agency, Appendix B - Potential Environmental Impacts of Hardrock Mining. This appendix is available as a Printable Document Format (PDF) file on the Internet at http://www.epa.gov/aml/policy/app_b.pdf

EPA, 2004. U.S. Environmental Protection Agency Abandoned Mine Lands Team, Reference Notebook.

Erickson, D.L., 2004. The relationship of historic city form and contemporary greenway implementation: a comparison of Milwaukee, Wisconsin (USA) and Ottawa, Ontario (Canada), Landscape and Urban Planning 68: 199-221.

Ernst, W.H.O., 1996. Bioavailability of heavy metals and decontamination of soils by plants. Applied Geochemistry 11: 163-167.

ESRI, 2005. ArcView 3.2 Software. Environmental Systems Research Institute, Redlands, CA.

EEB, 2000. European Environment Bureau. The Environmental Performance of the Mining Industry and the Action Necessary to Strengthen EU Legislation. In Hontelez, J. (Ed.). Document no. 2000/016, Brussels, 28 pp. http://www.eeb.org/publication/2000/Environmental_Performance_of_Mining_Industry.pdf.

European Greenways Info 15, 2012. European Greenways Association, 5 pp.

Fabos, J.G., 1995. Introduction and overview: the greenway movement, uses and potentials of greenways. Landscape and Urban Planning 33: 1-13.

F.A.O.-I.S.R.I.C., 2006. Guidelines for Soil Description. 4th edition (revised). F.A.O. Roma, 97pp.

Faz, A., Lozano R.A., Conesa, H.M., García, G., 2001. Soils affected by mining and industrial activities in Cartagena (SE Spain): classification problems. European Soil Bureau, Research Report No. 7: 165-170.

Faz, A., Martínez-Martínez, S., Acosta, J.A., Peñas, J., Aracil, E., Alcaraz, M., Conesa, H., García, G., García, C., Manteca, I., Martínez, P., Martínez, M., Rodríguez, T., Rodríguez, R., Trigueros, E., 2004. Risk assessment and restoration possibilities of some abandoned mining silt ponds in the region de Murcia: study case “El Lirio”. Fourth International Conference on Land Degradation. Cartagena. 357 pp.

Faz, A., Martínez-Pagan, P., Acosta, J.A., Carmona, D.M., Martínez-Martínez, S., Zornoza, R., Kabas, S., 2012. Risk Assessment in tailing ponds: Use of Electrical Tomography Tecnique. IRIS Working Document. 29 pp.

Felson, A.J., Pickett, S.T.A., 2005. Designed experiments: new approaches to studying urban ecosystems. Frontiers in Ecology and the Environment 3(10): 549-556.

Ferguson, C.C., 1998. Techniques for Handling Uncertainty and Variability in Risk Assessment Models. Umweltbundesamt, Berlin.

Fernandez-Caliani, J.C., Barba-Brioso, C., Gonzalez, I., Galan, E., 2009. Heavy metal pollution in soils around the abandoned mine sites of the Iberian Pyrite Belt (Southwest Spain). Water Air Soil Pollution 200: 211-226.

Fisher, T., 2006. The Art and Science of Mining Reclamation: An Integrated Approach to the Design of the Post-mined Landscape. Master of Landscape Architecture Department of Landscape Architecture University of Oregon. 117 pp.

Frischenbruder, M.T. M., Pellegrino, P., 2006. Using greenways to reclaim nature in Brazilian cities. Landscape and Urban Planning 76: 67-78.

Fundación Sierra Minera, 2001. Medio ambiente y empleo en la Sierra Minera de Cartagena-La Unión. Fundación Sierra Minera. 256 pp.

Fundación Sierra Minera, 2007. *Patrimonio Cultural y Yacimientos de Empleo en la Sierra Minera de Cartegena-La Unión*. Gráficas Alamo, S. L., Fuente-Alamo, Murcia.

Ganuza, A., Almendros, G., 2003. Organic carbon storage in soils of the Basque Country (Spain): the effect of the climate, vegetation type and edaphic variables. Biology and Fertility of Soils 37: 154-162.

Garcia-Fernández, G., Romero-Díaz, A., 2009. Environmental risks associated to wind erosion in a metal mining area from SE Spain. Congresos Científicos de la Universidad de Murcia, Congreso Internacional sobre Desertificación, Topic 2: Soil Erosion and desertification, 251-254.

García, G., Faz, Á., Conesa, H.M., 2003. Selection of autochthonous plant species from SE Spain for soil lead phytoremediation purposes. Water, Air and Soil Pollution 3: 243-250.

García, G., Faz, A., Cunha, M., 2004. Performance of *Piptatherum miliaceum* (Smilo grass) in edaphic Pb and Zn phytoremediation over a short growth period. International Biodeterioration & Biodegradation 54(2-3): 245-250.

García, G., Manteca, J.I., Faz, A., 2003. Riesgos y calidad ambiental de los terrenos del antiguo distrito minero de La Unión-Cartagena, Murcia. III Congreso Internacional sobre Patrimonio Geológico y Minero. Cartagena. Rábano, I., Manteca, I. and García, C. (Eds), 301-306.

