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ASSESSMENT OF ENVIRONMENTAL IMPACT OF TAILING DUMPS IN CHADAK MINING AREA, UZBEKISTAN

Presented by
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ASSESSMENT OF ENVIRONMENTAL IMPACT OF TAILING DUMPS IN CHADAK MINING AREA, UZBEKISTAN

Memorandum presented by OBIDJON KODIROV, under the supervision of Prof.Dr. Francisco J. Martín Peinado and Dr. Nosir Shukurov, to obtain the International PhD Degree.

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DEDICATED

To

My Beloved Father
An honest man with big heart who supported and
encouraged me in all my endeavors. "God bless his soul
and makes the resting place of Paradise"

My Beloved Mother
A strong and gentle soul who loves her children with
all their faults and keeping praying for our prosperity

My Beloved Wife and Children
For endless love, great support and continuous care

To my Brothers and sisters
For their help and criticism when necessary

To all of my nephews and nieces
For having joyful and funny moments

Corruption has appeared throughout the land and sea by [reason of] what the hands of people have earned; so He may let them taste part of the consequences of what they have done that perhaps they will return [to righteousness] (Quran, 30:41)

بسم الله الرحمن الرحيم

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ABSTRACT

Of all the diversity of man-made wastes, the problems associated with mining wastes have a great concern. The characterization is the first step to find a solution to the potential pollution related to these areas and to prevent environmental risk to living organisms. A set of processes that adversely affect the environment is associated with mine wastes that include pollution of adjacent soils, water and air with toxic elements. In this work, the assessment of potential trace elements contamination in tailing dumps and soils was characterized in the Chadak mining area (Uzbekistan). Hence, the main objective of this work is to assess the environmental impact of metals and metalloids coming from waste rock piles and tailing dumps generated during processing of the Chadak Au-Ag deposit, by characterizing the potentially contaminating elements and assessing their toxicity. The studies and results obtained have covered a knowledge gap in relation to the evaluation of the potential pollution of the environment in this area.

Concentrations of trace elements (V, Cr, Co, Ni, Cu, Zn, As, Cd, Sb, Pb) were determined by X-ray fluorescence analysis and compared with background (BC) and intervention values (IV). The concentrations of As, Zn, Sb, and Pb exceeded the BC in most cases and were higher in the abandoned than in the active tailing dump, ranging from 42–1689 mg/kg for As, 73–332 mg/kg for Zn, 14–1507 mg/kg for Sb, and 27–386 mg/kg for Pb. Moreover, As and Sb showed mean values strongly exceeding the IV (up to 20- and 62-fold, respectively), indicating a high risk of pollution in the area for these two elements.

Physico-chemical properties of soils and tailing samples showed a moderate critical load of pollutants related to the alkaline pH and calcium carbonate content, low EC, CEC and OC. The moderate presence of calcium carbonate in the tailings, along with the high acidification potential, results in the potential acid generation in the active tailing dump, while the abandoned tailing dump is not susceptible to generate acidification over time.

Mineralogical studies of the tailings by XRD showed that the samples were dominated by quartz, feldspars, calcite, micas and chlorite. The SEM-EDS imaging

made on the tailings and open pit waste materials identified primary and secondary minerals consisting of sulfides, silicates and secondary precipitations of Fe and Mn oxyhydroxides. The presence of yukonite-like precipitation of Ca–Fe–As phases were also detected and could be related to potentially available forms of As.

Selective extractions were applied in order to assess the mobility and availability of metal(loid)s in samples. Oxyanion-forming elements such as As and Sb were immobilized by Fe oxides, although to some extent also extractable with acetic acid and soluble-in-water forms were detected, indicating potential bioavailability that can impose a potential toxicity risk for the environment. Selective extractions data also showed that Zn and Pb were relatively immobile, although in higher contamination sites significant amounts of these elements were also extractable with acetic acid. In tailing materials Zn and Pb mobility were negatively correlated by the cation-exchange capacity (CEC) and clay content, indicating the importance of these factors in the reduction of the potential toxicity for these elements. Total concentration of As, Sb, and Pb were also negatively correlated with soil pH, indicating that the oxidation process of sulphide tailings and thus the generation of acidic conditions may lead to release of contaminants over time. However, due to the calcium carbonate content, the acid neutralization capacity of the tailings is not yet exhausted and contaminant concentrations in soil-pore water are still relatively low.

Three toxicity tests (plant accumulation, toxicity bioassays and human health risk) were performed to evaluate the toxicity of metal(loid)s. The test of plants accumulation indicated that *Artemisia absinthium* can be suitable plant for phytoextraction of Cu, Zn and Sb in polluted areas, and *Phragmites australis* may be efficiently utilized for metal removal (mainly Cu) and, in any case, can also both be used for phytostabilization of contaminated sites. The toxicity bioassays made with the soluble-in-water phase using *Lactuca sativa* and *Vibrio fischeri* showed no risk of toxicity in the short-term, indicating that the metal(loid)s in tailings are mainly associated to secondary phases related to carbonates and iron/manganese forms that reduce the mobility and toxicity of these soluble phases. The results of human health risk assessment indicate a high potential of toxicity by accidental ingestion route for As, Sb and Pb. Special high risk was detected in the case of urban soils exposed to children (gardens or parks) and in agricultural soils.

The results of our investigation suggest that environmental risk associated with these wastes in semi-arid climate is therefore not a short-term problem but rather requires constant monitoring. In addition, remediation actions are recommended in order to mitigate or prevent the risk of toxicity to the population close to the mining area.

RESUMEN

De toda la diversidad de residuos generado por los seres humanos, los problemas asociados con los residuos mineros son motivo de gran preocupación. La caracterización es el primer paso para encontrar una solución a la contaminación potencial relacionada con estas áreas y para prevenir el riesgo ambiental para los seres vivos. Entre los procesos asociados con los residuos mineros que afectan negativamente el medio ambiente se incluyen los relacionados con la contaminación de suelos, agua y aire por elementos potencialmente tóxicos. En este trabajo, la evaluación de la contaminación potencial de elementos traza en vertederos y suelos se caracterizó en el área minera de Chadak (Uzbekistán). El objetivo principal de este trabajo es evaluar el impacto ambiental de los metales y metaloides provenientes de las balsas de residuos generados durante el procesamiento minero del depósito de Chadak Au-Ag, caracterizando los elementos potencialmente contaminantes y evaluando su toxicidad. Los resultados obtenidos en este estudio han supuesto un avance en el conocimiento en relación con la evaluación de la contaminación potencial del medio ambiente en esta zona de estudio.

Las concentraciones de elementos traza (V, Cr, Co, Ni, Cu, Zn, As, Cd, Sb, Pb) se determinaron mediante análisis de fluorescencia de rayos X y se compararon con los valores de fondo geoquímico (BC) y los valores de intervención (IV). Las concentraciones de As, Zn, Sb y Pb superaron el BC en la mayoría de los casos y fueron más altas en la balsa abandonada que en la activa, con valores que varían entre 42–1689 mg / kg para As, 73–332 mg / kg para Zn, 14 –1507 mg / kg para Sb, y 27–386 mg / kg para Pb. Además, As y Sb mostraron valores medios que superaron con creces los IV (hasta 20 y 62 veces, respectivamente), lo que indica un alto riesgo de contaminación en el área para estos dos elementos.

Las propiedades fisicoquímicas de los suelos y las muestras de lodos mostraron una moderada carga crítica de contaminantes relacionada con el pH alcalino y el contenido de carbonato de calcio, y los bajos valores de EC, CEC y OC. La presencia moderada de carbonato de calcio en los lodos, junto con el alto potencial de acidificación, da lugar a una generación potencial de ácido en la balsa de lodos

activa, mientras que la balsa de lodos abandonada no es susceptible de generar acidificación a lo largo plazo.

Los estudios mineralógicos de los lodos mediante DRX mostraron que las muestras estaban dominadas por cuarzo, feldespatos, calcita, micas y clorita. Los análisis por SEM-EDS realizados en los lodos y en los residuos analizados en la explotación a cielo abierto identificaron minerales primarios y secundarios que consisten en sulfuros, silicatos y precipitaciones secundarias de oxihidróxidos de Fe y Mn. Se detectó la presencia de precipitados tipo Yukonita en las fases de Ca-Fe-As lo que podría estar relacionada con la presencia de formas biodisponibles de As.

Se aplicaron también extracciones selectivas para evaluar la movilidad y disponibilidad de metal(loid)es en las muestras. Los elementos formadores de oxianiones como As y Sb fueron inmovilizados por los óxidos de Fe, aunque en cierta medida también se detectaron formas extraíbles con ácido acético y solubles en agua, lo que indica una posible biodisponibilidad que puede suponer un riesgo potencial de toxicidad para el medio ambiente. Los datos de las extracciones selectivas también mostraron que Zn y Pb eran relativamente inmóviles, aunque en las zonas de mayor contaminación, se extrajeron también cantidades significativas de estos elementos con ácido acético. En los lodos, la movilidad de Zn y Pb se correlacionó negativamente con la capacidad de intercambio catiónico (CEC) y el contenido de arcilla, lo que revela la importancia de estos factores en la reducción de la toxicidad potencial para estos elementos. Las concentraciones totales de As, Sb y Pb también se correlacionaron negativamente con el pH del suelo, lo que indica que el proceso de oxidación de los lodos ricos en sulfuros y, por lo tanto, la generación de condiciones ácidas, puede conducir a la liberación de contaminantes a lo largo del tiempo. Sin embargo, debido al contenido en carbonato cálcico, la capacidad de neutralización ácida de los lodos aún no se ha agotado y las concentraciones de contaminantes en la solución del suelo aún son relativamente bajas.

Finalmente, se realizaron tres bioensayos (acumulación en plantas, bioensayos de toxicidad y ensayo de riesgo para la salud humana) para evaluar la toxicidad de los metal(loid)es presentes en la zona. La prueba de acumulación en plantas indicó que

Artemisia absinthium puede ser una planta adecuada para la fitoextracción de Cu, Zn y Sb en áreas contaminadas, y *Phragmites australis* se puede utilizar de manera eficiente para la eliminación de metales (principalmente Cu) y, en cualquier caso, también se pueden usar ambas para fitoestabilización de los suelos de la zona. Los bioensayos de toxicidad realizados con la fase soluble en agua utilizando *Lactuca sativa* y *Vibrio fischeri* no mostraron riesgo de toxicidad a corto plazo, lo que indica que los metal(loid)es en los lodos se asocian principalmente a fases secundarias relacionadas con carbonatos y formas de hierro / manganeso que reducen la movilidad y la toxicidad de las fases solubles. Los resultados de la evaluación del riesgo para la salud humana indican un alto potencial de toxicidad por vía de ingestión accidental para As, Sb y Pb. Se detectó un riesgo especialmente alto en el caso de suelos urbanos expuestos a niños (jardines o parques) y en suelos agrícolas.

Los resultados de nuestra investigación sugieren que el riesgo ambiental asociado con estos residuos mineros en clima semiárido no es, por lo tanto, un problema a corto plazo, pero se requiere un seguimiento constante. Además, se recomienda el estudio y aplicación de acciones de remediación para mitigar o prevenir el riesgo de toxicidad en los suelos del entorno y para prevenir el riesgo de exposición a la población cercana al área minera.

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Part I

Introduction, Objectives and Justification

CHAPTER 1. INTRODUCTION

1.1. What are mine wastes

Mining is one of the most powerful factors of anthropogenic transformation of the environment. It is defined as an activity that focuses on the selective extraction, through mining techniques, of substances and minerals existing in the earth's crust, in an economically profitable manner. It is primarily manifested in the withdrawal and mechanical damage of considerable masses of land. Modern technology makes it possible to use only a small part of the extracted mass of rocks (usually a few percent). All the rest is accumulated in the form of waste piles and tailing dumps, which are dissipated by natural migration processes and are a source of pollution of the environment by chemical elements. In the last decades, a very important demand for mineral raw materials has been generated, motivated by the strong economic growth produced worldwide, which has made even more relevant, if possible, the strategic value of this extractive activity. It is estimated that the current volume of mining waste production amounts to several billion tons per year, and that it continues to increase as demand and exploitation of lower quality deposits or by the search for new materials such as Rare Earth Elements (Hudson-Edwards and Dold, 2015). In the case of tailings,14 billion tones were produced by the mining industry in 2010 (Jones and Boger, 2012).

The term "mining waste" is a generic term that encompasses all waste and by-products from mining activity, whether or not these are included in specific deposits. Mine wastes can also be defined as waste products originating, accumulating and present at mine sites, which are unwanted and have no current economic value" (Lottermoser, 2010). Mine wastes include waste piles, tailings, smelter slag, used processing solutions, particulate emissions and mine drainage waters. The chemical properties of mine wastes depend on the type of mineral mined, as well as from chemicals used in the extraction or enrichment processes. Historically, wastes were disposed often without regard for safety and often with significant environmental consequences. (Bell and Donnelly, 2006).

This Chapter is partially based on the publication: O.Kodirov, Kersten M., Shukurov N., Martín-Peinado F.. 2018. Trace metal(loid) mobility in waste deposits and soils around Chadak mining area, Uzbekistan. Science of the Total Environment, 622–623, 1658–1667.

In Uzbekistan various minerals are mined in several fields by open-pit and underground mining methods generating 25 million m^3 of waste annually (UNECE, 2001). According to the State Committee for Nature Protection of the Republic of Uzbekistan (2001), about 42 million tons of tailings and 300,000 tons of metallurgical slag are accumulated annually in Uzbekistan. Tailings represent, therefore, the most voluminous waste at metal mine sites.

Mining and foundry activities are the main anthropogenic sources of metals in the environment (Uzu et al., 2009). One of the main concerns with regard to mining activity is the production of a large amount of wastes, which are usually stored in the vicinity of mines. Since these industrial waste materials contain inorganic contaminants, such as metals, they in turn represent secondary sources of contamination for soil, water and the atmosphere.

1.2. Environmental impact of mining wastes

The main feature of the current stage of the development of the biosphere is the constant increase in the role of the anthropogenic factor in the formation of migration flows of elements. Unfortunately, man often intervenes without due attention in the established interrelationships between natural phenomena and disturbs most of the main ecological cycles, leading to unpredictable consequences and malfunctions in the environment.

The exploitation of mineral resources results in the production of large volumes of mining wastes containing metals or metalloids at elevated concentrations (Lottermoser, 2010). Environmental contamination and pollution as a result of improper mining, smelting and waste disposal practices have occurred and still occur around the world. Significance of contamination risk induced by mining is also highlighted by large mine accidents such as in Aznalcollar, Spain in 1998 (Simon et al., 2001). Mining waste is the most important source of impacts on the populations and ecosystems of mining areas and their areas of influence. In addition to its potential risk of contamination on the site itself, these residues are often susceptible to being eroded by wind (wind erosion) and runoff water (water erosion). Filtration to groundwater and discharge of surface water can lead to contamination of both ground and surface water. Therefore, extractive activities, such as mining, usually cause large impacts on their environment, since, as is particularly important in metal mining, they become zones from which contaminants can be dispersed, in addition to affect soils, aquifers and surface waters (Collon et al., 2006).

Tailings contain a combination of phenomena that adversely affect the environment. This is the contamination of the air basin, the high aggressiveness of technogenic waters, the ecotoxicity of elements and the probability of emergency situations at sites that make up the tailings (Hudson-Edward et. al, 2011). Pollution of the air basin is caused by intensive processes of dust formation on the surfaces of tailing dumps, which are mostly in a dry state.

Today Uzbekistan has to handle significant environmental problems associated with development of deposits in past and present time. The increase in mining activities in recent decades inevitably exerts a negative influence on the environment. In particular, opencast mining activities may therefore have a negative environmental impact on soils and watersheds. Sulphide-rich minerals represent a major ore deposit for extracting metals and metalloids worldwide, generating millions of tons of tailings and acid mine drainage (Dudka and Adriano, 1997).

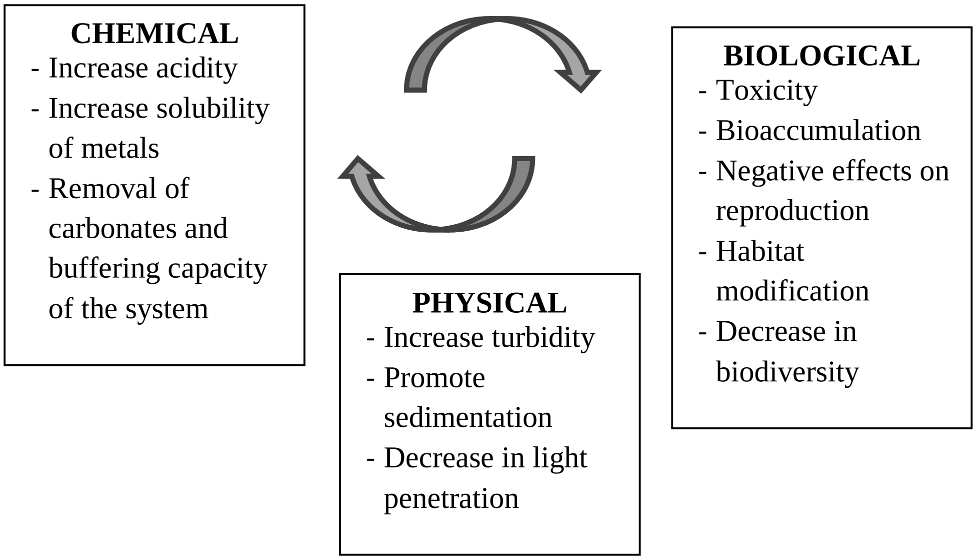


Figure 1.Acid Mine Drainage: main impacts on the environment (adapted from Gray, 1997)

Strongly related to waters draining active and, in particular, abandoned mines and mine wastes coming from sulphide-rich minerals, acid mine drainage (AMD) is one of the most serious environmental problems in sulphide mineralized areas, causing the solubilization and dispersion through the environment of trace metals and related toxic elements (Astrom, 1998). The main impacts on the environment affects to essential properties and cycles (Fig. 1), producing strong changes in the ecosystem. Most of the environmental-impact assessment and remediation efforts related to AMD generation have been focused on temperate climates, and few on mine sites exposed to semi-arid climates where AMD is not an immediate problem (Razo et al., 2004; Hayes et al., 2012). In these areas, the presence of soils with high buffering capacity is common, and when the AMD infiltrates the soil, the acidity is neutralized and most of the pollutants precipitate (Simón et al., 2005). In any case, although AMD generation in a semi-arid climate is not a short-term problem, the pollution can persist for thousands of years due to the slow time course of the processes related to oxidation, hydrolysis and acidification (Kempton and Atkins, 2000), which poses a long-term risk and even a chemical time-bomb for environment and human health.

1.2.1. Pollution by metals and metalloids

The fundamental difference between mankind and the animal world is the creation of a technosphere. Mankind, representing an insignificant share of the biomass of the planet, at the expense of its technological activity, intensively changes the spectrum of elements and their concentration in the environment.