Geebelen, W., Adriano, D.C., van der Lelie, D., Mench, M., Carleer, R., Clijsters, H., Vangronsveld, J., 2003. Selected biovailability assays to test the effect of amendment-induced immobilization of lead in soils. Plant and Soil 249: 217-228.

Gobster, P.H., 1999. An ecological aesthetic for forest landscape management. Landscape Journal 18: 54-64.

Gómez-Sal, A., Belmontes, J. A., Nicolau, J. M., 2003. Assessing landscape values: a proposal for a multidimensional conceptual model. Ecological Modelling 168: 319-341.

González-Alcaraz, M.N., Miguel Conesa H., Álvarez-Rogel J., 2013. When liming and revegetation contribute to the mobilisation of metals: Learning lessons for the phytomanagement of metal-polluted wetlands. Journal of Environmental Management 15: 72-80.

Goovaerts, P., 1998. Geostatistical tools for characterizing the spatial variability of microbiological and physico-chemical soil properties. Biology and Fertility of Soils 27: 315-334.

Gosar, M., 2004. Environmental impacts of metal mining. RMZ - Materials and Geoenvironment 51(4): 2097-2107.

Gutiérrez-Galindo, E.A., Muñoz-Barbosa, A., Walter, L., Macías-Zamora, J.V., Segovia-Zavala, J.A., 2007. Sources and factors influencing the spatial distribution of heavy metals in a coastal lagoon adjacent to the San Quintín volcanic field, Baja California, Mexico. Marine Pollution Bulletin 54: 1962-1989.

Hamon, R.E., McLaughlin, M.J., Cozens, G., 2002. Mechanisms of attenuation of metal availability in situ remediation treatments. Environmental Science & Technology 36: 3991-3996.

Hartig, J. H., Krueger, A., Rice, K., Niswander, S. F., Jenkins, B., Norwood, G., 2012. Transformation of an industrial brownfield into an ecological buffer for Michigan's only Ramsar wetland of international importance. Sustainability 4: 1043-1058.

Hatje, V., Payne, T.E., Hill, D.M., McOrist, G., Birch, G.F., Szymczak, R., 2003. Kinetics of trace element uptake and release by particles in estuarine waters: effects of pH, salinity, and particle loading. Environment International 29: 619-629.

Hepcan, S., Coskun Hepcan, Ç., Bouwma, I. M., Jongman, R. H. G., Özkan, M. B., 2009. Ecological networks as a new approach for nature conservation in Turkey: A case study of Izmir Province. Landscape and Urban Planning 90: 143-154.

Heywood, V.H.,1993. Flowering plants of the world. Oxford University Press Oxfordshire, UK. 336 pp.

Hoctor, T.S., Carr, M.H., Zwick, P.D., 2000. Identifying a Linked Reserve System Using a Regional Landscape Approach: the Florida Ecological Network. Conservation Biology 14 (4): 984-1000.

Hüttl, R.F., Gerwin, W., 2005. Landscape and ecosystem development after disturbance by mining, Ecological Engineering 24: 1-3.

Jacob, D.L., Otte, M.L., 2004. Influence of *Typha latifolia* and fertilization on metal mobility in two different Pb-Zn mine tailings types. Science of the Total Environment 333: 9-24.

Ji, P., Sun, T., Song, Y., Ackland, M.L., Liu, Y., 2011. Strategies for enhancing the phytoremediation of cadmium-contaminated agricultural soils by *Solanum nigrum* L. Environmental Pollution 159: 762-768.

Johnson, M.S., Bradshaw, A.D., 1977. Prevention of heavy metal pollution from mine wastes by vegetative stabilisation. Transactions of the Institution of Mining and Metallurgy A 86: 47-55.

Jongman, R. H. G., Külvik, M., Kristiansen, I., 2004. European ecological networks and greenways. Landscape and Urban Planning 68: 305-319.

Kabas, S., Faz, A., Carmona, D. M., Martinez-Martinez, S., Zornoza, R., Acosta, J. A., 2010. A landscape design approach for the sustainable reclamation activities of a post-mining area in Cartagena, SE Spain. Tailings and Mine Waste´10. Vail, Colorado, USA. 419-426

Kabas, S., Acosta, J.A., Zornoza, R., Faz Cano, A., Carmona, D.M., Martínez-Martínez, S., 2011. Integration of landscape reclamation and design in a mine tailing in Cartagena - La Unión, SE Spain. International Journal of Energy and Environment 5(2): 301-308.

Kabas, S., Faz, A., Acosta, J.A., Zornoza, R., Martinez-Martinez, S., Carmona, D.M., Bech, J., 2012. Effects of marble waste and pig slurry on the growth of native vegetation and heavy metal mobility in a mine tailing pond. Journal of Geochemical Exploration 123: 69-76.

Kabata-Pendias, A., Pendias, H., 1992. Trace elements in soils and plants. 2nd. ed. CRC Press, USA.

Kabata-Pendias, A., Pendias, H., 2001. Trace Elements in Soils and Plants, 3rd ed. CRC Press, Boca Raton, Florida.

Kabata-Pendias, A., 2004. Soil-plant transfer of trace elements - an environmental issue. Geoderma 122: 143-149.

Knoot, R., de Waal, R., 2009. Brown coal mining and rehabilitation: a landscape chronicle. Designing the rehabilitation of brown coal mines in Lusatia by integrating landscape narration with a landscape based approach to rehabilitation. Landscape Architecture Master Thesis, Wageningen University, Netherlands.

Kumar, P.B.A.N., Dushenkov V., Motto, H., Raskin, I., 1995. Phytoextraction: The use of plants to remove heavy metals from soils. Environmental Science and Technology 29(5): 1232-1238.

Kumpiene, J., Lagerkvist, A., Maurice, C., 2008. Stabilization of As, Cr, Cu, Pb and Zn in soil using amendments – A review. Waste Management 28: 215-225.

Land Information Bulletin, 1998. Land Information & Computer Graphics Facility. Technical Paper No. 1, University of Wisconsin- Madison.

Lasat, M.M., 2000. Phytoextraction of metals from contaminated soil: A review of plant/soil/metal interaction and assessment of pertinent agronomic issues. Journal of Hazardous Substance Research 2: 1-25.

Lefèvre, I., Corréal, E., Lutts, S., 2005. Cadmium tolerance and accumulation in the noxious weed *Zygophyllum fabago.* Canadian J Botany 83: 1655-1662.

Lefèvre, I., Corréal, E., Lutts, S., 2010. Impact of cadmium and zinc on growth and water status of *Zygophyllum fabago* in two contrasting metallicolous populations from SE Spain: comparison at whole plant and tissue level. Plant Biology 12: 883-894.

Leitão, A.B., Ahern, J., 2002. Applying landscape ecological concept and metrics in sustainable landscape planning. Landscape and Urban Planning 59: 65-93.

Lewis, P., 1964. Quality Corridors in Wisconsin. Landscape Architecture: 100-107.

Li, M. S., 2006. Ecological restoration of mineland with particular reference to the metalliferous mine wasteland in China: A review of research and practice. Science of the Total Environment 357: 38-53.

Lindsay, W.L., Norvell, W.A., 1978. Development of a DTPA soil test for Zn, Fe, Mn, and Cu. Soil Science Society of American Journal 42: 421-428.

Liu, L., Chen, H., Cai, P., Liang, W., Huang, Q., 2009. Immobilization and phytotoxicity of Cd in contaminated soil amended with chicken manure compost. Journal of Hazardous Materials 163: 563-567.

Liu, H., Probst, A., Liao, B., 2005. Metal contamination of soils crops affected by the Chenzhou lead/zinc mine spill (Hunan, China). Science of the Total Environment 339: 153-166.

Loures, L., Horta, D., Santos, A., Panagopoulos, T., 2006. Strategies to Reclaim Derelict Industrial Areas. WSEAS Transactions on Environment and Development 5(2): 599-604.

Loures, L., Panagopoulos, T., 2007. Sustainable reclamation of industrial areas in urban landscapes. Sustainable Development and Planning III. WIT Transactions on Ecology and the Environment 102: 791-800.

Loures, L., Panagopoulos T., Burley, J., 2010. Postindustrial land transformation: from theory to practise and vice-versa. In Proc. 3rd WSEAS International Conference on Urban Rehabilitation and Sustainability, Algarve, Portugal, 153-158.

Lutts, S., Lefevre, I., Delperee, C., Kivits, S., Dechamps, C., Robledo, A., Correal, E., 2004. Heavy metal accumulation by the halophyte species Mediterranean saltbush. Journal of Environmental Quality 33: 1271-1279.

Luymes, D.T., Tamminga, K., 1995. Integrating public safety and use into planning urban greenways. Landscape and Urban Planning 33: 391-400.

Manta, D.S., Angelone, M., Bellanca, A., Neri, R., Sprovieri, M., 2002. Heavy metals in urban soils: a case study from the city of Palermo (Sicily), Italy. Science of the Total Environment 300: 229-243.

Manteca, J., Berrocal, M., 1997. Sobre la creación de un parque geominero y arqueoindustrial en La Unión (Murcia) como medida de protección y puesta en valor del patrimonio histórico-minero. II Congreso Empresarial COEC. Desarrollo Turístico-Económico de la comarca de Cartagena. Cartagena, 20-21 February of 1997. 181-199 pp.

Markus, J., McBratney, A.B., 2001. A review of the contamination of soil with lead: II. Spatial distribution and risk assessment of soil lead. Environmental International 27: 399-411.

Martínez-Coronado, A., Oyarzun, R., Esbrí, J. M., Llanos, W., Higueras, P., 2011. Sampling high to extremely high Hg concentrations at the Cerco de Almadenejos, Almadén mining district (Spain): The old metallurgical precinct (1794 to 1861 AD) and surrounding areas. Journal of Geochemical Exploration 109: 70-77.