In the last decades, interest in assessing chemical elements as pollutants has increased dramatically. A number of elements, in particular Pb, Cd, Fe, Cu, Zn, As, Hg, Sb, etc., due to human activities, already now far exceed the level of dispersion of these elements associated with geological processes. The major concern of contamination of soil, sediments, and waters by metals and metalloids is their toxicity and threat to human life and the environment (Nriagu et al., 2007). Trace elements are found naturally in the earth's crust (natural source), but the use by the human beings (anthropogenic source), generate a high diversity of chemical forms (Table 1). Many elements like arsenic, mercury, cadmium, lead, selenium, etc., are considered priority pollutants (Sparks, 2005), because they are transformed to chemical forms that can produce acute toxic effects in living organisms.

Unlike most organic pollutants, inorganic elements (like metals and metalloids) are not affected by natural degradation processes, and due to their low mobility under oxidizing conditions, they are persistent in the environment over time. Their presence in soils at long-term, can produce that they incorporate into the biological cycle, inevitably leading to contamination of the other most important life-supporting natural environments: water, air and living organisms.

Table 1. Natural and anthropogenic sources and common forms in wastes of trace elements as priority pollutant.

Element	Natural source or metallic minerals	Anthropogenic sources	Common forms in wastes
Ag	Free metal (Ag), chlorargyrite (AgCl),acanthite (Ag_2S), copper, lead, zinc ores	Mining, photographic industry	Ag metal,Ag–CN complexes, Ag halides, Ag thiosulfates
As	Metal arsenides and arsenates, sulfide ores (arsenopyrite), arsenolite (As_2O_3), volcanic gases, geothermal springs	Pyrometallurgical industry, spoil heaps and tailings, smelting, wood preserving, fossil fuel combustion, poultry manure, pesticides, landfills	As oxides(oxyanions), organo-metallic forms, $H_2AsO_3CH_3$ (methylarsinic acid), $(CH_3)_2$-AsO_2H (dimethylarsinic acid)
Be	Beryl ($Be_3Al_2Si_6O_{18}$), phenakite (Be_2SiO_4)	Nuclear industry, electronic industry	Be alloys, Be metal, $Be(OH)_2$
Cd	Zinc carbonate and sulfide ores, copper carbonate and sulfide	Mining and smelting, metal finishing, plastic industry, microelectronics, battery manufacture, landfill sand refuse disposal, phosphate fertilizer, sewage sludge, metal scrap heaps	Cd^{2+}ions, Cd halides and oxides, Cd–CN complexes, $Cd(OH)_2$ sludge
Cr	Chromite ($FeCr_2O_4$), eskolaite (Cr_2O_3)	Metal finishing, plastic industry, wood treatment refineries, pyrometallurgical industry, landfills, scrap heaps	Cr metal, Cr oxides (oxyanions),Cr^{3+} complexes with organic/inorganic ligands
Cu	Native metal (Cu), chalcocite (Cu2S), chalcopyrite (CuFeS2)	Mining and smelting, metal finishing, microelectronics, wood treatment, refuse disposal and landfills, pyrometallurgical industry, swine manure, pesticides, scrap heaps, mine drainage	Cu metal, Cu oxides, Cu humic complexes, alloys, Cu ions
Hg	Native metal (Hg), cinnabar (HgS), degassed from Earth's crust and oceans	Mining and smelting, electrolysis industry, plastic industry, refuse disposal/landfills, paper/pulp industry, fungicides	Organo-Hg complexes, Hg halides and oxides, Hg^{2+}, $(Hg_2)^{2+}$, Hg^0
Ni	Ferromagnesian minerals, ferrous sulfide ores, pentlandite	Iron and steel industry, mining and smelting, metal finishing, microelectronics, battery manufacture	Ni metal, Ni^{2+} ions, Ni amines, alloys
Pb	Galena (PbS)	Mining and smelting, iron and steel industry, refineries, paint industry, automobile exhaust, plumbing, battery manufacture, sewage sludge, refuse disposal and landfills, pesticides, scrap heaps	Pb metal, Pb oxides and carbonates, Pb-metal–oxyanion complexes
Sb	Stibnite (Sb_2S_3), geothermal springs	Microelectronics, pyrometallurgical industry, smelting, mine drainage	Sb^{3+} ions, Sb oxides and halides
Se	Free element (Se), ferroselite (FeSe2),	Smelting, fossil fuel combustion, irrigation waters	Se oxides (oxyanions), Se-organic complexes

	uranium deposits, black shales, chalcopyrite–pentlandite–pyrrhotite deposits		
Tl	Copper, lead, silver residues	Pyrometallurgical industry, microelectronics, cement industry	Tl halides, Tl–CN complexes
Zn	Sphalerite (ZnS), Willemite (Zn_2SiO_4), smithsonite ($ZnCO_3$)	Mining and smelting, metal finishing, textile, microelectronics, refuse disposal and landfills, pyrometallurgical industry, sewage sludge, pesticides, scrap heaps	Zn metal, Zn^{2+} ions, Zn oxides and carbonates, alloys

Source: Sparks (2005); Adriano(2001); mineral nomenclature after Mandarino and Back (2004).

Metals and metalloids are transferred to the environment via fly ash, dust, and leachates coming from point-source pollution such as mine quarries, dumps, and tailings (Shukurov et al., 2014; Martín et al., 2007), and may become a problem of diffuse pollution due to the widespread partitioning of these elements through the ecosystem (Martín et al., 2010).

1.2.2. Trace elements in plants

The disposal of mining wastes resulting from metalliferous and processing wastes release toxic metals into the environment and has harmful effects on soil, terrestrial and aquatic plants, organisms and ecological cycles causing alteration and damage to plants, animals and ecological biodiversity (Ives and Cardinale 2004; Hsu et al. 2006; Anawar et al.2013). Therefore, a better knowledge about the soil processes of these mining soils will provide, in addition to scientific knowledge, better information on how to deal with the processes of recovery and environmental restoration of these environments (Smithet al., 1987; Wong, 2003).

It is known that the chemical composition of plant communities is closely related to the concentration of a number of elements in the soil substrate (Kabata-Pendias, 2011). Plants have developed a range of mechanisms to obtain metals from the soil solution and transport these metals within the plant, accumulating both in roots as in aerial parts (Zhou et al., 2016). Plants are recognized as critical elements of terrestrial ecosystems and must be considered as part of any environmental impact assessment.

Plant ability to take up chemical elements from growth media is evaluated by a ratio of element concentration in plants to element concentration in soils and is called Biological Absorption Coefficient (BAC), Index of Bioaccumulation (IBA), or Transfer

Factors (TF). To provide an effective evaluation of the pool of bioavailable trace elements, therefore, techniques based on both soil tests and plant analyses should be used together. An assessment of toxic concentrations and effects of trace elements on plants is very complex because it depends on so many factors that it cannot be measured on a linear scale (Kabata-Pendias, 2011).

In recent decades, in order to combat the consequences of pollution from mining activities, a large number of researches have taken place for plant species tolerant of heavy metals, for phytoextraction and/or phytorestoration of affected sites and stabilize the mining waste dumps (Wong 2003).

Phytoremediation is a relatively new approach to removing contaminants from the environment. It may be defined as the use of plants to remove, destroy or sequester hazardous substances from environment (Zu, 2003). It has become a attractive method due its safe and potentially cheap nature compared to traditional methods of remediation (Glick, 2003; Pulford and Watson, 2003). The process of phytostabilization leads to the stabilization of metal contaminants in polluted soils and the reduction of the transfer of metal from the soil to the plants (Blaylock and Huang, 2000).

Despite the impact of mining activities on community structure and biodiversity, ancient as well as recent mine spoils can still support populations of metal-tolerant taxa and some wild plants that grow on metal contaminated soil can accumulate significant amounts of metals. Some plants have mechanisms for accumulation and tolerance or alleviation of high levels of metals in contaminated soils (Khan et al. 2000); for example, native plants such as *Artemisia absinthium* (Badea, 2015) and *Phragmites australis* have been used successfully in phytoremediation (Stoltz and Greger, 2002) due to excellent tolerances to various contaminants and specific biochemical, physiological and anatomical adaptations. Identification of those plants native to such areas with reasonably high biomass and capacity to accumulate heavy metals is essential for phytoremediation (Fitamo, 2010).

Anyway, the use of phytoextraction in the restoration of mine sites or soil polluted by heavy metals is usually restricted due to the high concentration of heavy metals and the potential toxicity of the soil solution. Therefore, in most cases, the use of phytostabilization is frequently applied to these areas. The use of metal tolerant plants together with different amendments like organic materials, liming agents, or other inorganic products to reduce metal mobility and bioavailability in soils, appears a viable strategy for restoration of sites contaminated with high levels of metals when phytoextraction is not a feasible option (Alcorta et al., 2010).

1.2.3. In vitro bioaccessibility assay for metals

Heavy metals in mine-impacted areas may enter to the human body through direct inhalation or ingestion of particulates (Hayes et al., 2012). Accordingly, some methods have been developed to evaluate the health risks of heavy metals (Wang et al. 2005) which depend on the fraction that is soluble in the gastrointestinal environment and available for absorption (Paustenbach, 2000; Oomen et al. 2002).

In order to define the amount of an element that is actually readily available for uptake, is desirable the use of human bioaccessibility tests (Wragg and Cave, 2003). *In vitro* bioaccessibility analysis measures the potential hazard from ingestion of metals in soil, dust or other solid-like waste material. The bioaccessibility test of contaminants that have entered the gastro-intestinal tract by direct ingestion of soil should provide quantification of the dissolution under ‘‘realistic worst conditions’’ (Poggio et al, 2009).

There are various methods of *in vitro* bioaccessibility tests ranging from very simple chemical extraction or leaching tests to advanced multi-step tests simulating the human digestion process in detail (Ruby et al.,1996, 1999; Yang et al., 2003). In these assays, soil is incubated in an acid solution for a period corresponding to the residence time of ingested soil particles in the human stomach. The analysis is highly controlled in terms of temperature as well as pH of the fluid.

Statistical relationships between human bioaccessible fractions and various soil properties were found by Ruby et al. (1999), suggesting that this approach could be useful for assessing bioaccessible fractions, especially for preliminary, non-legally binding investigations (Poggio et al, 2009). However, the relationship between bioaccessibility and its fractionation in soils remains to be better characterized (Tang et al., 2018), so this important aspect is going to be addressed in this study.

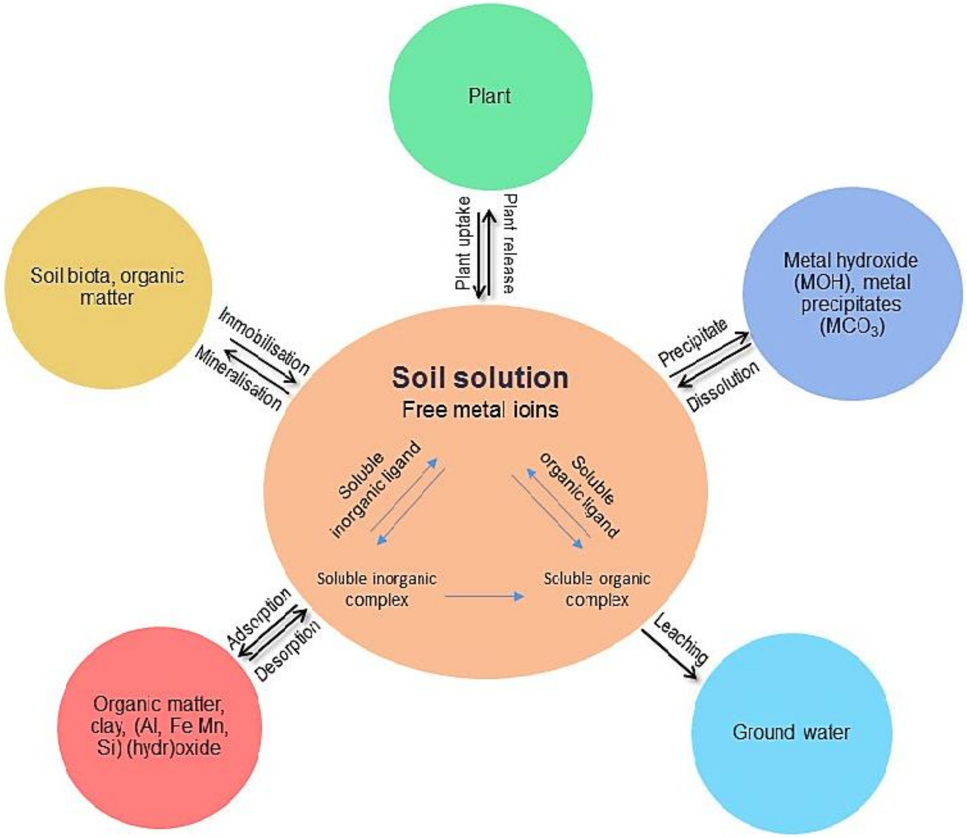
1.3. Soil properties in relation to pollution

Soil is one of the basic elements of the environment because is the component on which ecosystems and most anthropic activities are installed and developed. In this sense, soil is an element that interacts with the other natural components (geological substrate, atmosphere, water component and living organisms), performing ecosystemic and human use functions, including agriculture, industry and mining. Moreover, its dynamic nature extends these function to many other environmental, socioeconomic and cultural scopes, many of which are of great importance for the the functioning and health of ecosystems (Hamilton, 2000).

However, in mining areas soils are heavily disturbed, resulting in a strong alteration of their main properties and constituents. According to the World Reference Base (WRB, 2015), these soils in mining areas were within the Technosols Group. These soils combine soils whose properties and pedogenesis are dominated by their technical origin. They include soils formed by materials that, strictly, have not undergone edaphogenetic processes (e.g.: those previously confined in the subsoil: sterile mines or all kinds of excavation products below the original soil profiles, and sometimes also the byproducts of the treatments like landfills, sludge, residues from mines and ash. Otherwise, Tecnosols also may include surface materials that have undergone edaphogenetic processes, which, in turn, may have been subjected to the mixture of horizons when removed and that, in any case, have been altered their properties during the handling.In the U.S. Soil Taxonomy, any class of soil may be modified by the “technic” or “anthropic” qualifier, so they are included in the Orthent suborder; in the Russian soil classification system they are recognized as surface Technogenic formations and in the Australian soil classification they are considered to be included within Anthroposols.

Heavy metals can be retained in the soil but can also be mobilized by different and chemical mechanisms. Mobilization processes are complex and strongly related to soil properties and constituents, but is especially sensitive to those reactions that affect transfer from solid to liquid phases (Alloway, 1995). The most important factors that influence the mobilization of heavy metals in soils are related to the main soil characteristics like: pH, redox potential, ionic composition of the soil solution, ion change capacity, presence of carbonates, iron forms, organic matter, texture, etc. (Sauquillo et al., 2003).

Figure 2. Possible reactions of metal(loid)s in soils



The possible dynamic of metal(loids) in soils involved in physical, chemical and biological transformation (Fig. 2), although environmental conditions such as acidification, changes in redox conditions, or variation of temperature and humidity, play a key role in the mobility and availability of these potentially pollutant elements into the ecosystem.

In this regard, it is of main interest determining the general behavior of heavy metals in various soil conditions, such as acid soils (Birkefeld et al., 2006; Chen et al., 2005) or alkaline, as well as in a carbonated context (Fotovat and Naidu, 1998, Boussen et al., 2013). In this sense, the behavior of the chemical elements can be evaluated by sequential or selective extraction procedures, which provide essential information on therelations between soil components and pollutants,while providing information on their mobility and bioavailability in relation to the soil properties (Van Herreweghe et al., 2003; Anju and Banerjee, 2010; Uzu et al., 2011; Boussen et al., 2013). The use of these chemical procedures with a mineralogical approach, such as DRX, SEM, TEM, etc., allows the determination of the different metallic phases in the soils (Kovács et al., 2006; Otones and Álvarez-Ayuso, 2011; Chiang et al., 2010), allowing to predict and evaluate their stabilityin the medium and long term.

1.3.1. Soil fractionation of metals and metalloids

Traditionally, in environmental studies the total content of toxic elements is analyzed, but only mobile forms of toxicants can be dangerous for ecosystems, while immobile forms are of less danger. It is now widely recognized that the mobility and bioavailability of trace metals in soils depend not only on the total concentration, but also on their specific chemical form or binding state in relation to soil properties and constituents (Dang et al., 2002; Sauve et al., 2000; Nyamangara, 1998; Romero-Freire et al., 2014). However, changes in environmental conditions such as acidification, changes in the redox potential conditions or increases in organic-ligand concentrations can result in trace-element mobilization from the solid to the liquid phase and cause contamination of surrounding waters (Gleyzes et al., 2002).

To assess the mobility and bioavailability of potentially polluting elements, several extraction schemes have been developed and described in the literature (Rauret et al., 1989; Kersten, 2001; Gleyzes et al., 2002; Quevauviller, 2002). These extraction schemes are based on operationally defined fractions that allow the assessment of distinct reagent-extractable forms (distilled water, single salts, acetic acid, complexing agents, etc.), which are usually defined as pool-extractable forms (soluble, exchangeable, carbonate associated, Fe/Mn oxide-associated, organic associated, residual, etc.). The most insoluble forms (extracted only by strong acids) are usually defined as residual forms (Beckett, 1989). In this way, a set of selective extraction techniques are used to determine the most leachable and thus potentially the most bioavailable compounds, while the total abundance of potentially harmful elements was determined by strong acid digestion (Anju and Banerjee, 2010). Despite the uncertainties associated with non-selectivity of the extractants, readsorption, and redistribution problems, extraction schemes remain widely used as an essential tool in element fractionation in soil and sediments (Kersten, 2001; Gleyzes et al., 2002).

However, not all the processes or reactions of trace elements with the properties and constituents of the soil that determine their bioavailability (MO, oxides, carbonates, clays etc.) are equally important for each element; although most of these processes are usually affected by the pH of the soil and biological processes (Fageria et al., 2002). In this sense, it is essential to know which processes or reactions are the most important for each element to be able to propose the appropriate solutions to avoid toxicity in organisms and dispersion of pollution.

1.3.2. Soil assessment of toxicity by bioassay tests

To solve the issue of further use of the territories near the areas of past environmental damage, an estimation of soil toxicity is necessary. The assessment of toxicity in soils based on the results of the chemical analysis is not reliable, because the chemical-analytical control cannot detect the actual toxicity of polluted soils, but only shows the presence of a concentration of pollutants that are compared with existing sanitary and hygienic standards (usually called "intervention levels"). This problem can be solved if the methods of bioassay testing are introduced into the environmental control system, which allows obtaining an integral ecotoxicological assessment of the soils in the zone of influence of industrial facilities.