Martinez-Martinez, S., Acosta, J. A., Faz Cano, A., Carmona, D. M., Zornoza, R., Cerda, C., 2012. Assessment of the lead and zinc contents in natural soils and tailing ponds from the Cartagena-La Unión mining district, SE Spain. Journal of Geochemical Exploration 124: 166-175.

Martínez, Pérez, 2007. Niveles de fondo y niveles genéricos de referencia de metales pesados en suelos de la Región de Murcia. Murcia. 304 pp.

Martínez-Sánchez, M.J., García-Lorenzo, M.L., Pérez-Sirvent, C., Bech, J., 2012. Trace element accumulation in plants from an aridic area affected by mining activities. Journal of Geochemical Exploration 123: 8-12.

Martos-Miralles, P., 2007. Patrimonio cultural y yacimientos de empleo en la Sierra Minera de Cartagena-La Unión (Cultural heritage and mine sites in the Sierra Minera de Cartagena-La Unión). Fundacion Sierra Minera, 2nd. ed, Cartagena, Spain.

McBride, M.B., 1994. Environmental chemistry of soils. Oxford University Press, New York.

McBride, M., Sauve, S., Hendershot, W., 1997. Solubility control of Cu, Zn, Cd and Pb in contaminated soils. European Journal of Soil Science 48: 337-346.

Mchaina, D.M., 2001. Environmental planning considerations for the decommissioning, closure and reclamation of a mine site, International Journal of Surface Mining, Reclamation and Environment 15(3): 163-176.

Melendo, M., Benítez, E., Nogales, R., 2002. Assessment of the feasibility of endogenous Mediterranean species for phytoremediation of lead-contaminated areas. Fresenius Envirnomental Bulletin 11: 1105-1109.

Mendez, M.O., Maier, R.M., 2008. Phytostabilization of Mine Tailings in Arid and Semiarid Environments-An Emerging Remediation Technology. Environmental Health Perspectives 116 (3): 278-283.

Mendiguchía, C., Moreno, C., Galindo, R.M.D., García-Vargas, M., 2004. Using chemometric tools to assess anthropogenic effects in river water. A case study: Guadalquivir River (Spain). Analytica Chimica Acta 515: 143-149.

Merino, A., Macías, F., García-Rodeja, E., 1998. Aluminium dynamics in experimentally acidified soils from a humid-temperate region of South Europe. Chemosphere 36: 1137-1142.

Mertens, J., Vervaeke, P., De Schrijver, A., Luyssaert, S., 2004. Metal uptake by young trees from dredged brackish sediment: limitations and possibilities for phytoextraction and phytostabilisation. Science of the Total Environment 326: 209-215.

Michelutti, B., Wiseman, M., 1995. Engineered wetlands as a tailings rehabilitation. In: Environmetnal restoration of the industrial city. Lal, R., Stewart, B.A. (Eds.) Springer-Verlag, Berlin. 135-141.

Micó, C., Recatalá, L., Peris, M., Sánchez, J., 2006. Assessing heavy metal sources in agricultural soils of an European Mediterranean area by multivariate analysis. Chemosphere 65: 863-872.

Micsak, R.W., 2008. The legal landscape. In Designing the reclaimed landscape, A. Berger, Ed. New York, 154-164.

Miller, W., Collins, M. G., Steiner, F. R., Cook, E., 1998. An approach for greenway suitability analysis. Landscape and Urban Planning 42: 91-105.

Ministerial Decree, 1999. Italian Official Gazzette no. 293, 15. December 1999.

Ministry of Housing, 1994. Spatial Planning and the Environment. Intervention and Target Values-Soil Quality Standards. The Netherlands.

National Research Council, 2003. Bioavailability of Contaminants in Soils and Sediments: Process, Tools and Applications. The National Academies Press, Washington, DC.

Newson, T.A., Fahey, M., 2003. Measurement of evaporation from saline tailings storages: Third British Geotechnical Society Geoenvironmental Engineering Conference. Eng Geol 70: 217-233.

Nieratko, P.E., Burley, J.B., 2003. Surface Mine Reclamation Settings: Facilitating Landscape Planning, Design, and Management Education, 2003 National Meeting of the Amerikan Society of Mining and Reclamation and the 9th Billings Land Reclamation Symposium, Billings MT, June 3-6, 2003. Published by ASMR, 3134 Montavesta Rd., Lexington, KY 40502.

Norusis, M.J., 1993. SPSS for Windows Base System User's Guide Release 6.0, SPSS Inc.

Norvell, W.A., 1984. Comparison of chelating agents as extractants for metals in diverse soil materials. Soil Science Society of America Journal 48, 1285-1292.

Oen, I.S., Fernández, J.C., Manteca, J.I., 1975. The lead-zinc and associated ores of La Unión, Sierra de Cartagena, Spain. Economy Geology 70, 1259-1278.