In recent years, a large number of cost effective and more environmentally friendly remediation techniques have been developed (Kulshreshtha et al., 2014). Remediation of polluted areas is important to prevent environmental degradation, as well as to control the impact of people and other living organisms on hazardous chemicals. Pollution and toxicity in polluted soils by metal(loid)s are generally evaluated by the means of bioassays (García-Carmona et al., 2017).

Toxicity bioassays, are used to determine the toxicity in organisms when exposed to potentially contaminating elements. They are crucial to determine the ecological risk, since they can foresee the potential risk of contamination in living organisms in the ecosystem (Petänen et al., 2003). Bioassays are experiments in which selected test organisms are exposed to a soil to bediagnosed, and some biological response is measured. For terrestrial ecosystems, the most commonly used tests for toxicity assessment include the most important groups of soil organisms: plants, soil microorganisms and mesofauna (Romero-Freire, 2015).

Generaly, extractions remove soluble in water contaminants; subsequently, they reflect the behaviour of the mobile phases and assess the short-term risk of dispersion, solubilization and bioavailability of pollutants in the soil. To evaluate soil toxicity, the use of a diverse set of exposure routes, as well as anumber of bioassays is recommended, jointly take into account exposure to both the solid and the soluble phases of the soil (Romero-Freire et al., 2016).

There are very diverse toxicity tests that can be applied in case of soil contamination assessment. They are divided mainly into two groups: those that use the liquid phase (the saturation extract of the soil), and those that use the solid phase (Farré and Barceló, 2003). There is a high correlation between bioassays that use both phases, although it is not always direct (Lors et al., 2011). The bioassays that use the soil extract seem to better reflect the behavior of the mobile phases, which allows to evaluate in the short term the risks of dispersion, solubilization and bioavailability of the contaminants in the soil (Romero-Freire et al., 2014).

1.4. Justification of the problem

In recent decades, the problem of pollution of natural systems by toxic components of technogenic origin is becoming increasingly important due to the growing influence of metals and metalloids sources in the environment and, as a consequence - in the food chain and the human organism.

We are increasingly confronted with the phenomenon of which Vernadsky (1960) spoke: "...humanity becomes the leading geological force, and its activity determines the formation of a modern geological environment in the atmosphere, the hydrosphere and the upper zones of the lithosphere.". This particularly applies to the mining industry, as a result of which the Earth’s surface in some regions is changed beyond recognition and turns into "lunar landscapes". In fact, over 6 billion ha (66 percent of the world’s soil surface) has been affected by degradation, leaving roughly only a third of the world’s surface in good condition (Gibbs y Salmon, 2015).

In most deposits related to mining activities, the rich ore is mainly involved in industrial development, while the low-grade ore mass is stored in the form of mining wastes or tailing dumps. Extracted to the surface and stored ore-rock association on one hand inevitably experiences the influence of natural factors, modifying and transforming under their influence, and on the other hand exerts an active influence on the surrounding natural components. Mine wastes are often a major source of heavy metal pollution in the local environment owing to direct dispersion of potentially polluted particles by dust blow (eolic erosion) or water erosion, and from the leaching of the products of mineral weathering into nearby soils and watercourses (Tordoff et al., 2000). This pollution may have serious detrimental effects upon crops and public health in the surrounding areas both in active as in abandoned mines.

In this regard, the problem of assessing the impact of unclaimed part of mineral raw materials in the process of mining deposits on the surrounding environment and human health is very relevant, since ore deposits are natural geochemical anomalies, which are potential and real sources of toxic elements. Among the most ecotoxic deposits, gold ore deposits occupy one of the first places, since their ores contain a wide range of toxic elements, most of which classified as 1 and 2 hazard groups (highly and moderately hazardous, respectively) according to the Russian general toxicological standard (GOST 17.4.1.02-83). Taking into account the fact that the main attention is paid to one (Au), maximum of two components (Au + Ag) during the mining of these deposits, the questions of identification the potential environmental risk of pollution of unused ore minerals are of particular importance.

CHAPTER 2. AIM AND OBJECTIVES

2.1. General aim of thesis

As a result of the large-scale mining activities several environmental problems such as land degradation, poor soil and water quality, tailings disposal, high metal contamination, limited vegetation and geological hazards are observed as "point-source" pollution. In this case, contaminants are directly released to the soil, and the source and of the pollution is easily identified (Hernández and Pastor 2008; Takeuchi and Shimano 2009; Anawar et al. 2011.). Otherwise, in arid and semi-arid regions usually occurs at the same time "diffuse pollution", this involving the spread of contaminants over wide areas, mainly related to wind erosion, which involves the transport of pollutants via air to soil-water systems (Rodríguez-Eugenio et al., 2018).

The mining industry is the main national wealth of Uzbekistan. The relevance of the topic is determined by the fact that in the mining regions of Uzbekistan huge amounts of mining wastes have accumulated.

In general, under the socialist system, main attention was paid to the intensive development of minerals and due attention was not paid to the protection of the natural environment and to the sustainable or rational use of resources. After gaining independence and transition to a market economy, Uzbekistan began working on economic incentives for mining enterprises, focusing on the rational and integrated use of mineral raw materials. However, technogenically disturbed territories continue to grow from year to year, producing an increasing degradation of the environment (mainly air, water and soils) which adversely affects the development of livestock, agriculture and public health. However, mining and technical reclamation of disturbed areas was and remains at a very low level of development.

Taking into account the above described, the general aim of this research is to contribute to identify and characterize the potential problems associated with the tailing dumps of the Chadak mine (Uzbekistan), and to support information to be used in further studies related to environmental safety of the population by preventing the negative consequences of the development of activities related to the exploitation of mineral deposits.

2.2. Main objective

The main objective of this work is to assess the environmental impact of metals and metalloids coming from waste rock piles and tailing dumps generated during processing of the Chadak Au-Ag deposit, by characterizing the potentially contaminating elements and assessing their toxicity. The final goal is to generate useful data and information to be used in the development of remediation strategies for alleviate of recovery the environmental problems in Chadak area.

To achieve this objective, the following specific objectives will be carried out:

2.3. Specific objectives

1. Characterize the total concentration and distribution of metals and metalloids (As, Sb, Zn, Pb and others) in surrounding soils and wastes deposits in and around the tailing dumps of Chadak mining area, to evaluate the potential risk of pollution as the first step in an environmental risk assessment of the area;

2. Analyze of physico-chemical parameters (grain size, pH, EC, CEC, etc.) and mineralogical composition of soils and tailings materials, to be considered as they create conditions for changing the forms of metals.

3. Assessment of the mobility and potential bioavailability of the main contaminants (As, Pb, Zn and Sb) by selective chemical extractions.

4. Identification of phytoremediation potential of plants (*Phragmites australis*, *Artemisia absinthium*) growing in and around tailing dumps;

5. Evaluation of the potential toxicity of metals and metalloids in soils and tailings materials using bioassays and if necessary develop remediation strategies.

6. Determination of bioaccessibility of metal(loid)s in tailings material and evaluate associated human health risk from its ingestion.

The overall goal of the project is thereby contribution to more secure livelihoods, increased environmental sustainability, and greater social harmony.

Part II

Results and Discussion

CHAPTER 3. PHYSICO-CHEMICAL AND MINERALOGICAL CHARACTERISTICS OF SOILS, SEDIMENTS AND WASTE MATERIALS OF CHADAK MINING AREA

3.1. INTRODUCTION

The study of physicochemical and mineralogical properties of soils, sediments and waste materials allows us to understand the processes that largely control superficial geochemical cycles. Moreover, these studies are important in understanding contaminative character of trace metals, to assess the pollution levels and the distribution of these elements among solid-phase fractions (Usman et al., 2017), since their interactions are mainly controlled by these properties. Metal(loid)s are significant natural components in the environment, and their presence in the mineral fraction indicates a store of potentially-mobile species as important components of clays, minerals and iron and manganese oxides that have a key influence on soil geochemistry (Gadd, 2008).

Most of the trace metal(loid)s that enter the environment from anthropogenic sources eventually reach the soil. When metal(loid)s get into the soil, they enter into a series of physico-chemical, biochemical and other interactions during which they accumulate, leach out, perform interphase transitions, and enter plant and animal organisms (Violante et al., 2010). During these interactions, the mobility, availability and potential toxicity of metal(loid)s for living organisms can vary significantly.

The degree of mobility of trace metals in soils is determined by a number of soil physico-chemical characteristics, namely: the granulometric composition, pH, the content of clay minerals, the amount of organic matter, electrical conductivity cation exchange capacity, the content of the oxides of iron (Fe), aluminum (Al), and manganese (Mn), the oxidation-reduction potential and biological activity (Kabata-Pendias, 2001). Soils have different responses against pollution depending on their characteristics, and a way to assess this response, the critical load of contaminats is usually estimated (Jiménez Ballesta et al., 1996). The critical load is defined as the concentration below which significant harmful effects on specified sensitive elements

This Chapter is partially based on the publication: O.Kodirov, Kersten M., Shukurov N., Martín-Peinado F.. 2018. Trace metal(loid) mobility in waste deposits and soils around Chadak mining area, Uzbekistan. Science of the Total Environment, 622–623, 1658–1667.

of the environment do not occur. When this critical load of metal(loid)s is exceeded, the soil no longer be able to effectively protect the ecosystem and can even function as a source of toxic substances (Díez et al, 2008).

The most essential soil properties affecting metal(loid)s mobility summarized by US EPA guide (Cameron, 1992) are as follows:

pH - has a significant effect on solubility by alteration of solution equilibria and direct participation in redox reactions, chemical and microbial reactions occurring at a waste site. The ability of soil to immobilize metal(loid)s increases with rising pH and peaks under mildly alkaline conditions. Although in alkaline conditions there is the possibility of metal(loid)s complex anions formation with an increased mobility and bioavailability (Fijalkowski et al., 2012). Although arid zone climatic and soil properties may limit movement of applied liquids, other properties will increase potential for release and movement (e.g., sudden rainfall, flooding, runoff, and erosion by water and wind). A large change in soil pH will result in a radical modification of the soil environment, being one of the most important factors determining the concentration of metals in the soil solution and their mobility and availability to plants (Alkorta et al., 2004).

Redox potential - oxidation-reduction processes influence contaminant behavior in soils as much as any biological or chemical factor. In general terms, the mobility of most metals is low under reducing conditions and increase in a variable way in oxidizing environments (Plant and Raiswell, 1983). Otherwise, biogeochemical redox processes strongly influence also metalloids mobility such as As and Sb (Violante et al., 2010). The mobility of other metals whose redox state is not affected by the redox conditions is nevertheless indirectly affected by the availability of complexing agents, adsorbing Fe and Mn (hydr)oxides and redox-sensitive anions which can induce precipitation of these metals (e.g. reduced sulfur forms) (Bourg and Loch, 1995). Moreover, redox conditions produce changes in the chemical species which can be related to different degrees of toxicity depending on the specific metal oxidation state; for example, Cr^{6+} is toxic to plants, animals and humans, whereas Cr^{3+} is not toxic to plants and is necessary in animal nutrition (Fendorf, 1995).

Organic matter - plays an important role in the accumulation and transport of metals as well as in delaying their circulation in the soil. Trace metals tend to form complexes with organic matter in the soil. Organic matter not only forming complexes, but also retaining trace metals in an exchangeable form. The binding of heavy metals by organic matter involves a different group of complex processes, strongly related to the interactions between organic matter and the mineral phase. Usually, increasing the amount of organic matter in the soil, helps to minimize the absorption of metal(loid)s by plants (Fijalkowski et al., 2012). Otherwise, the presence of organic acids may produce the formations of ligands with many metal ions, increasing their mobility along the soil profile (Gamng et al., 2010).

Ion exchange capacity - corresponds to adsorption reactions that occurs at the interface between the solid and aqueous phase in the matrix of the soils. The main constituents responsible for these surface reactions are organic matter, clay minerals, iron and manganese oxides and hydroxides, carbonates, and amorphous aluminosilicates (McLean and Bledsoe, 1996). The ion exchange capacity (IEC) is one of the general indicators characterizing the buffering capacity of the soil; the higher the IEC, the greater the ability to retain trace metals (van Rensburg et al., 2009). Anyway, the complex interactions among constituents can produce different processes; for example, clay minerals have an important role as carriers of associated oxides and humic substances forming organo-mineral complexes, which present specific sorption capacities different from those of each single soil constituent. Otherwise, variable charge minerals (crystalline and short range ordered Fe-, Al-, Mn-oxides, allophanes, imogolite) strongly retain trace heavy metals for their dependency on pH. On these materials a hydroxylated or hydrated surface, positive or negative charge is developed by sorption or desorption of H^+ or OH^- ions (Violante et al., 2010). Moreover, the competitive anion exchange effects of other elements like P, can displace adsorbed metalloids like As, increasing the mobility of As into the soil (Peryea and Kammereck, 1997).

The type and quantity of the mineral phase largely determines the buffer capacity of a soil in relation to metal(loid)s. Particularly important is the mineralogical analysis with the separation of hypergene stages of mineral formation for the evaluation of tailings as sources of environmental pollution, since the minerals of the sulfate group (transition phase) have the maximum solubility. On the other hand, minerals of initial (sulfides) and final (oxides, hydroxides) stages are most resistant to dissolution (Grehnev, 2011). The latter circumstance is important for the characterization of pollution sources and evolution over time, since the mineralogy determines the potential of geochemical pollution. In mine wastes, Jamieson (2011) describes four groups of minerals and other solid compounds:

1) **Primary sulfide minerals** – comprising or accompanying ore, affect the sulfide oxidation rate and the degree and nature of the released potentially toxic elements.
2) **Primary non-sulfide minerals** – mainly carbonate and silicate minerals that are in ore deposits or their host rocks; in most cases they can provide neutralizing capacity.
3) **Compounds produced by ore processing** – on-site processing such as roasting, heap leaching and pressure oxidation produce new solid compounds that may convert sulfide minerals to oxides and reduce the acid-generating potential of the wastes.
4) **Secondary minerals formed by weathering** – majority of these minerals are fine grained with high capacity for adsorption of potentially toxic metals. Secondary minerals can provide information on the environmental condition they formed (pH, redox, etc.)

In this way, physicochemical and mineralogical studies of potentially polluted materials by trace elements are essential to find and apprise the source of pollution, to understand and predict the behavior of the contaminants in the environment, and to propose remediation actions. Therefore, the objective of this chapter is to conduct physicochemical and mineralogical characterization of soil, sediment and mine waste materials to evaluate the potential risk of pollution as the first step in the environmental risk assessment in Chadak area.

3.2. MATERIALS AND METHODS

3.2.1. Study area

The present study is focused on the Chadak mining area, one of the main gold-producing sites in Uzbekistan. The Chadak ore area has been known since antiquity and was in use up to the 12th century, with mining traces (abandoned open-pit mines and placer fields) preserved in the lower Chadak village and other surrounding areas. However, in the 12th and 13th centuries the mining activity declined and was revived only in the 20th century (Kuldashev and Abdurahmanov, 2009).

Figure 3. Location map of the study area

The history of the Chadak deposits without exaggeration is the history of the formation of the gold industry in the Republic of Uzbekistan. The discovery of the

Chadaks gold deposit was the reason for carrying out large-scale prospecting and exploration throughout the territory of Uzbekistan.

3.2.2. Site description

Samples were collected from the vicinity of the Chadak ore field which is located in the Pap district of Namangan region (eastern, Uzbekistan), in the north-eastern slopes of the Kurama ridge in Chadak basin (Fig. 3). Chadak ore field includes gold-silver deposits (Pirmirab and Guzaksay) and a number of other occurrences of gold and other exploitable minerals. System of gold-silver veins of the Chadak deposits (low sulphidation type) is hosted by Carboniferous andesite volcanites. Veins are associated with quartz-sericite-pyrite alteration. The main gangue minerals are quartz, calcite, adularia, sericite, wollastonite and tremolite. The main ore minerals are pyrite and hematite, but galena, chalcopyrite and sphalerite are common (Smirnova et al., 2009).

The area is characterized by a relatively developed mining industry, operated since 1970 by the Chadak gold-extracting plant (GEP) with the capacity of 180,000 t/y. The plant treats gold bearing ore from the Pirmirab and Guzaksai deposits. Mining is conducted by an underground and open pit method, and two tailing dumps were settled to storage the waste from the mineral extraction procedures. The first tailing dump which operated from 1970 to 1979 is abandoned (AbT), while the new tailing dump operating from 1979 to the present time is active (AcT). According to Filimonov (2009) the amount of wastes stored in tailing dumps is 3 Mt. The technological scheme includes: three-stage crushing, one-stage grinding in a closed cycle with two-stage ore classification, hydrocyclone overflow thickening; cyanidation of thickened product; filtration of gold bearing solutions; precipitation of precious metals onto zinc dust and drying of zinc precipitates. The waste products, after their sterilization with liquid chlorine, are delivered to the tailing dump.

The nearest railway stations are the cities of Kokand (65 km), Pop (60 km), Namangan (75 km) and Angren (120 km), with which there is an asphalt road. The source of the active labor force of the mining company and Chadak exploration works group are the villages Altynkan, Chadak and Gulistan.

The relief is mountainous and is represented by a system of low ridges, sometimes rocky forms, with slopes between 10 - 30°. Elevations range from 1000 m to 1700 m. The main watercourse in the area is Chadak river and its tributaries Kokinsay, Uryuklisay, Dzhulaysay and Pirmirab. Supply of streams occurs at the expense the melting of snow, rain and springs. The closest source of technical water supply is Dzhulaysay, the source of drinking water is Chadak river.