Oorts, K., Vanlauwe, B., Merckx, R., 2003. Cation exchange capacities of soil organic matter fractions in a Ferric Lixisol with different organic matter inputs. Agriculture, Ecosystems and Environment 100: 161-171.

Ordoñez, A., Alvarez, R., Charlesworth, S., De Miguel, E., Loredo, J., 2011. Risk assessment of soils contaminated by mercury mining, Northern Spain. Journal of Environmental Monitoring: 13, 128-136.

Orozco, J.M.M., Huete, F.V., Alonzo, S.G., 1993. Environmental problems and proposals to reclaim the areas affected by mining exploitations in the Cartagena Mountains (southeast Spain). Landscape and Urban Planning 23: 195-207.

Ortega, M., Nicolás, E., Esteve, M., Torres, A., Ramírez-Díaz, L., 1993. Prioridades en la restauración e integración paisajística de la Sierra Minera de La Unión y Cartagena (Murcia, Sureste de España): inventario, cartografía y tipología de cortas, balsas y escombreras. Problemática ambiental y desarrollo. V Reunión Nacional de Geología ambiental y Ordenación del Territorio. Murcia, 1993. Otiz Silla, R. (Ed.). 307-316.

Ottenhof, C.J.M., Faz Cano, Á., Arocena, J.M., Nierop, K.G.J., Verstraten, J.M., van Mourik, J.M., 2007. Soil organic matter from pioneer species and its implications to phytostabilization of mined sites in the Sierra de Cartagena (Spain). Chemosphere 69: 1341-1350.

Paalman, M.A.A., van der Weijden, C.H., Loch, J.P.G., 1994. Sorption of cadmium on suspended matter under estuarine conditions: competition and complexation with major seawater ions. Water, Air, and Soil Pollution 73: 49-60.

Pastor, J., Martín-Aparicio, A., Gutierrez-Maroto, A., Hernández, A.J., 2007. Effects of two chelating agents (EDTA and DTPA) on the autochthonous vegetation of soil polluted with Cu, Zn and Cd. Science of the Total Environment 378: 114-118.

Pavloudakis, F., Galetakis, M., Roumpos, Ch., 2009. A spatial decision support system for the optimal environmental reclamation of open-pit coal mines in Greece, International Journal of Mining, Reclamation and Environment 23(4): 291-303.

Peech, M., 1965. Hidrogen-ion activity. In C.A. Black (ed.). Methods or Soil Analisis. American Society of Agronomy. Madison, Wisconsin, U.S.A. 2, 914-916.

Penrod, K., Cabanero, C. R., Beier, P., Luke, C., Spencer, W., Rubin, E., Sauvajot, R. M., Riley, S., Kamradt, D., 2006. South coast missing linkages project. A linkage design for the Santa Monica–Sierra Madre Connection. South Coast Wildlands and National Park Service, p. 107.

Pérez-Esteban, J., Escolástico, C., Ruiz-Fernández, J.,Masaguer, A., Moliner, A., 2011. Bioavailability and extraction of heavy metals from contaminated soil by *Atriplex halimus*. Environmental and Experimental Botany 88: 53-59

Pérez de Mora, A., Burgos, P., Madejón, E., Cabrera, F., Jaeckel, P., Schloter, M., 2006. Microbial community structure and function in a soil contaminated by heavy metals: effects of plant growth and different amendments. Soil Biology & Biochemisty 38: 327-341.

Pérez de Mora, A., Ortega-Calvo, J.J., Cabrera, F., Madejón, E., 2005. Changes in enzyme activities and microbial biomass after “in situ” remediation of a heavy metal-contaminated soil. Applied Soil Ecology 28: 125-137.

Peris, M., Recatalá, L., Micó, C., Sánchez, R., Sánchez, J., 2008. Increasing the knowledge of heavy metal contents and sources in agricultural soils of the European Mediterranean region. Water, Air Soil Pollution 37: 192-25.

Peters, T.H., 1984. Rehabilitation of mine tailings: A case of complete ecosystem reconstruction and revegetation of industrially stressed lands in the Sudbury Area, Ontario, Canada, in: Sheehan, P.J., Miller, D.R., Butler, G.C., Bourdeau, Ph. (Eds.), Effects of pollutants at the ecosystem level. John Wiley & Sons Ltd, Norwich, UK, 403-421.

Peu, P., Birgand, F., Martinez, J., 2007. Long term fate of slurry derived nitrogen in soil: A case study with a macro-lysimeter experiment having received high loads of pig slurry (Solepur). Bioresource Technology 98: 3228-3234.

QERM, 1995. Queensland Government, Department of Environment and Resource Management. Determination of Post-Mining Land Use. 1-6. (This guideline is available as a Printable Document Format (PDF) file on the Internet at http://www.derm.qld.gov.au/register/p01206ad.pdf)

Rauret, G., 1998. Extraction procedures for the determination of heavy metals in contamined soils and sediment. Talanta 46: 449-455.

Real Decreto 1310/1990, de 29 de octubre, por el que se Regula la Utilización de los Lodos de Depuración en el Sector Agrario. BOE nº 262 de 1 de noviembre de 1990, Madrid, 32339-32340.