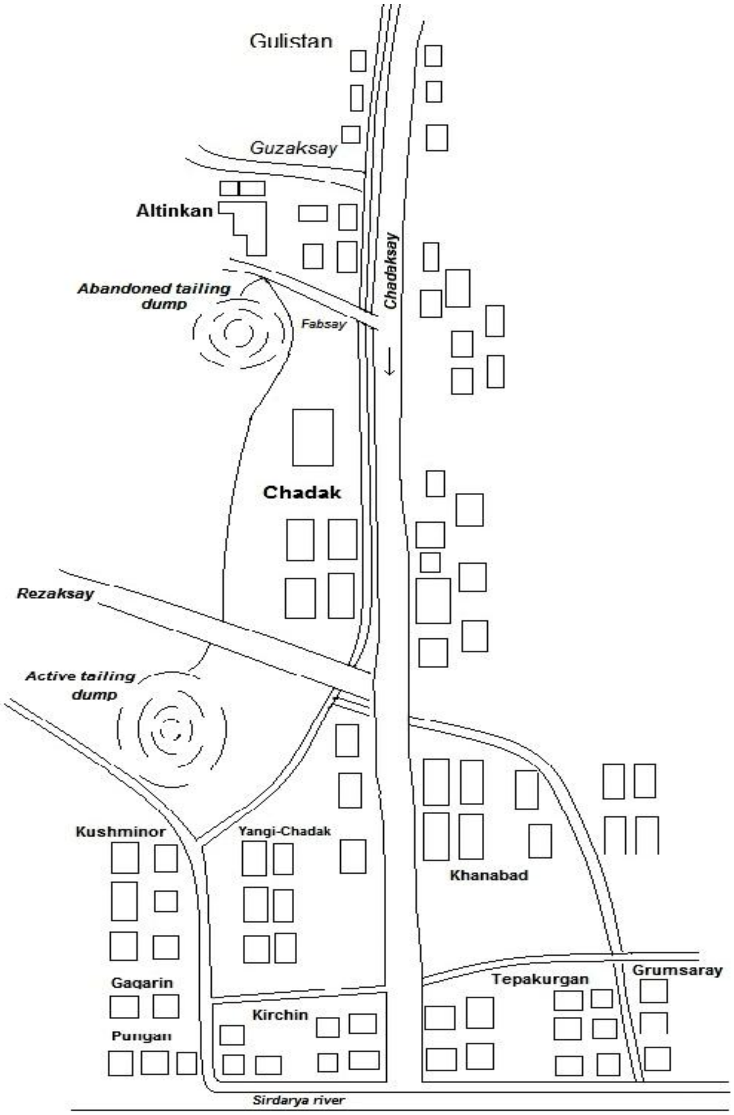


Figure 4. Schematic map of the Chadak village with production facilities

The capacity of the Chadak river is 0.12-0.2 m^3/s in the summer-autumn period, and reaches 30 - 62 m^3/s in the spring flood (April-May). The climate is continental with long hot summers and short, but relatively cold winters with little snow. The average annual air temperature is +14°C. The hottest months are July - August with maximum temperatures between +30°C and +42°C. In winter, the lowest recorded temperature ranging from -5°C to -25 °C. The distribution of seasonal rainfall is very uneven: the maximum amount of precipitation falls in the spring, whereas winter and autumn account for about 50% of the total precipitations, while the summer is characterized by dry weather. Snow falls rarely, and it does not cover more than 30 cm in thickness. Total annual precipitation is also highly variable 250 - 460 mm.

Soils in the area are characterized by low organic matter (<1%), a high level of calcium, often associated with gypsum, alkaline pH, and a low agricultural potential. They usually have poor structural characteristics, and often a high level of compaction. Most of the soils have evolved from alluvial, colluvial or aeolian loessic deposits with little weathering of the parent material. They have been intensively studied for their agricultural development potential because of the availability of irrigation water, mainly from the Amu-Darya river (Letolle and Mainguet, 1993). Three main groups of soils may be distinguished among all the soil types recorded in Uzbekistan (Odintsova and Toyniontsova, 1999): i) sandy aeolian soils (located on the adyr on the piedmont of the eastern mountains); ii) grey-brown soils (located on pre-desert and steppe, on the chol and the adyr); iii) solonchak and solonetz soils (mainly located in depressions, and takyr with a high saline water table).

The area is quite poor in relation to vegetation. The extreme arid to semi-arid and continental climate, the abrupt slopes of the rocky valleys, and the low development of soils support a very poor vegetation cover with a very low diversity. In the semi-arid areas, the vegetation cover consists of various shrub-ephemeral plant communities, with xerophytic-dwarf shrub vegetation predominating in the foothill areas (Gintzburger et al., 2003). The dominant species are *Artemisia diffusa*, *Carex pachystylis*, *Poa bulbosa*, annual *Salsola* spp., *Gamanthus gamocarpus* and *Climacoptera lanata* with annual herbaceous species such as *Bromus tectorum*, *Eremopyrum orientale*, *Malcolmia* spp. and others. Woody vegetation is scarce and the most abundant species are related to rare wild rose bush (Genus *Rosa*),

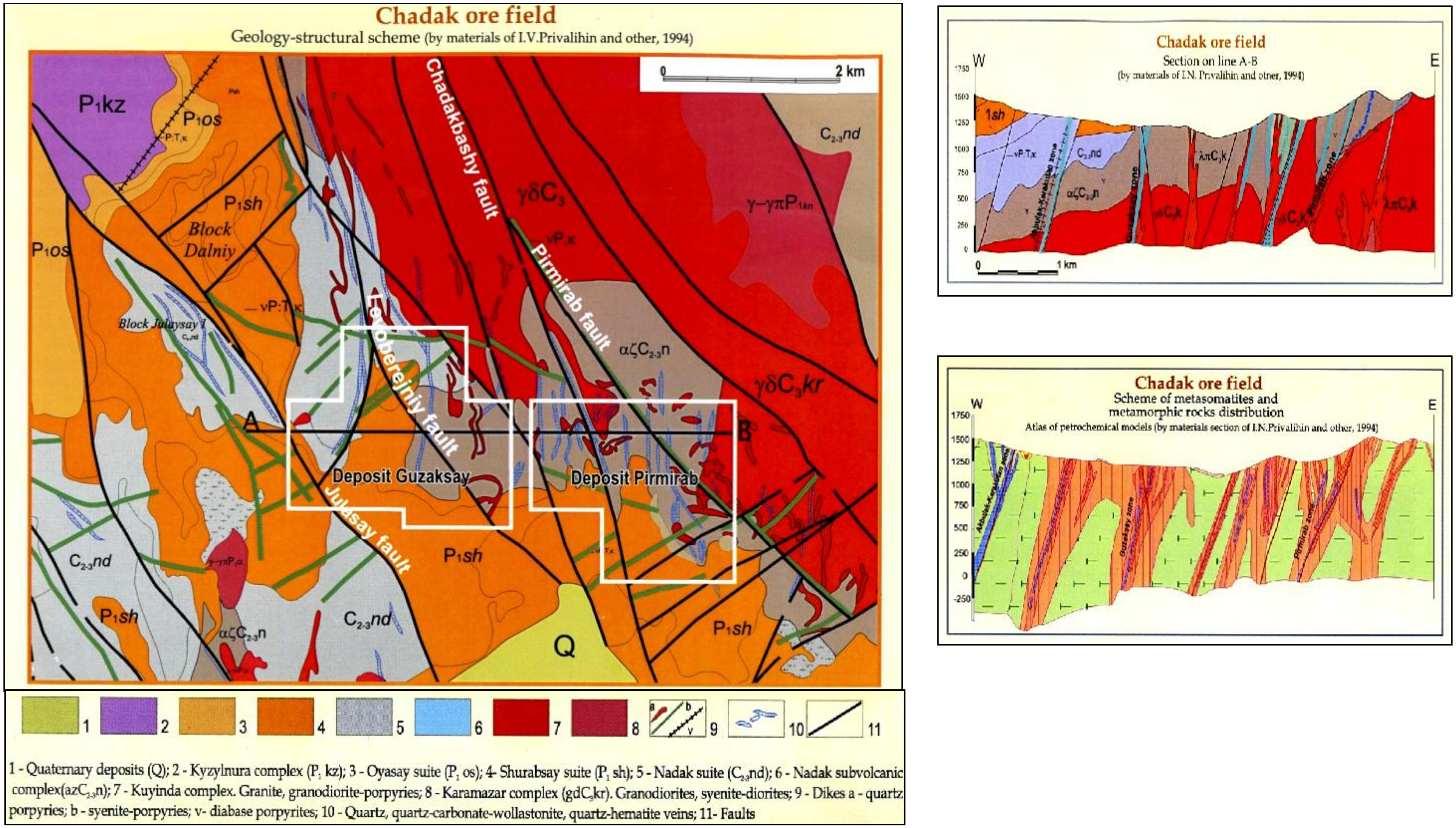


Figure 5. Geology-structural scheme (adopted from Mirkamalov et al., 2011)

mountain cherry and almond (Genus *Prunus*). is represented by thawed, poplar (Genus *Populus*), hawthorn (Genus *Crataegus*).

Power supply of work facilities is carried out by the power line capacity of 35 kW. Carrying out survey and exploitation works on the fields of the ore area is possible all the year round. Opening in 1953, of the gold deposit Pirmirab intensive exploration works (1953-1962), construction and commissioning of Chadak mining and processing plant, a complex of two mines and a gold mill in 1970 led to a sharp change in the region infrastructure. There was a separate mining district, where the overwhelming majority of the population (2 thousand people) is associated with the exploration, extraction and processing of gold. Such infrastructure is preserved until today.

Production facilities of mining group includes: mines, beneficiation plant, tailing dumps, administrative-domestic premises, as well as villages Oltinkon and Chadak located on the banks of the river Chadaksay (Fig. 4). The river Chadaksay is the only source of water for mining administration, as well as for residents of villages on its banks.

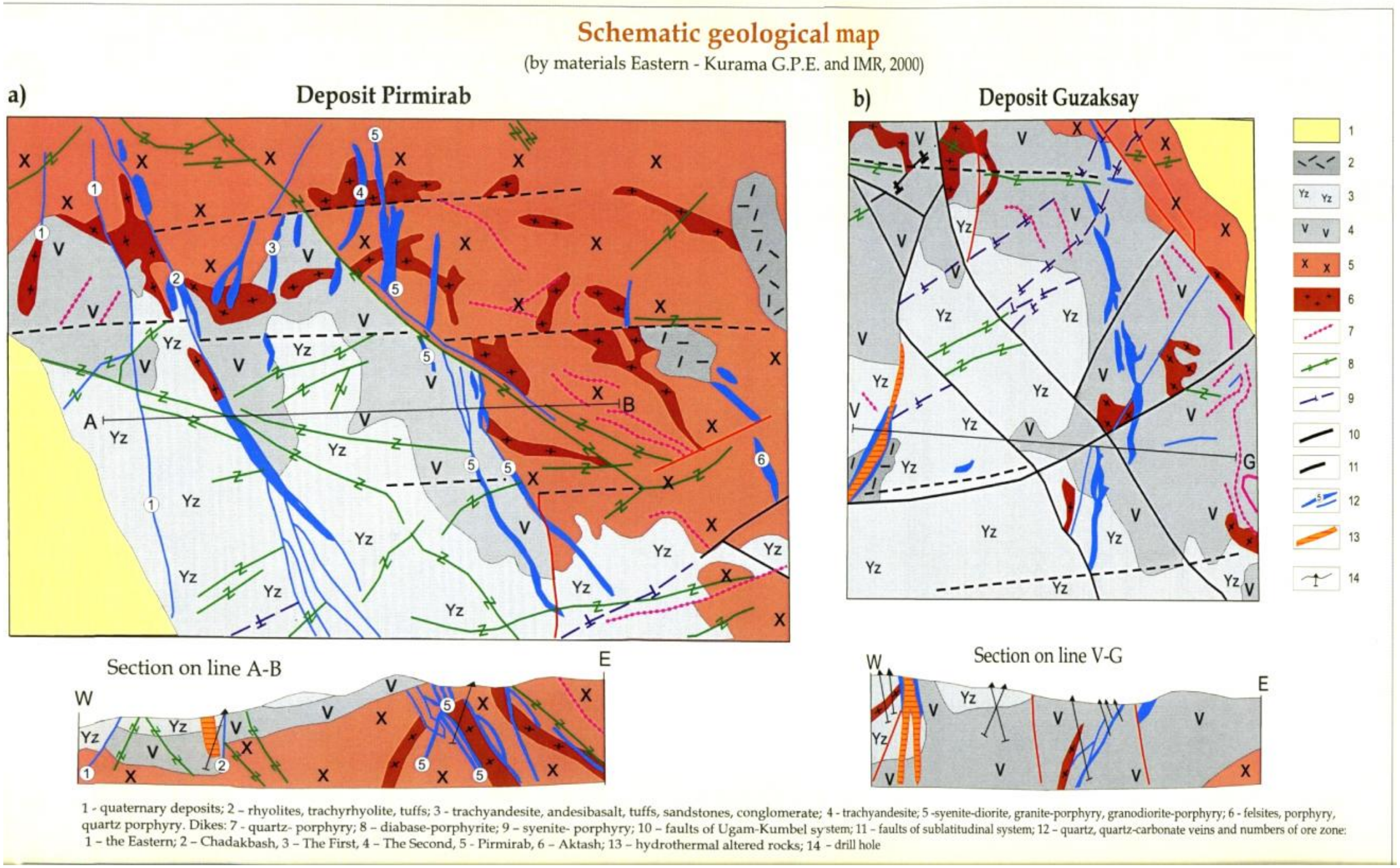
3.2.3. Geological structure of the ore area

Among the set of conditions that determine the state of the soil and the environment as a whole, geochemical factors associated with the geological history of the area and the chemical composition of its constituent rocks and soils, play an important role.

Chadak ore field consists of gold-silver deposits Pirmirab and Guzaksay. It is located on the southern slope of the eastern end of Kurama Mountains, in the middle of the river Chadak, in the Pap district of Namangan region (Mirkamalov et al., 2011). Ore field is located in a part of volcano-plutonic belt, where manifested very intensive late Carboniferous and Permian supersubduction intraplate volcanism in the junction zones of Ugam-Kumbel thrust and North Fergana upthrust. Within the ore field, the following volcanic structures established: Uryukly dome uplift, Chadak near-fault depression, southern edge of the Babaytaudor caldera (Averin, 1969).

Major role in the placement of mineralization played faults. On the area of the ore field are distinguished following systems: sublatitudinal – the earliest, poorly expressed on the surface; the north-western, the largest ones, block dividing have a complicated structure, often accompanied by magmatic hydrothermal vein formations, and also submeridional, mainly branch structures of larger faults of the previous system and are characterized by intense hydrothermal processing of the surrounding rocks, accompanied by quartz, quartz-carbonate veins bearing sometimes commercial gold mineralization. In addition, north-east faults were established, which are intersecting dislocations of the previous system (Majidov and Egamberdiyev, 1992).

Geological formation of the ore field belongs to Hercynian structural stage, subdivided into two substages – Middle-Upper Carboniferous and Permian (Fig.5). Middle – Upper Carboniferous stage (Median Tien-Shan volcanic-plutonic belt of active margin C_1-C_3) presented by sediment of rhyolite-dacite-trachyandesite complex, which is complicated by two subsuites – lower and upper Nadak. Lower Nadak subsuite composed by sandstones, tuffs of acid composition, banded limestones, tuffs and porphyrites of andesite-dacite and dacite composition. Upper Nadak subsuite represented by acid composition tuffs with interbedded sandstone and argillites. Subvolcanic facies of complex – bodies of andesite and trachyandesite composition. Middle Carboniferous intrusive complex consists of granodiorites of Karamazar type and presented by hornblend-biotite granodiorites. Upper Carboniferous Gushsay-Kuyundy intrusive complex is represented by lakkolite shape, flat-lying body granite porphyry and granodiorite porphyries. At the final stage of formation of the complex took place intrusion of quartz porphyry dike bodies. Rocks of the complex build up a significant portion of the area of deposits Pirmirab and Guzaksay. Among them are the main quartz-gold ore bodies of deposits (Averin et al. 1972). Otherwise, Permian structural stage (Chatkal-Kurama areals of interpolate magmatism P) presented by deposits of Shurabsay, Ravash and Kyzylnura complexes and their subvolcanic facies. Mineralization formed in three stages of hydrothermal activity: early hydrothermal of Upper Carboniferous age; skarn-hydrothermal and late hydrothermal of Upper-Permian age. Basic mass of gold and silver is associated with adular-calcite-quartz gold ore phase of



Schematic geological map

(by materials Eastern - Kurama G.P.E. and IMR, 2000)

a) Deposit Pirmirab

b) Deposit Guzaksay

Section on line A-B

Section on line V-G

1 - quaternary deposits; 2 – rhyolites, trachyrhyolite, tuffs; 3 - trachyandesite, andesibasalt, tuffs, sandstones, conglomerate; 4 - trachyandesite; 5 -syenite-diorite, granite-porphyry, granodiorite-porphyry; 6 - felsites, porphyry, quartz porphyry. Dikes: 7 - quartz- porphyry; 8 – diabase-porphyrite; 9 – syenite- porphyry; 10 – faults of Ugam-Kumbel system; 11 – faults of sublatitudinal system; 12 – quartz, quartz-carbonate veins and numbers of ore zone: 1 – the Eastern; 2 – Chadakbash, 3 – The First, 4 – The Second, 5 - Pirmirab, 6 – Aktash; 13 – hydrothermal altered rocks; 14 - drill hole

Figure 6. Schematic geological map (adopted from Mirkamalov et al., 2011)

early hydrothermal stage and chlorite-carbonate-quartz (with adular), gold-silver phase of skarn-hydrothermal stage (Averin et al. 1972). By typomorphic features of minerals and their associations in the area of the ore field is revealed vertical zoning. Above and upper-ore horizons characterized by quartz, calcite, chlorite. Metasomatic quartz marks “blind” ore zones (Barkhudarov, 1975). Structural-tectonic and lithological factors significantly predetermined localization of gold mineralization within Chadak ore field (Majidov and Egamberdiyev, 1992).

3.2.3.1. Pirmirab deposit.

In its area (Fig.6) widely spreaded deposits of Nadak and Shurabsay complexes. From the south, deposits of bearing mineralization Nadak complex, with a sharp azimuthal disconformity in the course are overlapped by basal layers of Shurabsay complex. Shurabsay formations are characterized by variable composition.

Intrusive formations presented by granite-porphyries, quartz and felsite porphyries of Karamazar and Kuyindy complexes, and diabase – granophyre complex, represented by quartz syenite porphyries and dikes of acid, subalkaline and basic composition. Diabase porphyries are the most common formations. In the area of Pirmirab deposit are distinguished vein mineralized zones with north-western, close to the meridional trend:

- Eastern mineralized zone – presented by bodies of quartz-carbonate and quartz-chlorite with pyrite composition;
- Chadakbashy mineralized zone presented by quartz-chlorite with pyrite veins with non-industrial gold content. On the southern flank of the zone the veins thin out rapidly and can be traced to the south under volcanites of Shurabsay complex and some sites are characterized by concentrations of gold;
- Pirmirab vein zone includes the veins, which are concentrated almost all prospected commercial reserves of gold. All the veins are prospected into depth 150-250mm, have a complex morphology, different mineral composition and the uneven distribution of gold;

- Aktash mineralized zone is represented by a series of thick (20m) quartz-carbonate-chlorite with hematite and magnetite veins. The length of the zone is over 900 m (Mirkamalov et al., 2011).

3.2.3.2. Guzaksay deposit.

Deposit Guzaksay (Fig. 6) is composed by volcanic-sedimentary deposits of Nadak and Shurabsay complexes. Major faults are distinguished: the north-north-western, submeridional (Guzaksay, Akbulak-Karakutan, etc.), north-western and north-eastern.

Practically all ore bodies are concentrated in the zones of Guzaksay and Akbulak-Karakutan faults. In the southern part of the Guzaksay fault situated Main Zone (vein), which has a meridional trend with the dip to the west at angles of 60-70^0. South-western vein has extent 400 m, the industrial part of the vein along strike – 40-50 m, dip- 85-100 m, with gold content from 0,6 to 27,2 g/t.

In the zone of Akbulak-Karakutan fault two main ore-bearing zones were identified, which contain more than 90% of the deposit reserves. In addition, structures that carry commercial gold-silver mineralization – Small Dzhulaysay fault and the southern end of the Levoberezhny fault (South-Eastern site) was also identified. Vein mineralized zones presents bundles and clusters of an echelon like quartz veins, poorly continued by thickness from 0,3 to 6 m, with variable azimuths and dip angles (Mirkamalov et al., 2011).

3.2.4. Field investigations

3.2.4.1. Soil sampling.

Two replicates of soil samples were taken in a systematic-random pattern (grid of 100 x100 m) from the upper soil layer (0-10 cm) around the active (20 samples, Fig. 7) and abandoned (13 samples, Fig. 8) tailing damps. Moreover, 13 soil samples were collected in the vicinity of Guzaksay open pit area (Fig. 9).

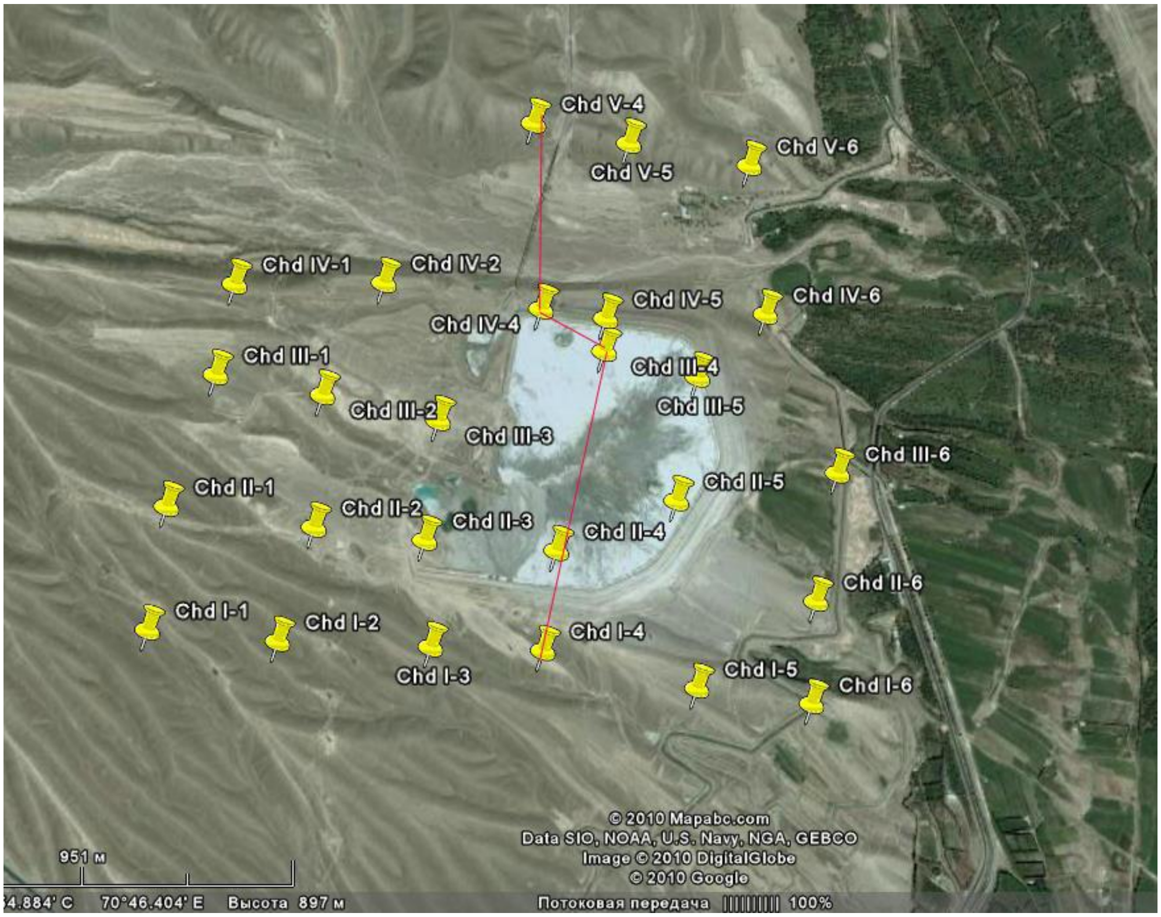


Figure 7. Sampling points at the Active tailing dump

3.2.4.2. Sampling of waste and tailings materials.

A set of 5 samples were collected from the waste piles resulted from the exploration of Guzaksay open pit (Fig. 9). Tailing materials from the surface layer of the active (AcT – 12 samples) and abandoned (AbT – 9 samples) tailing dumps (Fig. 7, 8) as well as a vertical profile of 1.5 m depth in the abandoned tailing dump (Fig. 10) was sampled at different depth (A: 0-30, B: 30-80, C: 80-150 cm, 12 samples).

3.2.4.3. Sediment sampling.

Four replicates for each 9 samples were collected along the Chadaksay river (Fig. 11) in order to assess the impact of contamination to the river banks. A distance between sampling points were 200 m for a total of 18 km profile along the river.

Figure 8. Sampling points at the Abandoned tailing dump

Figure 9. Sampling points at the vicinity of Guzaksay open pit

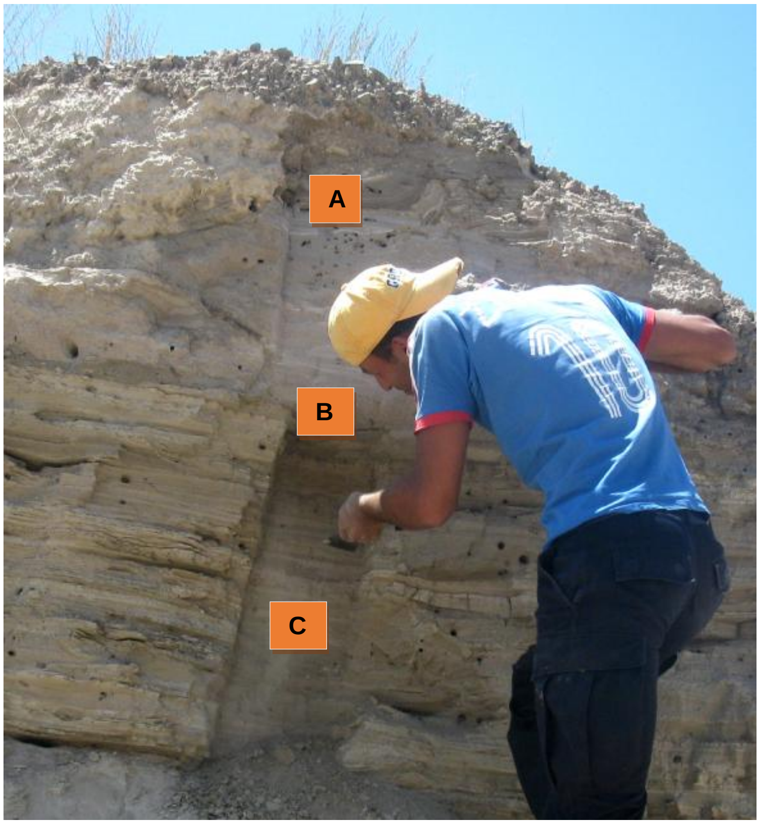


Figure 10. Sampling a vertical profile at the Abandoned tailing dump

3.2.5. Equipments and their application

3.2.5.1. Ion chromatography (DIONEX DX-120)

A Dionex DX-120 Ion Chromatograph equipment was used to perform isocratic ion analysis of extracts using conductivity detection. The DX-120 is an integrated system, which includes a pump, detector, and injection valve. Ion chromatography is used for water chemistry analysis and water extracts coming from soil, sediments or waste materials. Ion chromatographs are able to measure concentrations of major anions, such as fluoride, chloride, nitrate, nitrite, and sulfate, in the parts-per-billion (ppb) range.

3.2.5.2. Atomic absorption spectroscopy (VARIAN SpectrAA220FS)

Atomic absorption spectrometry is an element analysis technique that uses absorption of electromagnetic radiation to detect the presence of the elements of interest. This technique has been applied to the determination of numerous elements and is a major tool in studies involving trace metals in the environment and in

Figure 11. Sampling profile along the Chadaksay river sediments

biological samples. It is also frequently useful in cases where the metal is at a fairly high concentration level in the sample but only a small sample is available for analysis. The SpectrAA 220 optics feature four lamp positions with automated wavelength and slit selection, and high intensity deuterium background correction as standard. Conventional AA systems still determine one element at a time, repeating all samples for each element in turn. SpectrAA-220 FS provides complete results for each sample in minutes.

3.2.5.3. Inductively coupled plasma – mass spectrometry (PE SCIEX ELAN-5000A)

Inductively coupled plasma-mass spectrometry (ICP-MS) is a powerful tool for analyzing trace metals in environmental samples. A large range of elements can be detected using an ICPMS. The ICP-MS system can quantitatively measure simultaneously a high range of trace elements and give a measurement of the total amount of the specific element of interest. The benefits of using plasma compared to other ionization methods, such as flame ionization, are that ionization occurs in a chemically inert environment, preventing oxide formation, and ionization is more complete. Also, the temperature profile of the torch is relatively uniform, reducing self-absorption effects.

3.2.5.4. X-Ray fluorescence spectrometer (MagiX Pro XRF)

An X-ray fluorescence (XRF) spectrometer is an x-ray instrument used for routine, relatively non-destructive chemical analyses of rocks, minerals, sediments and fluids. It works on wavelength-dispersive spectroscopic principles that are similar to an electron microprobe (EPMA). However, an XRF cannot generally make analyses at the small spot sizes typical of EPMA work (2-5 microns), so it is typically used for bulk analyses of larger fractions of geological materials. The relative ease and low cost of sample preparation, and the stability and ease of use of x-ray spectrometers make this one of the most widely used methods for analysis of major and trace elements in rocks, minerals, soils and sediments.

3.2.5.5. X-ray diffraction (XRD Philips PW-1710)

X-ray diffraction (XRD) is an important tool for determining the intercrystalline structures of minerals and chemical compounds. The method is non-destructive (although in our study samples were grinded) and mineral species can be identified (‘fingerprinted’) in bulk samples even if only in very small particles. Mineralogical make-up of sediments and sedimentary rocks can also be estimated (for species with concentrations in excess of about 5%). For total mineralogy of the samples, powdered samples were used, and for clay mineralogy, oriented aggregates of this fraction were analysed.

3.2.5.6. Scanning electron microscopy (ZEISS-SUPRA 40VP SEM)

The Zeiss Supra 40VP scanning electron microscope (SEM) provides high resolution surface imaging. It scan a sample with a focused electron beam and deliver images with information about the sample’s morphology and composition. It operates in both high vacuum and variable pressure modes with a high resolution. This equipment has a X-ray Dispersive Energy Microanalysis System (EDX) with X-Max large surface detector 50 mm. The analysis can be done on solid materials having a resistance to incident electron beam (< 30 kV).

3.2.5.7. Microwave Accelerated Reaction System (CEM MARS 230/60 Xpress)

The CEM MARS 230/60 Microwave Accelerated Reaction System is designed for laboratory use in digesting, dissolving, hydrolyzing, extracting or drying a wide range of materials. Its primary purpose is the rapid preparation of samples for analysis by atomic absorption (AA) and inductively coupled plasma (ICP) emission spectroscopy and gas or liquid chromatography. Using microwave energy to heat samples, the MARS rapidly heats and elevates pressures, causing the sample to digest or dissolve quickly and efficiently. Samples were grinded before acid digestion.

3.2.6. Chemical and analytical works

3.2.6.1. Preparation of soils, sediments and waste materials for analysis

The main physico-chemical properties of the samples were measured by standard soil-analysis techniques (MAPA, 1994): the pH was measured in a pH-meter (CRISON digit 501) in a 1:2.5 (w:v) soil-water suspension ratio; electrical conductivity (EC) was measured using a EUTECH XS Con 700 meter in extracts prepared by filtering the 1:10 soil:water suspensions through 0.45 µm cellulose acetate membrane filter; organic carbon (OC) was determined by wet oxidation method; cation exchange capacity (CEC) was determined by 1 N sodium acetate solution at pH 8.2 measured by atomic absorption spectroscopy using the VARIAN SpectrAA 220FS instrument; particle size distribution was determined by the pipette method; and calcium carbonate content was determined manometrically upon HCl digestion.

The neutralization potential (NP) of tailing samples were evaluated with the modified Sobek acid-base accounting (ABA) method (Lawrence and Scheske, 1997). The acid potential (AP) and net neutralization potential (NNP) was calculated according to SRK (1989).

3.2.6.2. Measurement of major anions

Major anions such as fluoride, chloride, nitrate, nitrite, phosphate and sulfate were measured with a means of Dionex DX-120 Ion Chromatograph. A calibration curve was prepared with multi-anions standards (Merck, Darmstadt, Germany) containing all the analytes of interest at five different levels of concentration. Measurements were performed according to the Method 300.1 (US Environmental Protection

Agency EPA, 1997). The detection limits for undiluted anion samples ranged in all cases from 0.02 to 0.05 ppm (using an IonPac AS9-HC column).

3.2.6.3. Total concentration of trace elements

The total concentration of trace elements (V, Cr, Co, Ni, Cu, Zn, As, Cd, Pb, Sb) was measured using X-ray fluorescence (XRF) analysis of the powder pellets (MagiX Pro XRF with rhodium anode X-ray tube). The total concentration of major elements was determined by XRF using glass pellets of subsamples melted with lithium tetraborate fluxer (0.6:5.5). QA/QC criteria were fulfilled by the use of geochemical standard reference materials GSS-2 and GSS-4 (Table 2); the experimental average values ranged within the certified reference values in both cases.

Table 2. Analysis of geochemical standard reference materials GSS-2 (n=4) and GSS-4 (n=2) measured by XRF.

Element	**GSS-2**				**GSS-4**			
	Certified		**Experimental**		**Certified**		**Experimental**	
	Mean	S.D.	Mean	S.D.	Mean	S.D.	Mean	S.D.
V	62	2	62.0	1.4	247	6	261.5	0.7
Cr	47	1.6	44	1.2	370	6	385	1.4
Co	8.7	0.3	8.5	1.7	22.3	0.6	24.5	2.1
Ni	19.4	0.5	19.5	0.6	64.2	1.7	68.5	0.7
Cu	16.3	0.4	14.5	0.6	40.5	0.1	39.5	0.7
Zn	42.3	1.2	41.0	0.1	210	5	218	1.4
As	1.37	0.6	1.35	0.7	58	3	63.0	0.1
Cd	0.07	0.01	bdl*	-	0.35	0.03	0.20	0.10
Sb	1.3	0.1	bdl*	-	6.3	0.6	6.0	0.1
Pb	20.2	1.0	20.0	1.4	58.5	2.1	61.0	1.0

*bdl – below detection limit; S.D. – standard deviation

3.2.6.4. Mineralogical studies

The mineralogy was studied by X-ray diffraction (XRD) in a Philips PW-1710 instrument with CuKα radiation, Ni-filter and graphite monochromator. For total mineralogy determination, powder method was used (Azaroff and Buerger, 1958), and for clay mineralogy, oriented aggregates of clay after three specific treatments (heating at 550ºC, and solvation with ethylene glycol and dimethyl-sulfoxide) were analysed according to the Moore and Reynolds (1989) method. Interpretation of diagrams was made according to the software XPowder ver.2004.04 (www.xpowder.com).

Selected subsamples were prepared for scanning electron microscopy (SEM Supra 40VP, ZEISS, Germany). The imaging was performed at an acceleration voltage of 30 kV in both conventional secondary electron and backscattered electron mode. For the elemental microanalysis of mineral particles, an energy-dispersive X-ray microanalysis (EDX) spectrometer with X-Max large surface detector 50 mm, was used in pinpoint mode (diameter 1 µm), resolution of 10 eV/channel, and a full-spectrum collection time of 100s.

3.2.7. Statistical analysis of geochemical data

Geochemical background values of trace elements for the studied area were calculated from surrounding soil samples collected in the vicinity of tailings dumps with statistical methods using mean (Mf) ± twice the standard deviation (σ) of the calculated distribution function (Matschullat et al., 2000).

Statistical analyses of the data were carried out after testing the fit of the data set to a normal distribution by a Kolmogorov-Smirnov test. Mean comparison study was made by one-way analysis of variance (ANOVA) and Tukey’s test, the significant differences were considered when $p<0.05$. The relationship between variables was investigated using Varimax-rotation Principal component analysis (PCA). All statistical treatments were made using SPSS v.20.0 software.

3.3. RESULTS AND DISCUSSION

3.3.1. Total content of major and trace elements and their distribution in the horizontal and vertical profiles

The results of the major elements analysis for waste and sediment samples are given in Table 3. The main component of all samples is SiO_2, ranging from 53.34% to 73.68%, followed by Al_2O_3 (fluctuations from 7.18 to 17.88%), Fe_2O_3 (3.06-8.44%) and CaO (0.88-11.58%).

The values of the total content of elements in the soil allows us to estimate the general contamination in the study area. The total content of all analyzed trace elements are given in Annex-1 and Annex-2. The mean total concentration of most important trace elements of environmental concern are summarized in Table 4 for soils and tailing dump material, and in Table 5 for Guzaksay open pit and Chasaksay river sediments samples. The results were compared with the calculated background concentration (BC) of the soils in the area, and the intervention values (IV) reported by the Ministry of Environment of the Regional Government in Andalusia (Spain), based on a review of the intervention values in many countries worldwide (Aguilar et al., 1999) and the Dutch Target and Intervention Values (RIVM, 2000).