Ribeiro, L., Barao, T., 2006. Greenways for recreation and maintenance of landscape quality: five case studies in Portugal. Landscape and Urban Planning 76: 79-97.

Risser, J.A., Baker, D.E., 1990. Testing soils for toxic metals. In R. L. Westerman (ed) Soil Testing and plant analysis. Soil Sci. Soc. Amer. Spec. Publ. 3. 3rd ed., Madison, Wisconsin, 275-298.

Roche, C., 1991. Syrian beancaper (*Zygophyllum fabago* L.) Pacific Northwest Extension Publication PNW-370. WSU Cooperative Extension, Pullman, Wash.

Rochette, P., Angers, D. A., Cote, D., 2000. Soil carbon and nitrogen dynamics following application of pig slurry for the 19th consecutive year: I. Carbon dioxide fluxes and microbial biomass carbon. Soil Science Society of American Journal 64: 1389-1395.

Rodrigues-Ramos, B., Panagopoulos, T., 2007. Integrating Aesthetic and Sustainable Principles in Stream Reclamation Projects. WSEAS Transactions on Environment and Development 11(3): 189-195.

Rodriguez, L., Ruiz, E., Alonso-Azcarate, J., Rincon, J., 2009. Heavy metal distribution and chemical speciation in tailings and soils around a Pb-Zn mine in Spain. Journal of Environmental Management 90: 1106-1116.

Roig, A., Romero, M., Lax, A. and Fernández, F.G., 1980. Estudio comparativo de métodos de determinación de capacidad de cambio catiónica en suelos calizos. Anales de Edafología y Agrobiología 39: 2021-2032.

Romic, M., Romic, D., 2002. Heavy metals distribution in agricultural topsoils in urban area. Environmental Geology 43: 795-805.

Ros, M., 1997. Estudio de paisajes para una aproximación a la ordenación ambiental de la minería a cielo abierto en la Región de Murcia. Tesis doctoral. Univ. Murcia. 494 pp.

Ross, S.M., 1994. Retention, transformation and mobility of toxic metals in soils. In: Ross, S.M. (Ed.), Toxic Metals in Soil–plant Systems. John Wiley and Sons Ltd, Chichester, UK, 63-152.

Ross, C., 1999. Mine revegetation in Nevada: the state of the art in the arid zone. In: Closure, remediation and management of precious metal heap leach facilities. Kosich, D., Miller, G. (eds). Center for Environmental Sciences and Engineering, University of Nevada, Reno. 71-76.

Sáez, A., 1998. Libro de La Unión. 171 pp.

Sasmaz, A., Sasmaz, M., 2009. The phytoremediation potential for strontium of indigenous plants growing in a mining area. Environmental and Experimental Botany 67: 139-144.

Satherley, S. D., 2006. Reconnecting the interrupted landscape: a theoretical framework to support ethically responsible design. People, Methods, Application, Brisbane, Qld.

Schulz, F., Wiegleb, G., 2000. Development options of natural habitats in a post-mining landscape. Land Degradation and Development 11: 99-110.

Serrano, M., Sanz, L., Puig, J., Pons, J., 2002. Landscape fragmentation caused by the transport network in Navarra (Spain) Two-scale analysis and landscape integration assessment. Landscape and Urban Planning 58: 113-123.

Shannon, C., 1948. A mathematical theory of communication. The Bell System Technical Journal 27: 379-423.

Sims, J.T., Johnson, G.V., 1991. Micronutrients soil tests, second ed. In: Mortvedt, J.J., Cox, F.R., Shuman, L.M., Welch, R.M. (Eds.),Micronutrients in Agriculture, vol. 4 Soil Science Society of America Inc., Madison, Wisconsin, United States, 427-476.

Six, J., Bossuyt, H., Degryze, S., Denef, K., 2004. A history of research on the link between aggregates, soil biota, and soil organic matter dynamics. Soil and Tillage Research 79: 7-31.

Sklenicka, P., Prikryl, I., Svoboda, I., Lhota, T., 2004. Non-productive principles of landscape rehabilitation after long-term opencast mining in north-west Bohemia. The Journal of the South African Institute of Mining and Metallurgy: 83-88.

Smith, R.A.H., Bradshaw, A.D., 1979. The use of metal tolerant plant populations for the reclamation of metalliferous wastes. Journal of Applied Ecology 16: 595-612.

SMMPE, 1983. Sociedad Minero Metalúrgica Peñarroya España. Libro del centenario 881-1981. ISBN: 84-398-0334-6. Madrid. 757 pp.

SMRE, 2000. U.S. Office of Surface Mining Reclamation and Enforcement. Post Mining Land Use, Exceptions to Approximate Original Contour Requirements for Mountaintop Removal Operations and Steep Slope Mining Operations, June 2000, http://www.dmme.virginia.gov/DMLR/Adobe/mtpmlureport.pdf

Sobek, A. A., Schuller, W. A., Freeman, J. R., Smith, R. M., 1978. Field and Laboratory Methods Applicable to Overburdens and Minesoils. Report EPA-600/2-78-054, U.S. National Technical Information Report PB-280 495.