Table 3. Total concentration of major elements, (%)

Sample	SiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5	Zr (ppm)
Abandoned tailing dumps											
CTX I-3	**64,02**	**12,96**	**4,68**	**0,11**	**1,39**	**4,47**	**1,66**	**3,83**	**0,46**	**0,16**	**168,1**
CTX II-2	**60,17**	**13,24**	**6,34**	**0,19**	**2,03**	**5,15**	**1,12**	**3,65**	**0,54**	**0,20**	**154,5**
CTX II-5	**59,05**	**13,75**	**5,30**	**0,09**	**1,97**	**6,24**	**1,82**	**3,44**	**0,53**	**0,16**	**166,3**
CTX IV-3	**61,93**	**11,25**	**7,13**	**0,23**	**2,01**	**6,70**	**0,44**	**3,40**	**0,33**	**0,16**	**79,5**
Active tailing dump											
Chd I	**62,57**	**13,23**	**5,13**	**0,13**	**2,01**	**4,84**	**1,55**	**3,83**	**0,64**	**0,20**	**250,8**
Chd II	**73,68**	**9,01**	**4,33**	**0,12**	**1,14**	**3,55**	**0,70**	**3,23**	**0,39**	**0,17**	**116,5**
Chd III	**70,72**	**8,28**	**7,09**	**0,14**	**1,20**	**4,27**	**0,50**	**2,90**	**0,33**	**0,14**	**96,9**
Chd IV	**64,40**	**13,23**	**3,96**	**0,10**	**1,79**	**2,82**	**1,85**	**3,80**	**0,59**	**0,25**	**256,0**
Chd V	**71,14**	**8,38**	**5,53**	**0,13**	**0,98**	**5,29**	**0,37**	**2,84**	**0,33**	**0,13**	**92,0**
Vertical profile in abandoned tailing dump											
Chd IV-1	**60,16**	**14,34**	**5,74**	**0,12**	**1,85**	**5,26**	**1,51**	**3,68**	**0,69**	**0,20**	**197,2**
Chd IV-2	**66,28**	**11,09**	**5,93**	**0,10**	**1,40**	**4,12**	**1,32**	**3,28**	**0,87**	**0,17**	**273,3**
Chd IV-3	**68,64**	**10,20**	**5,23**	**0,13**	**1,25**	**4,29**	**0,93**	**3,54**	**0,62**	**0,15**	**196,5**
Chd IV-4	**68,06**	**8,19**	**3,89**	**0,20**	**0,87**	**7,82**	**0,50**	**3,44**	**0,22**	**0,10**	**107,4**
Chd IV-5	**64,71**	**7,18**	**3,46**	**0,26**	**0,84**	**11,58**	**0,34**	**2,81**	**0,18**	**0,08**	**96,8**
Chd IV-6	**65,54**	**8,34**	**3,06**	**0,21**	**1,00**	**9,63**	**0,74**	**3,30**	**0,21**	**0,09**	**119,3**
Chadak river sediment											
CHDS-0	**71,66**	**13,75**	**3,17**	**0,07**	**0,75**	**1,64**	**2,40**	**4,20**	**0,31**	**0,11**	**119,3**
CHDS-3	**66,40**	**14,51**	**4,26**	**0,09**	**1,21**	**1,63**	**2,21**	**4,24**	**0,51**	**0,19**	**219,1**
CHDS-5	**71,29**	**13,75**	**3,57**	**0,07**	**0,78**	**1,54**	**2,38**	**4,31**	**0,34**	**0,12**	**143,6**
CHDS-8	**67,18**	**13,62**	**4,01**	**0,08**	**0,99**	**2,01**	**2,12**	**4,24**	**0,54**	**0,18**	**257,6**
Guzaksay open pit area											
KP I-1	**55,15**	**17,88**	**8,44**	**0,22**	**2,11**	**1,65**	**0,76**	**4,60**	**1,01**	**0,48**	**144,8**
KP II-1	**56,25**	**17,48**	**8,76**	**0,23**	**3,22**	**1,18**	**1,42**	**4,34**	**0,95**	**0,33**	**163,2**
KP III-1	**61,79**	**16,09**	**5,84**	**0,15**	**1,77**	**2,27**	**1,19**	**3,85**	**0,65**	**0,26**	**192,4**
KP IV-1	**53,34**	**18,85**	**5,81**	**0,13**	**2,39**	**6,05**	**0,86**	**3,35**	**0,73**	**0,24**	**173,1**
KP IV-3	**58,95**	**14,89**	**7,09**	**0,20**	**2,14**	**4,47**	**0,52**	**3,92**	**0,56**	**0,22**	**131,7**
KP IV-5	**60,57**	**15,57**	**5,76**	**0,18**	**1,46**	**4,21**	**0,60**	**4,42**	**0,50**	**0,18**	**145,9**

Table 4. Total element concentrations in mg/kg^{-1} (mean ± SD; n = 3) in the surface sampling (0–10 cm) at active (AcT) and abandoned (AbT) tailing dumps and in the vertical profile (AbT). Letters (a, b) indicate significant differences ($p<0.05$); nd: not determined.

Area	**Subarea**	**V**	**Cr**	**Co**	**Ni**	**Cu**	**Zn**	**As**	**Cd**	**Sb**	**Pb**
AcT	Soil	85.0±12.7 (a)	46.5±2.1 (a)	10.5±2.1 (ab)	25.0±2.8 (ab)	24.5±0.7 (a)	84.0±1.4 (a)	10.5±2.1 (a)	1.3±0.7 (a)	0.0 ±0.0 (a)	36.0±0.0 (a)
	Tailing	62.7±2.5 (abc)	13.6±1.5 (b)	9.0±3.0 (ab)	5.7±1.5 (a)	37.0±9.8 (a)	233.7±98.6 (a)	27.5±5.0 (a)	1.0±1.8 (a)	3.3±0.6 (a)	137.3±68.6 (a)
AbT	Soil (cover)	81.7±4.9 (ab)	30.8±13.5 (ab)	12.2±1.5 (a)	15.0±6.4 (ab)	29.5±9.4 (a)	215.7±109.4 (a)	132.2±71.1 (a)	1.1±1.0 (a)	7.5±5.8 (a)	126.5±123.3 (a)
Profile (AbT)	A	89.7±14.5 (a)	35.9±13.9 (ab)	11.1±0.3 (a)	26.3±12.1 (b)	23.97±0.1 (a)	207.8±91.6 (a)	1032.6±928.8 (a)	2.4±1.9 (a)	924.0±824.7 (a)	246.3±198.2 (a)
	B	47.5±26.2 (bc)	29.3±1.4 (ab)	7.0±1.0 (ab)	16.2±5.4 (ab)	42.4±27.6 (a)	201.9±29.4 (a)	385.3±405.7 (a)	1.5±0.7 (a)	362.1±257.2 (a)	191.5±5.5 (a)
	C	27.6±1.0 (c)	15.3±0.4 (b)	4.7±0.6 (b)	11.8±1.0 (ab)	38.4±3.4 (a)	229.7±38.9 (a)	347.2±144.8 (a)	1.5±0.3 (a)	68.1±18.2 (a)	293.1±103.3 (a)
Background		131	51	19	31	37	135	15	nd	4	48
Interv. Value*		-	450	300	300	500	1000	50	10	-	500
Interv. Value**		250	380	240	210	190	720	55	12	15	530

* Intervention value according to the proposal of Aguilar et al. (1999) to the Ministry of Environment of the Board of Andalusia (Spain).

** Dutch Target and Intervention Values (The New Dutch List, 2000).

Table 5. Total element concentrations in mg/kg^{-1} (mean ± SD; n = 3) in the soils (0–10 cm) at open pit area and Chadaksay river sediments. Letters (a, b) indicate significant differences ($p<0.05$); nd: not determined.

Area	V	Cr	Co	Ni	Cu	Zn	As	Sb	Cd	Pb
Open pit area soils	126.3±51.1 (a)	26.9±10.0 (a)	19.3±9.5 (a)	15.2±6.0 (a)	52.6±55.4 (a)	101.9±36.9 (a)	32.1±32.1 (a)	1.6±1.7 (a)	0.9±0.7 (a)	41.4±16.9 (a)
River sediments	45.9±10.1 (a)	12.8±4.8 (a)	5.8±2.4 (a)	5.8±2.5 (a)	26.8±7.4 (a)	72.1±14.0 (a)	5.9±1.7 (a)	0.4±0.6 (a)	0.2±0.3 (a)	40.8±8.7 (b)
Background	131	51	19	31	37	135	15	nd	4	48
Interv. Value*	-	450	300	300	500	1000	50	10	-	500
Interv. Value**	250	380	240	210	190	720	55	12	15	530

* Intervention value according to the proposal of Aguilar et al. (1999) to the Ministry of Environment of the Board of Andalusia (Spain).

** Dutch Target and Intervention Values (The New Dutch List, 2000).

The mean concentrations of V, Cr, Co, Ni, Cu, and Cd in all surface samples (soils and tailings) were in the range of the background concentrations (BC) in the area. On the other hand, Zn, As, Sb, and Pb showed significantly higher mean concentrations (Table 4) both in tailings of AcT (exceeding 1.7-, 1.8-, 0.8-, and 2.8-fold the BC values, respectively), and in the covering soils of AbT (exceeding 1.5-, 8.8-, 1.8-, and 2.6- fold the BC values, respectively).

In the vertical profile of AbT, trace metals V, Cr, Co, and Ni presented significant differences although these values were in the range of BC (Table 4). Layer A had the highest concentrations of these elements, which decreased in the next two layers. On the other hand, concentrations of Cu, Zn, and Cd were slightly above the BC but below the intervention values (IV) and presented no significant differences along the vertical profile. The Pb concentrations in the vertical profile were higher than the BC (between 3.9- and 6.1-fold), but also below the IV. However, the mean values of Zn and Pb revealed an inverse trend in vertical distribution, showing the highest mean concentrations in the deepest C layer. High values of these elements in tailings could be attributed not only to the presence of sulphide and suphosalt minerals (pyrite, sphalerite, arsenopyrite, galena, and tetrahedrite) in ores of the Chadak deposits, but also to the concentration related to the metal-extraction procedure in the mining activity of the Chadak ore field. The two elements with the highest concentrations in all three layers were As and Sb, with mean values strongly exceeding the IV (up to 20-fold for As, and 62-fold for Sb), with the highest concentrations in the surface A layer (1030 and 920 mg/kg, respectively). A comparison of these concentrations with the ecotoxicological threshold levels reported of 55 mg/kg for As (Van den Berg et al., 1993) and 60 mg/kg for Sb (Sheppard et al., 2005) indicate a high risk of pollution in the area. The problem is exacerbated by the fact that these wastes are located up-stream of the main population area (Chadak city), which poses a serious potential pollution risk over time.

The mean concentrations of all elements in the Chadaksay river sediments were in the range of the BC of the area (Table 5). Similarly, the mean concentration of trace elements in the Guzaksay open pit soil samples were in the range of the BC except for Cu and As. However, the latter elements are below the IV and not presenting an immediate risk for the area. The comparison of open pit and river sediments results showed no significant differences with the exception of Pb.

As the total content of some trace elements of environmental concern were higher in the tailings materials and the surface soils samples, exceeding the intervention values used to assess the potential risk of pollution, a detailed physico-chemical study was conducted in this samples.

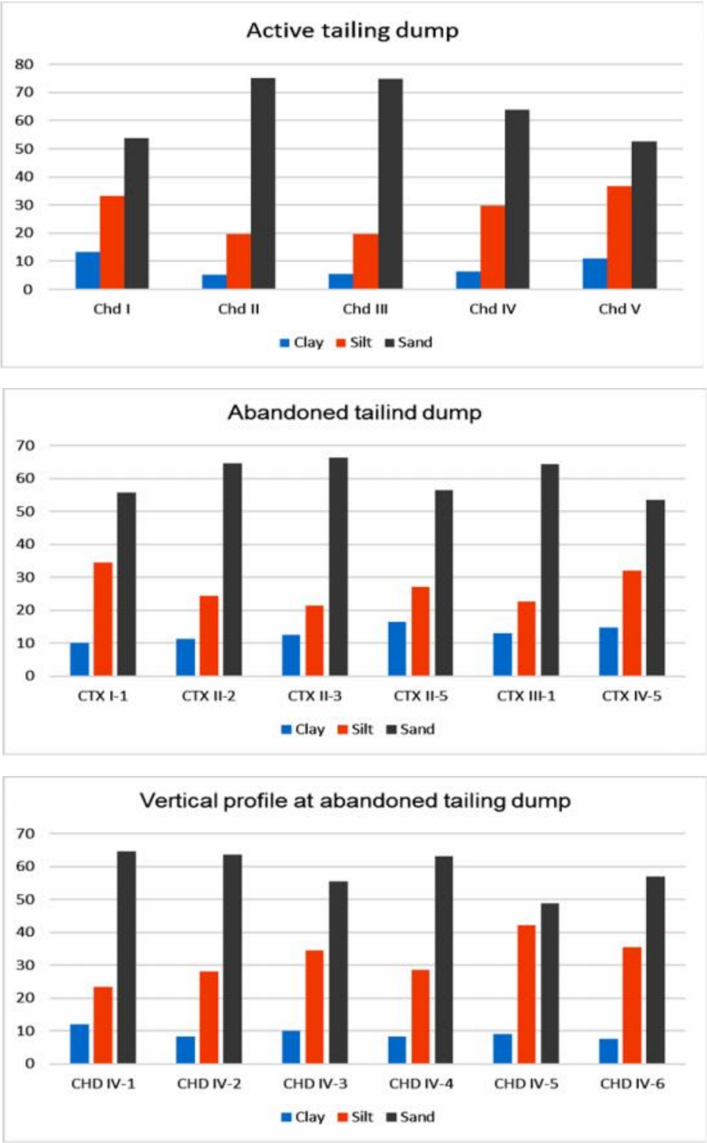


Figure 12. Granulometric distribution of Chadak mine tailings, %

3.3.2. Grain size distribution

Tailings of enrichment area consisting of a mixture of solid and liquid phases. The solid phase is represented by a mixture of mineral particles of different sizes (from a micron fraction to 3 mm). According to the granulometric distribution, the tailings pond is mainly represented by sandy material, and also contains a large amount of dust particles (<5 µm). The results of studying the granulometric composition of the tailings of the Chadak mine are shown in Figure 12. As can be seen from the figure, the sand fractions is predominating with an average content of more than 50% in all samples. The output of the silt fraction is followed by the sand fraction averaging more than 20%. The clay fraction is the least among all, averaging 10%. Thus, the grain size of tailing materials is represented by sandy-loam texture.

3.3.3. Physio-chemical properties of soil and tailings

The general physico-chemical properties of soils and tailing samples are summarized in Table 6, and the properties of the vertical profile collected on AbT in Table 7. The pH values of soil samples collected in the vicinity of AcT and soils covering AbT showed mean values of 8.2 and 8.4, respectively. The moderately alkaline conditions are presumably related to the presence of carbonate minerals calcite, ankerite, and dolomite (Iavazzo et al. 2012), and can be also related to the arid climate in the study area. In any case, calcium carbonate content in soil and tailings was moderately low (mean values < 15%), with minimum concentrations in tailings ranging from 2.9 to 4.2%.

The analysis of the soluble salts by ion chromatograpy was made in the abandoned tailing dump from the water-soluble extract of the samples. Tailings presented a very high concentration in sulfates (224.3 ±150.2 mg/kg), with lower amounts of chlorides (9.1 ±1.4 mg/kg) and nitrates (8.1 ±6.8 mg/kg); while soil covering the abandoned tailing dumps presented a lower concentration of sulfates (44.9 ±26.9 mg/kg) in relation to the tailings, low concentration of chlorides (14.4 ±3.0 mg/kg) and very low of nitrates (2.6 ±0.9 mg/kg). The high deviation of the data did not indicate significant differences between both type of samples.

Soil samples from both areas showed very low EC values (SSDS, 1993), very low

CEC (Marañés, 1998), sparse OC content, and a sandy-loam texture, with no significant differences between active and abandoned tailing dumps. Tailings at AcT, registered similar values to soil samples for pH, EC, and OC, but significant lower values for CEC and clay content (Table 6), indicating a selection in the particle size towards the sand fraction and concomitant reduction in clay content that is directly related to the reduction in the CEC (Jung, 2008).

The comparison between tailings from vertical profile in AbT and active tailing dump (AcT) showed similar properties, with no significant differences in any of the main variables studied except $CaCO_3$, which showed significantly lower values from the A to C layers (Table 7).

3.3.4. Acid potential (AP) and Neutralization potential (NP) of the tailings

The presence of S was also detected in tailing samples, with values ranging from 1.70 to 0.45%. Therefore, the tailings possess a neutralization potential (NP) which can be balanced with the acid potential (AP) assessed for a worst case from the total S content (neglecting the minor sulphate mineral content as a product of previous oxidation). The acid-base accounting (ABA) of tailings and concentrates are shown in Table 8, where results related to AP, NP and net neutralization potential (NNP) are presented. The acid potential (AP) of tailings from AbT is 20.3 kg CaCO3/t, while for tailings from AcT is 53.1 kg CaCO3/t; meanwhile the mean neutralization potential (NP) of the tailings amount to 15.5 and 11.1 kg CaCO3/t, in AbT and AcT dumps, respectively. This indicates that both tailings have similar neutralization potential, but AcT has higher acid potential than AbT.

Thus, according to the criteria defined by SRK (1989: NNP <-20 kg CaCO3/t), the net neutralization potential (NNP = NP-AP) indicates that the active tailing dump is potentially acid generating (NNP = - 42.0 kg/t), while the abandoned tailing dump is not (NNP = - 4.8). In this sense, there is a risk of contamination related to the potential acidification of the tailings from AcT. The acidification by sulphide oxidation in presence of carbonate was previously reported in soils from other semi-arid areas (García et al., 2009; Sánchez-Marañón et al., 2015), where soils with similar range in CaCO3 (3.2 - 7.6%) and high amount of S (0.2 - 0.8 %) showed a sharp decrease in pH (from 7.4 to 3.1) after 10 years of continuous oxidation under natural conditions.

Table 6. Mean and standard deviations (n=3) of general physicochemical properties of surface samples (0-10 cm) in the active (AcT) and abandoned (AbT) tailing dumps. Letters (a, b) indicate significant differences between samples (p <0.05). EC: electrical conductivity; CEC: cation-exchange capacity; OC: organic carbon.

Area	**Subarea**	**pH**	**EC**	**CEC**	**$CaCO_3$**	**OC**	**Clay**	**Silt**	**Sand**
			(dS/m)	(cmol/kg)	(%)	(%)	(%)	(%)	(%)
AcT	**Soil**	8.2±0.2 (a)	0.17±0.04 (a)	10.4±2.7 (a)	4.8±2.6 (a)	1.1±0.9 (a)	12.0±1.6 (ab)	33.4±0.3 (a)	53.1±0.8 (a)
	Tailing	8.3±0.1 (a)	0.53±0.05 (a)	2.6±1.0 (b)	5.4±1.7 (a)	0.8±0.2 (a)	5.8±0.6 (b)	22.9±5.8 (a)	71.3±6.4 (a)
AbT	**Soil (cover)**	8.4±0.2 (a)	0.30±0.44 (a)	7.9±2.3 (ab)	10±1.4 (ab)	0.7±0.3 (a)	13.8±2.9 (a)	35.9±30.2 (a)	50.3±28.6 (a)

Table 7. Mean and standard deviations (n=3) of general physicochemical properties of samples collected from vertical profile in the abandoned tailing dump (AbT). Letters (a, b) indicate significant differences between layers (p<0.05). EC: electrical conductivity; CEC: cation-exchange capacity; OC: organic carbon.

Area	**Profile**	**pH**	**EC**	**CEC**	**$CaCO_3$**	**OC**	**Clay**	**Silt**	**Sand**
			(dS/m)	(cmol/kg)	(%)	(%)	(%)	(%)	(%)
AbT	A	8.1±0.3 (a)	0.52±0.57 (a)	6.1±1.6 (a)	6.0±2.5 (a)	0.4±0.1 (a)	10.2±2.5 (a)	25.7±3.3 (a)	64.0±0.8 (a)
	B	8.2±0.1 (a)	0.68±0.39 (a)	4.9±0.1 (a)	8.2±3.2 (ab)	0.2±0.1 (a)	9.2±1.2 (a)	31.6±4.1 (a)	59.3±5.3 (a)
	C	8.6±0.1 (a)	0.29±0.17 (a)	3.7±0.3 (a)	14.4±0.6 (b)	0.1±0.05 (a)	8.3±1.1 (a)	38.8±4.7 (a)	52.8±5.8 (a)

Table 8. Acid potential (AP), neutralization potential (NP) and net neutralization potential (NNP) in the tailings from active (AcT) and abandoned (AbT) tailing dumps.

	AP	**NP**	**NNP**
		(kg $CaCO_3$/t)	
Tailings at AcT	53.1	11.1	-42.0
Tailings at AbT	20.3	15.5	-4.8

NNP <0 indicate potential acid generation

3.3.5. Mineral composition of tailing dumps

The source of the materials of the tailing dump are the ores of the Pirmirab and Gusaksay deposits, as well as the imported ore from the Karakutan, Zarmitan, Kauldy, Yambek, Chakmaktash, Kochbulak and other deposits. The ore passed the stage of crushing and extraction of ore components at the Chadak gold extraction factory, and the underextracted material has been deposited into the tailings. These materials can contain significant amount of sulfide minerals which may oxidize and produce metal and acid contamination (Dold et al., 2009).

Below there is a list of primary and secondary minerals of the Chadak ore field (Table 9) according to Moiseeva (1969), that can provide a list of potentially pollutant elements when they were released to the soils and water after acidification processes occur.

Table 9. List of minerals of the Chadak ore field

Name of minerals	Formula	Frequency of occurence
Native		
Silver	Ag	+++
Kustelite	(Ag, Au)	+++
Electrum	(AuAg)	++++
Gold	Au	+
Copper	Cu	+
Bismuth	Bi	+
Iron	Fe	+

Tellurides, sulphotellurides		
Hessite	Ag_2Te	+
Altaite	PbTe	+
Aleksite**	$PbBi_2Te_2S_2$	+
Sulfides and sulfosalts		
Mckinstryite	$Ag_{5-x}Cu_{3+x}S_4$	++
Chalcocite	Cu_2S	++
Bornite	Cu_5FeS_4	++
Chalcopyrite	$CuFeS_2$	+++
Sphalerite	ZnS	+++
Pyrite	FeS_2	+++
Marcasite	FeS_2	++
Pyrrhotite	$Fe_{(1-x)}S$	++
Arsenopyrite	FeAsS	+
Molibdenite	MoS_2	+
Galena	PbS	+++
Cosalite	$Pb_2Bi_2S_5$	+
Bismuthinite	Bi_2S_3	+
Pekoite	$PbCuBi_{11}(S,Se)_{18}$	+
Gladite	$PbCuBi_5S_9$	+
Tennantite	$(Cu,Fe)_{12}As_4S_{13}$	+
Tetrahedrite	$(Cu,Fe)_{12}Sb_4S_{13}$	++
Polybasite	$(Ag,Cu)_{16}Sb_2Sn$	++
Pearceite	$[(Ag,Cu)_6(As,Sb)_2S_7][Ag_9CuS_4]$	+
Pyrargyrite	Ag_3SbS_3	+
Oxides and Hydrooxides		
Quartz	SiO_2	++++
Opal	SiO_2+H_2O	+
Hematite	Fe_2O_3	++++
Magnetite	Fe_3O_4	++
Mushketovite	$FeFe_2O_4$	+++
Goethite	α - FeO(OH)	+++
Lepidocrocite	γ - FeO(OH)	++
Pyrolusite	MnO_2	++
Rutile	TiO_2	++
Cassiterite	SnO_2	+
Fluorite	CaF_2	++
Carbonates		
Calcite	$CaCO_3$	++++
Dolomite	$CaMg[CO_3]_2$	++
Ankerite	$CaFe[CO_3]_2$	+++
Smithsonite	$ZnCO_3$	+
Cerussite	$PbCO_3$	++
Azurite	$Cu_3[CO_3]_2[OH]_2$	++
Malachite	$Cu_2[CO]_3\ [OH]_2$	++
Sulfates		
Baryte	$BaSO_4$	++
Jarosite	$KFe_3[SO_4]_2[OH]_6$	++
Anglesite	$PbSO_4$	+
Gypsum	$CaSO_4 2H_2O$	++

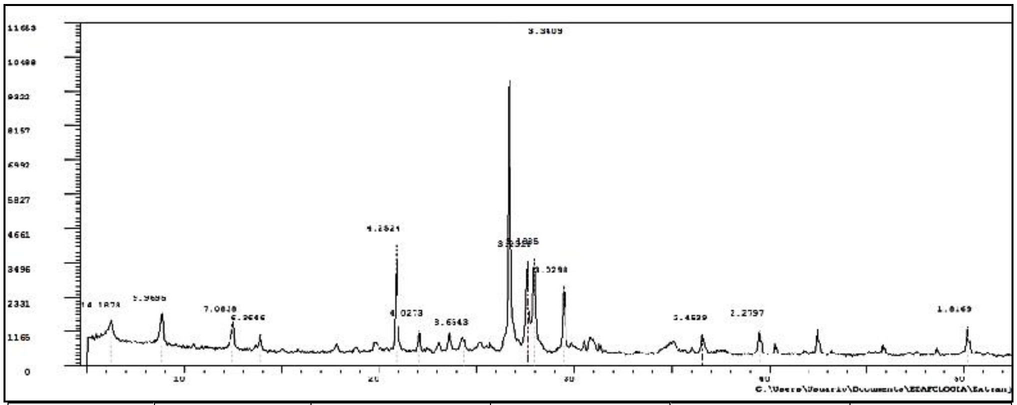
Alunite	$KA1_3[SO_4][OH]_6$	+
Molybdates, wolframite and Arsenates		
Wulfenite	$Pb\ [MoO_4]$	++
Scheelite	$CaWO_4$	+
Chalcophyllite	$Cu_{18}A_{l2}(AsO_4)_3(SO_4)_3(OH)_{27*33}H_2O$	+
Silicates and aluminosilicates		
Grossular	$Ca_3Al_2[SiO_4]_3$	+++
Andradite	$Ca_3Fe_2[SiO_4]_3$	+++
Hedenbergite	$CaFe^{2+}[Si_2O_6]$	++
Actinolite	$Ca_2(Mg,Fe)_5[Si_8O_{22}](OH)_2$	++++
Tremolite	$Ca_2Mg_5[Si_4O_{11}]_2[OH]_2$	+
Epidote	$Ca_2(Al, Fe)_3[Si_2O_7]\ [SiO_4]O[OH]$	+++
Zoisite	$Ca_2Al_3[Si_2O_7]\ [SiO_4]O[OH]$	++
Orthoclase	$K[AlSi_3O_8]$	+++
Adularia	$K[AlSi_3O_8]$	+++
Albite	$Na[AlSi_3O_8]$	+
Oligoclase	$(Na,Ca)(Si,Al)_4O_8$	++
Muscovite	$KAl_2[AlSi_3O_{10}][OH]_2$	++
Sericite	$KAl_2[AlSi_3O_{10}][OH]_2$	++++
Biotite	$K(Mg,Fe)_3\cdot[Si_3AlO_{10}]\ [OH]_2$	++
Pennine	$(Mg, Fe)Al[AlSi_3O_{10}]\ [OH]_8$	++
Serpentine	$Mg_6[Si_4\ O_{10}](\ OH)_8$	+
Montmorillonite	$(Na,Ca)_{0.33}(Al,Mg)_2(Si_4O_{10})(OH)_2 \cdot nH_2O$	++
Kaolinite	$Al_4[Si_4O_{10}][OH]_8$	++

++++ : main minerals (found in amounts of more than 10%);
+++ : minor minerals (the same, up to 10%);
++ : minerals distributed in small quantities (<1%);
+ : rare minerals, isolated finds.

Patterns and mineralogical composition obtained on the total fraction by XRD from selected soil and tailings materials are shown in Figure 12. All samples contained mainly quartz, feldspar group minerals, calcite, micas and chlorite, without detecting any other accompanying mineral species, probably due to the low concentrations.

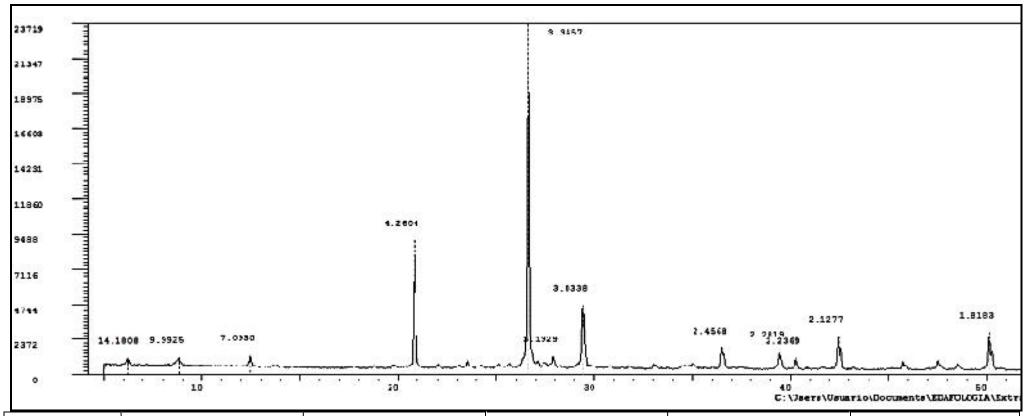
The mineralogical characterization of phyllosilicates from the clay fraction (<2 µm) in a surface sample in AbT with no treatment and treated with ethylene-glycol and dimethyl-sulfoxide is presented in Figure 13. The figure depicts that the mineralogy of phyllosilicates is dominated by micas, chlorite and smectite. The surface properties of phyllosilicates (high active surface areas and presence of electrical charge) is a key factor for the buffer and sink properties of soils (Kabata-Pendias, 2011), and therefore have a major positive effect on chemical and physical soil properties in relation to the dispersion of the pollution.

Surface soil at AbT



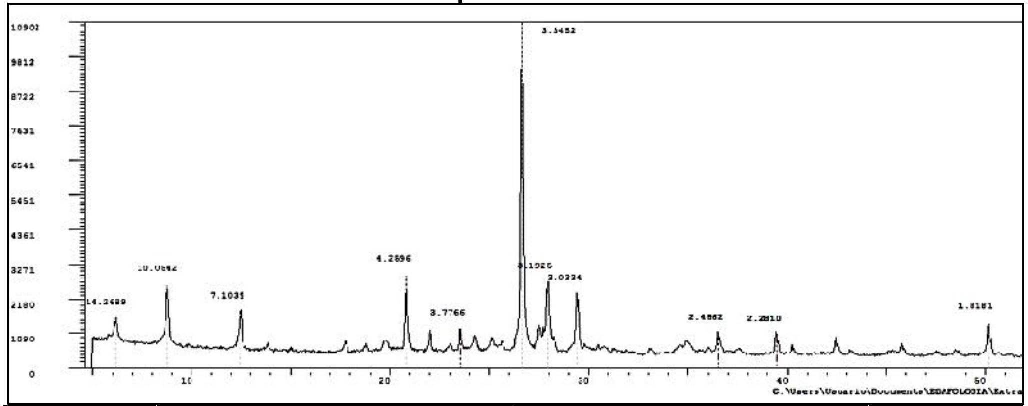
Surface soil at AbT	Quartz %	Calcite %	Felds. gr. %	Mica. %	Chlorite %
	40	10	20	20	10

AcT



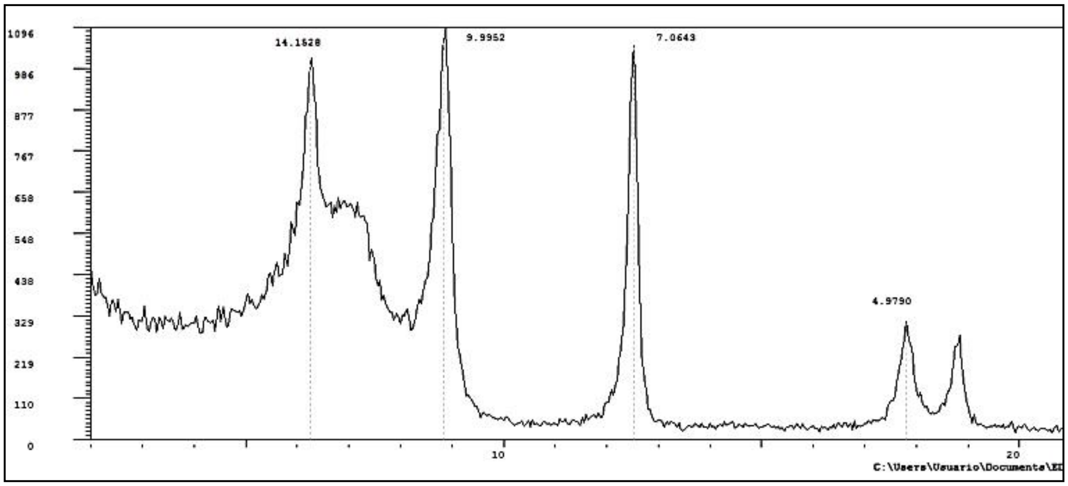
AcT	Quartz %	Calcite %	Felds. gr. %	Mica. %	Chlorite %
	60	20	5	10	5

Vertical profile at the AbT

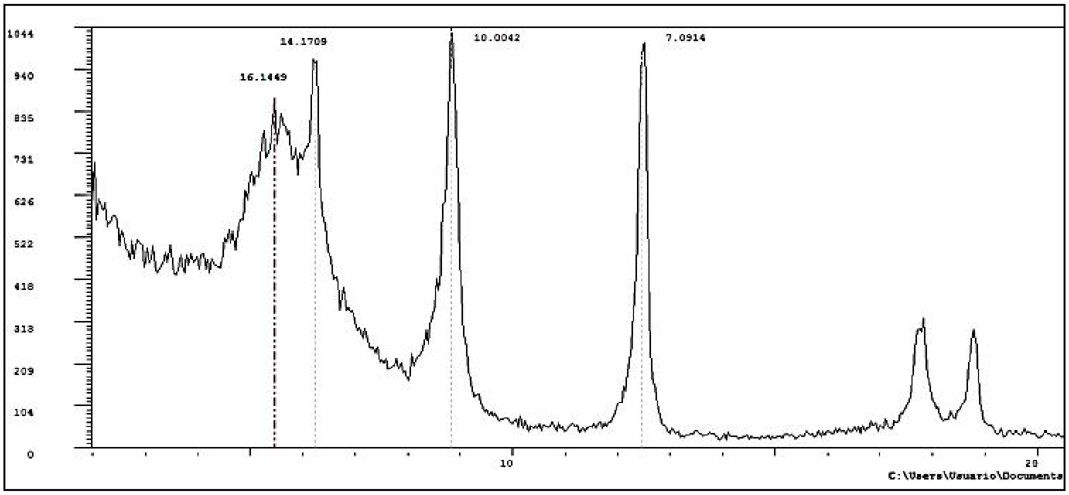


Vertical profile at AbT	Quartz %	Calcite %	Felds. gr. %	Mica. %	Chlorite %
	45	10	15	20	10

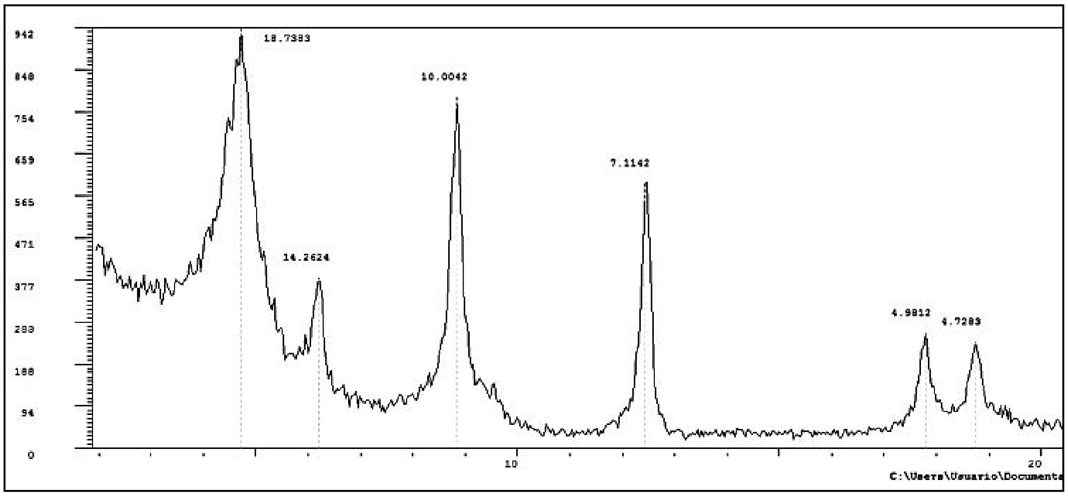
Figure 12. Mineralogical composition of selected soil and tailing materials



Normal difractogram (no treatment)



Ethylene glycol treatment



Dimethyl sulfoxide treatment

Figure 13. Mineralogical characterization of phyllosilicates from surface soil at AbT

The results of the SEM-EDS imaging made on the tailings and open pit waste materials is shown in Annex 3 (Figures 14 – 23). Microphotography of the sample grain from AcT material showed the presence of pyrite (FeS_2) in pyritohedron form (Fig.14 (1)) surrounded by foliate form of clinochlore ($Mg_5Al(AlSi_3O_{10})(OH)_8$) crystals (Fig.14 (2)). Massive calcite ($CaCO_3$) (Fig.14 (3)) and albite ($Na(AlSi_3O_8)$) (Fig.14 (4)) minerals also were detected in this sample. Primary non-sulfide minerals such as carbonates play an important role in neutralizing acid drainage. Silicates may dissolve slowly and they are usually not effective in controlling pH (Jambor et al., 2002), however, soluble silicates may largely influence the composition of drainage (Jamieson, 2011).

In the microphotography of the sample from vertical profile of AbT was identified partially oxidized grains of pyrite (Fig.15 (A-B)) and rare unaltered arsenopyrite (FeAsS) (Fig.15 (C)). Pyrite and arsenopyrite are common acid producing sulfide minerals in tailing dumps. Oxidation of pyrite may produce the formation of secondary products such as goethite ($FeO(OH)$), hematite (Fe_2O_3) and jarosite ($KFe_3(SO_4)_2(OH)_6$) (Dold, 2010) which were found in the studied area. Moreover, the amorphous grain from vertical profile of Abt contains mica, probably biotite (Fig. 16 (1)) with crystals of quartz (fig. 16 (2)) and rutile (fig. 16 (3)) which is consistent with the mineralogy of the area.