Soil Survey Division Staff, 1993. Soil survey manual. Soil Conservation Service. U.S. Department of Agriculture Handbook 18.

Soil Survey Staff, 2004. Soil survey laboratory methods manual. Version No. 4.0. USDA NRCS. Soil Survey Investigations Report No. 42. U.S. Govt. Print. Office, Washington D.C.

Sollins, P., Swanston, C., Kleberc, M., Filley, T., Kramere, M., Crowa, S., Caldwella, B.A., Lajthaa, K., Bowden, R., 2006. Organic C and N stabilization in a forest soil: evidence from sequential density fractionation. Soil Biol. Biochem. 38: 3313-3324.

Souflias, G., Kallithakas-Kontos, N., Gekas, V., 2008. “Removal of heavy metals from wastewaters using Greek coals,” in Proc. 4th IASME/WSEAS International Conference on Energy, Environment, Ecosystems and Sustainable Development (EEESD'08), Algarve, Portugal, 397-401.

StatSoft Inc., 2011. STATISTICA (data analysis software system), version 10. www.statsoft.com.

Stevenson, F.J., 1994. Humus Chemistry: Genesis, Composition, Reactions. 2nd ed. Wiley, New York.

Steward, A. L., Schiller, D., Tockner, K., Marshall, J. C., Bunn, S. E. (2012). When the river runs dry: human and ecological values of dry riverbeds. Front Ecol Environ 10(4): 202-209.

Sudhalakhsmi, C., Velu, V., Thiyagarajan T.M., 2007. Redox Potential in the Rhizosphere Soil of Rice Hybrid as Mediated by Crop Management Options. Research Journal of Agriculture and Biological Sciences 3(4): 299-301.

Sung-Hyun, K., Kyung, H.B., Hye, W.L., In-Sook, L., 2008. Microbial abundance and diversity during phytoremediation of military site. In Proc. 4th IASME/WSEAS International Conference on Energy,Environment, Ecosystems and Sustainable Development (EEESD'08),Algarve, Portugal, 315-317.

Swanson, D.A., Barbour, S.L., Wilson, G.W., 1997. Dry-site versus wetsite cover design. In: Proceedings of the Fourth International Conference on Acid Rock Drainage, 31 May–6 June 1997, Vancouver, Canada. Ottawa, Canada: Mine Environment Neutral Drainage Program. 1595-1610.

Sylvia, D.M., 1998. Mycorrhizal symbiosis. In: Sylvia DM, Fuhrmann JJ, Hartel PG, Zuberer DA eds. Principles and Applications of Soil Microbiology. Prentice Hall, New Jersey, USA, 408-426.

Tariq, S.R., Shah, M.H., Shaheen, N., 2006. Multivariate analysis of trace metal levels in tannery effluents in relation to soil and water:Acase study from Peshawar, Pakistan. Journal of Environmental Management 79: 20-29.

Termorshuizen, J.W., Opdam, P., Brink, A., 2007. Incorporating ecological sustainability into landscape planning. Landscape and Urban Planning 79: 374-384.

Tjasa, G.B., Maja, Z.J., Jaka, R., Alexis, Z., Marco, Z., 2007. Phytoremediation of Tannery Landfill Site. In Abstract Book of Cost 859 Phytotechnologies to promote sustainable land use and improve food safety, Vilnius, Lithuania.121-122.

Toccolini, A., Fumagalli, N., Senes, G., 2006. Greenways planning in Italy: The Lambro River Valley Greenways System. Landscape and Urban Planning 76: 98-111.

Toorn, M.v.d., 2007. Environmental Education and Design; The role of landscape architecture. In Proc. 5th WSEAS Int. Conf. on Environment, Ecosystems and Development, Tenerife, Spain. 451-462.

Tordoff, G.M., Baker, A.J.M., Willis, A.J., 2000. Current approaches to the revegetation and reclamation of metalliferous mine wastes, Chemosphere 41: 219-228.

Tuason, M.M.S., Arocena, J.M., 2009. Root organic acid exudates and properties of rhizosphere soils of white spruce (*Picea glauca*) and subalpine fir (*Abies lasiocarpa*). Canadian Journal of Soil Science 89: 287-300.

Uemura, G., Menezes, M.Â.B. C., 2007. Neutron Activiation, k0-Method, as a tool for phytoremediation studies and reclamation of degraded areas. In International Nuclear Atlantic Conference – INAC 2007, Santos, SP, Brazil, ISBN: 978-85-99141-02-1.

Unterbrunner, R., Puschenreiter, M., Sommer, P., Wieshammer, G., Tlustoš, P., Zupan, M., Wenzel, W.W., 2007. Heavy metal accumulation in trees growing on contaminated sites in Central Europe. Environmental Pollution 148: 107-114.

Urbano, P.,2001. Tratado de fitofecnia general. Ed. Mundi Prensa. Madrid. 895 pp.

US EPA, 2007. Drinking water standards and health advisories table. USA, San Francisco. 30 pp.

Vangronsveld, J., Cunningham, S., 1998. Introduction to concepts. In: *In situ* inactivation and phytorrestoration of metal contaminated soils. Vangronsveld, J., Cunningham, S. (eds). Springer-Verlag and RG Landes Company. Berlin and Georgetown. 1-15.

Vangronsveld, J., Sterckx, J., Van Assche, F., Clijsters, H., 1995. Rehabilitation studies on an old non-ferrous waste dumping ground: effects of revegetation and metal immobilization by beringite. Journal of Geochemical Exploration 52: 221-229.

Vilar, J., Egea, P., 1990. La minería murciana contemporánea (1840-1930). ISBN: 84-505-1119-4. 389 pp.

Vilar, J., Egea, P., Fernández, J., 1991. La minería murciana contemporánea (1930-1985). Instituto Tecnológico Geominero de España. ISBN: 84-7840-050-8. Madrid, España. 256 pp.

Walker, D.J., Clemente, R., Pilar Bernal, M., 2004. Contrasting effects of manure and compost on soil pH, heavy metal availability and growth of *Chenopodium album* L. in a soil contaminated by pyritic mine waste. Chemosphere 57: 215-224.

Wang, Y., Dawson, R., Han, D., Peng, J., Liu, Z., Ding, Y., 2001. Landscape ecological planning and design of degraded mining land, Land Degradation and Development 12: 449-459.

Warhurst, A., 2000. Mining, mineral processing, and extractive metallurgy: an overview of the technologies and their impact on the physical environment. In: Environmental Policy in Mining: Corporate Strategy and Planning for Closure. Warhurst, A., Noronha, L. (eds). Boca Raton, FL: CRC Press LLC.

WHO, 2011. Drinking water quality. Geneva, World Health Organization. 564 pp.

Wong, M.H., 2003. Ecological restoration of mine degraded soils, with emphasis on metal contaminated soils. Chemosphere 50: 775-780.

Wright, D.J., Otte, M.L., 1999. Wetland plant effects on the biogeochemistry of metals beyond the rhizosphere. Biology and Environment 99: 3-10.

Yin, Y., Impellitteri, C.A., You, S.J., Allen, H.E., 2002. The importance of organic matter distribution and extract soil:solution ratio on the desorption of heavy metals from soils. The Science of the Total Environment 287: 107-119.

Yokohari, M., Amemiya, M., Amati, M., 2006. The history and future directions of greenways in Japanese New Towns. Landscape and Urban Planning 76: 210-222.

Yu, K., Li, D., Li, N., 2006. The evolution of greenways in China. Landscape and Urban Planning 76: 223-239.

Zanuzzi, A., 2007. Reducción de impactos ambientales asociados a suelos contaminados por metales pesados mediante el uso de residuos antropogénicos (in Spanish). PhD Dissertation. Departamento de Ciencia y Tecnología Agraria. Universidad Politécnica de Cartagena. 468 pp.

Zanuzzi, A., Arocena, J. M., van Mourik, J. M., Faz Cano, A., 2009a. Amendments with organic and industrial wastes stimulate soil formation in mine tailings as revealed by micromorphology. Geoderma 154: 69-75.

Zanuzzi, A., Faz, A., Loring, T., 2009b. Recommendations for the phytostabilization of acidic mine tailings from SE Spain. Land Degradation and Rehabilitation–Drylands Ecosystems. Advances and GeoEcology 40. Catena Verlag publishers GMBH. 377-389 pp.

Zhang, C., Selinus, O., 1998. Statistics and GIS in environmental geochemistry some problems and solutions. Geochemical Exploration 64: 339-354.

Zornoza, R,. Carmona, D.M., Acosta, J.A., Martinez-Martinez, S., Weiss, N., Faz, A., 2011. The effect of former mining activities on contamination dynamics in sediments, surface water and vegetation in El Avenque Stream, SE Spain. Water, Air & Soil Pollution 223: 519-532.

Zornoza, R., Faz, Á., Carmona, D.M., Büyükkiliç, A., Kabas, S., Martínez-Martínez, S., Acosta, J.A., 2010. Long-term effects of mine soil reclamation using different amendments on microbial and biochemical properties in Southeast Spain. In Proc. 19th World Congress of Soil Science; Soil Solutions for a Changing World, R.J. Gilkes, N. Prakongkep, Ed. Brisbane, Australia, 173-176.

Zornoza, R., Faz, A., Carmona, D. M., Kabas, S., Martinez-Martinez, S., Acosta, J. A., 2012. Plant cover and soil biochemical properties in a mine tailing pond five years after application of marble wastes and organic amendments. Pedosphere 22: 22-32.

Zornoza, R., Faz, A., Parra, A., Martinez-Martinez, S., Gomez, M.D., Acosta, J.A., 2012b. Landscape rehabilitation of an abandoned tailing pond in southeast Spain. Proceedings Tailings and Mine Waste 2012, Colorado, USA. 493-501 pp.