However, apart from the primary minerals, the precipitation of Ca–Fe–As phases were found (Fig. 17 (1)), Fig.18 (A, B -1)), indicating the possible presence of yukonite-like or arseniosiderite-like minerals previously reported in oxidized As-bearing ores (Gomez et al., 2010) and in tailings of a gold-mining operation in Nova Scotia, Canada (Walker et al., 2009).

Tailings with a high Ca/As ratio found in some areas, provide neutral drainage and are less acid-generating and hence less risky to the environment (Jamieson, 2011). However, when we consider the possible oral ingestion of the fine dust, arsenate minerals such as yukonite pose high risk of toxicity (see Chapter 5).

Amorphous secondary precipitations of Fe and Mn with accompanying elements such as Ca, K, Si, P, As, Pb, Zn and Co were observed by SEM and EDS analyses in the vertical profile of AbT (Fig. 17 (2)), (Fig. 18 (B-2)), (Fig. 19 (2)) and in the open pit waste materials (Fig. 21 (1, 2)), (Fig. 22 (B-1, 2)) and (Fig. 23 (2, 3)), which could be resulted from the oxidation of sulfide (pyrite, arsenopyrite, sphalerite, galena), dissolution of oxyhydroxides and oxyhydroxide sulfates (hematite, goethite, jarosite) and aluminosilicate (feldspars and micas) minerals presented in Chadak ore area. Secondary precipitations of rounded (spherical) form of Fe with Ca is observed (Fig. 20 (1)) which have probably a microbial origin. Microbial activities largely enhance oxidation of sulfides and cause the release of metal(loid)s and the precipitation of iron oxyhydroxides sulfates (Lu and Wang, 2012).

The above mentioned secondary minerals can greatly affect the mobility of metal(loid)s in mine tailing dumps and acid mine drainage (AMD) affected areas. Secondary minerals are able to retain significant quantities of metal(loid)s by adsorption or sequestration on the large surface areas (Kabata-Pendias, 2011). On the other hand, the adsorbed or coprecipitated metal(loid)s are susceptible to remobilization resulted after transformation of these secondary minerals as environmental conditions change (Lu and Wang, 2012). Consequently, the geochemical and mineralogical characterizations of mine tailings are of high importance for the assessment of environmental impact of trace metals.

3.4. CONCLUSION

Chadak ore field is one of the main gold-producing sites in Uzbekistan. Abandoned and active tailing dumps with wastes enriched with metal(loid)s poses a potential pollution risk for this mining area and for populations living in the vicinity. Our data indicate that the total concentrations of As, Sb, Zn, and Pb exceeded the background concentrations in wastes at the active tailing (AcT) dump and in soils at abandoned tailings dump (AbT). Waste deposits at AbT have very high concentrations of As (mean > 1030 mg/kg) and Sb (mean > 920 mg/kg), exceeding intervention threshold values by 20- and 62-fold, respectively.

General physico-chemical properties of soils and tailing samples showed a moderately alkaline pH, low EC, CEC and OC. Due to the moderate presence of calcium carbonate in the tailings, the net neutralization potential (NNP = NP-AP) indicates that the active tailing dump is potentially acid generating, while the abandoned tailing dump is not. This is directly related to a higher amount of sulfide minerals with high acid potential in the AcT in relation to the AbT dump.

Mineralogy patterns from selected soil and tailings materials obtained by XRD presented that samples dominated by quartz, feldspars, calcite, micas and chlorite, and gives useful information in relation to the amount of neutralizing minerals (like calcite), although minerals bearing potentially pollutant elements are not detected by this technique. Otherwise, the results of the SEM-EDS analysis made on the tailings and open pit waste materials identified primary and secondary minerals consisting of sulfides, silicates and secondary precipitations of Fe and Mn oxyhydroxides. The presence of yukonite-like precipitation of Ca–Fe–As phases were also detected.

The geochemical and mineralogical characterizations of mine tailings are of high importance for the characterization of the potential toxicity of waste materials, the evaluation of the buffer capacity, and the assessment of the environmental impact of metal(loid)s in surrounding areas.

CHAPTER 4. ASSESSMENT OF MOBILITY AND AVAILABLILITY OF METAL(LOID)S AND THEIR RELATION TO SOIL AND TAILING PROPERTIES

4.1. INTRODUCTION

The analytical determination of the total content of metal(loid)s in soils, sediments and waste materials does not provide the necessary information to determine the physical-chemical state of these elements, nor does it allow the deduction of their potential mobilization capacity (Thomas et al., 1994). The application of selective extraction techniques allows us to deduce the distribution of the trace elements between the different fractions of a soil, while at the same time it allows us to deepen our knowledge of both the potential mobility of these elements and their biological availability. (Raksasataya et al., 1996; Breward et al., 1996).

Traditionally the method used to carry out studies of mobilization of heavy metal(loid)s is based on speciation studies, through operational fractionation methods such as selective, simple and / or sequential chemical extractions, since the direct determination is almost impossible (Van Herreweghe et al., 2003).

The sequential extractions are based on the selectivity of certain reagents, understanding this selectivity as the ability of that reagent to attack a single fraction of the metal(loid) in the material to analyze, remaining the other fractions unaltered to that attack; although there are authors who state that practically no reagent is totally specific (McCarty et al., 1998). These extractions depend on different factors such as the chemical nature of the extractant agents, the duration of the extraction, the solid / liquid ratio and the preparation and conservation of the sample, to the point that significant differences have even been found in the results when the same scheme has been applied by different analysts (Van Herreweghe et al., 2003). The first important works in the field of sequential chemical extractions were carried out by Tessier al. (1979); although later other methods of sequential extraction were developed, such as the BCR method (Thomas et al., 1994), and the method of Hall et al. (1996), as well as multiple methodological schemes based on the Tessier protocol or modifications thereof.

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One of the main problems of sequential extractions is that it has as a source of errors the handling and washing of solid samples between one extraction stage and the next, which can cause loss of solid material (Breward et al., 1996), generating that the degree of precision of the applied method decreases as the number of extraction steps increases in the procedure. Otherwise, the extractants applied are not fully selective and a considerable redistribution of heavy metals may take place upon the extraction procedure (Vodyanitskii, 2006).

On the other hand, single-selective extractions are used instead of sequential-selective extractions. In this case, the theoretical basis is similar in both cases, and the main difference is that for sequential extractions, the same sample is used in the successive steps, while for single extractions, different aliquots of a same sample are used to be reacted with different reagents. In the case of single extractions, a reagent is used to isolate the metal(loid)s associated or bound in a particular soil phase, fraction or component in a single extraction procedure. These single extractions allow us to estimate, both the natural mobility of heavy metals as the potential mobility in the face of changes in the environmental conditions in which they are found, according to the experiences carried out in similar environments (Martínez et al., 1996, García-Rizo et al., 1999, Pérez-Sirvent et al., 2003, Vidal et al., 2004, Navarro, 2004). In addition, single extractions are more used than sequential ones in studies of mobility and bioavailability in contaminated soils (Ure et al., 1995a). In any case, there is a wide variety of selective extraction protocols that leads to the absence of a standardized and unique extraction accepted procedure to evaluate the mobility and availability of metal(loid)s in soils, sediments or waste materials, which makes it difficult the comparison of the results obtained by different studies.

The aim of this chapter is to assess the mobility and availability of metal(loid)s found in tailings from the abandoned tailing dump by the use of single-selective extractions, and to correlate with the total concentrations and the main physicochemical properties to analyse the potential risk of pollution in the area in relation to the ability to disperse and move around the environment.

4.2. MATERIALS AND METHODS

4.2.1. Selective extraction of metal(loid)s

Selective extractions were applied to assess metal(loid)s mobility in sieved samples (< 2 mm) at the abandoned tailing dump site (AbT) with the following reagents: 1) distilled water (Sposito et al., 1982), 2) ammonium nitrate 1M (DIN 19730, 1997), 3) acetic acid 0.43M (Ure et al., 1993), and 4) oxalate buffer pH 3 (Schwertmann and Taylor, 1977). In general, metal(loid)s extracted with water (W) are the soluble fraction (Sposito et al., 1982). Those extracted with ammonium nitrate (AN) are considered as the readily available fraction (Gryschko et al., 2005). The extracted with acetic acid (AC) have been considered by many authors as bioavailable, although they are associated with the fraction bound to carbonates and also specifically linked to oxides and organic matter (Beckett, 1989). Those extracted with oxalic-oxalate (OX) are estimated to be linked to oxides (Ure, 1995). The extraction power of these reactants goes in increasing order as they have been presented here (W <AN <AC <OX), so that a solution is able to extract forms considered in the previous solutions, although this is not the case with all the elements or in all soil types.

The total concentration of trace elements was additionally determined by strong acid digestion (HNO_3/HF/HCl) using a Microwave Accelerated Reaction System (CEM MARS 230/60 Xpress). All extracted fractions (both strong acid digestion as single-selective extractions) were analyzed by inductively coupled plasma–mass spectrometry (ICP–MS) in a Perkin-Elmer Sciex-Elan 5000 instrument equipped with quartz torch, nickel sampler, and skimmer cones. Standard solutions were prepared from ICP single-element standard (Merck, Darmstadt, Germany) after appropriate dilution with 10% HNO_3. The accuracy of the method was evaluated by six replicate analyses of the certified reference material SRM 2711, average recoveries of the certified reference values ranged between 91% and 105% for the main pollutant elements (Martín Peinado et al., 2015).

4.3. RESULTS AND DISCUSSION

4.3.1. Geochemical fractionation of trace elements in tailings dumps material

Due to the elevated concentrations of metal(loid)s, mainly As and Sb, and the relatively high concentrations of Zn and Pb in the tailing samples analyzed from the vertical profile in the abandoned tailing dump (AbT), mobility and availability were assessed by selective extractions (water, ammonium nitrate salt solution, acetic acid, and oxalic-oxalate). The results of these selective extractions procedures of the soluble in water and ammonium nitrate extracted forms are shown in Tables 10 and 11 .

Table 10. Soluble in water extracted forms in tailings from the abandoned tailing dump (values in mg/kg)

Profile (AbT)		V_W	Cr_W	Co_W	Ni_W	Cu_W	Zn_W	As_W	Cd_W	Sb_W	Pb_W
A	Mean	0,046	0,082	0,023	0,091	0,059	0,775	4,056	0,005	1,482	0,431
	St. dev.	*0,051*	*0,025*	*0,003*	*0,002*	*0,055*	*0,603*	*2,362*	*0,005*	*0,291*	*0,583*
B	Mean	0,015	0,064	0,013	0,074	0,037	0,504	2,116	0,002	1,993	0,182
	St. dev.	*0,008*	*0,002*	*0,003*	*0,033*	*0,012*	*0,015*	*1,687*	*0,000*	*1,466*	*0,090*
C	Mean	0,013	0,065	0,015	0,045	0,047	0,526	6,848	0,001	0,465	0,159
	St. dev.	*0,002*	*0,001*	*0,008*	*0,010*	*0,016*	*0,170*	*4,709*	*0,001*	*0,029*	*0,187*
Total	Mean	0,025	0,070	0,017	0,070	0,048	0,602	4,340	0,003	1,313	0,257
	St. dev.	*0,028*	*0,014*	*0,006*	*0,026*	*0,028*	*0,311*	*3,263*	*0,003*	*0,965*	*0,308*

Table 11. Ammonium nitrate extracted forms in tailings from the abandoned tailing dump (values in mg/kg)

Profile (AbT)		V_AN	Cr_AN	Co_AN	Ni_AN	Cu_AN	Zn_AN	As_AN	Cd_AN	Sb_AN	Pb_AN
A	Mean	0,006	0,027	0,048	0,924	0,018	0,108	0,624	0,006	0,992	0,002
	St. dev.	*0,001*	*0,001*	*0,039*	*0,508*	*0,003*	*0,028*	*0,286*	*0,006*	*0,620*	*0,000*
B	Mean	0,005	0,028	0,047	0,975	0,044	0,137	1,554	0,003	2,073	0,002
	St. dev.	*0,001*	*0,001*	*0,004*	*0,350*	*0,033*	*0,018*	*1,363*	*0,001*	*1,430*	*0,001*
C	Mean	0,006	0,028	0,057	0,577	0,069	0,154	11,609	0,001	0,464	0,003
	St. dev.	*0,001*	*0,001*	*0,047*	*0,180*	*0,035*	*0,038*	*8,268*	*0,000*	*0,021*	*0,000*
Total	Mean	0,005	0,027	0,051	0,826	0,043	0,133	4,596	0,003	1,176	0,002
	St. dev.	*0,001*	*0,001*	*0,028*	*0,347*	*0,031*	*0,031*	*6,614*	*0,003*	*1,012*	*0,001*

Both soluble in water and ammonium nitrate extracted forms represent the readily soluble or available forms and are related the short-term mobility processes. The high variability of concentrations in all layers showed no significant differences in any case and for any element analyzed. There is no information about guideline values in readily mobile forms of metal(loid)s related to the soil solution of potentially polluted soils, so a comparison with Guideline values for water reuse (EPA, 2004) was made; according to this Guideline the concentration of most elements is below these reference values, with the exception of As which present a very high concentration (>4 mg mobile As / kg soil) above the reference value fixed in 0,1 mg/l, indicating a potential risk of pollution in relation to this element. In the case of Sb, readily mobile forms showed values above 1 mg mobile Sb / kg soil, but no guideline value was found for this element; according to the EPA drinking water regulations (EPA, 2009), the maximum level is fixed in 0.006 mg/l, which could indicate a high potential risk of toxicity for this element from the lixiviates derived from the tailings. Anyway, the potential implications of the high mobility of As and Sb in this area was discussed in Chapter 5, were toxicity and human-health concerns are discussed.

Acetic acid extracted forms, related to more strongly retained (but potentially long-term available) are presented in Tables 12. The high variability of concentrations in all layers showed no significant differences for any element analyzed. The elements extracted in greater concentrations were Zn (>56 mg/kg), As and Pb (>46 mg/kg for both elements), indicating that these elements could be partially uptaken by plants after slight acidification from the rhizosphere (Beckett et al., 1989) or leached from the tailing by the acidification caused by the sulphide oxidation (Simón et al., 2002). The extraction with acetic acid allows an estimation of the metal(loid)s fraction remobilised after acidification of the tailings (Van der Sloot et al., 1996), so long-term potential problems related to the acid potential of the tailings could be deduced.

Table 12. Acetic acid extracted forms in tailings from the abandoned tailing dump (values in mg/kg)

Profile (AbT)		V_AC	Cr_AC	Co_AC	Ni_AC	Cu_AC	Zn_AC	As_AC	Cd_AC	Sb_AC	Pb_AC
A	Mean	0,30	0,77	1,88	3,35	1,81	42,95	66,19	1,00	7,12	5,07
	St. dev.	*0,34*	*0,07*	*1,31*	*0,87*	*1,33*	*35,83*	*46,73*	*0,63*	*3,68*	*0,41*
B	Mean	0,18	1,00	1,47	2,86	7,66	58,90	35,90	0,83	14,63	60,23
	St. dev.	*0,19*	*0,12*	*0,70*	*0,32*	*5,59*	*15,56*	*22,41*	*0,05*	*11,17*	*50,26*
C	Mean	0,07	1,05	0,89	3,56	8,64	67,57	37,57	1,23	2,15	75,36
	St. dev.	*0,06*	*0,13*	*0,01*	*0,27*	*1,68*	*23,09*	*12,25*	*0,36*	*0,72*	*4,77*
Total	Mean	0,18	0,94	1,41	3,26	6,04	56,47	46,55	1,02	7,97	46,88
	St. dev.	*0,20*	*0,16*	*0,80*	*0,54*	*4,25*	*23,16*	*28,27*	*0,37*	*7,71*	*40,06*

Oxalic-oxalate extracted forms, related to more strongly retained fraction, are presented in Tables 13. The high variability of concentrations in all layers (high standard deviation) showed no significant differences for any element analyzed.

Table 13. Oxalic-oxalate extracted forms in tailings from the abandoned tailing dump (values in mg/kg)

Profile (AbT)		V_OX	Cr_OX	Co_OX	Ni_OX	Cu_OX	Zn_OX	As_OX	Cd_OX	Sb_OX	Pb_OX
A	Mean	5,52	3,40	4,31	7,21	8,29	103,57	794,58	0,16	202,85	27,43
	St. dev.	*3,55*	*2,32*	*1,06*	*4,82*	*3,11*	*79,10*	*720,04*	*0,16*	*192,78*	*29,81*
B	Mean	2,37	6,72	2,67	6,58	15,01	97,53	279,31	0,05	95,74	11,99
	St. dev.	*1,30*	*3,18*	*1,08*	*0,19*	*8,00*	*7,11*	*321,81*	*0,04*	*43,32*	*6,01*
C	Mean	1,85	7,66	1,85	6,72	22,79	135,38	313,39	0,03	17,51	5,90
	St. dev.	*0,28*	*1,12*	*0,54*	*1,34*	*4,60*	*47,45*	*135,82*	*0,00*	*7,30*	*1,59*
Total	Mean	3,25	5,93	2,94	6,83	15,36	112,16	462,43	0,08	105,37	15,10
	St. dev.	*2,46*	*2,71*	*1,33*	*2,26*	*7,81*	*45,19*	*441,05*	*0,10*	*121,43*	*16,85*

The oxalic-oxalate forms is related to the retention of metal(loid)s by the iron oxyhydroxide (mainly as non-crystalline forms) in the tailings. The element extracted in higher concentration was As, with mean values higher than 460 mg/kg, followed by Zn and Sb, with mean concentrations higher than 100 mg/kg; while Pb and Cu presented lower values (around 15 mg/kg) of these extracted forms. These values are related to the ability of iron to retain these elements; in these tailings, the iron released by oxidation of sulfides precipitated in amorphous or poorly crystallized forms adsorbing these elements presented in the acid solutions that are generated in the process (Simón et al., 2002). This mechanism of retention could be considered as a positive response to the potential release of pollutants, preventing the dispersion of these elements in the environment.

In the case of the four elements with the greatest potential for mobility or toxicity, a comparison has been made between the different forms extracted. Since the ammonium nitrate (AN) and the acetic acid (AC) also extract the water soluble forms (W), the calculations have been made by subtracting the soluble phase to these two extractions. In the case of oxalic-oxalate (OX) it is considered that it can extract elements associated with the same forms (oxides, inorganic precipitates, carbonates, etc.) as acetic acid, so this analysis has been carried out using the percentage of higher selective extraction for each element. The residual (insoluble) fraction was also calculated from be the difference between the total concentration of the element and the amount extracted by the most effective reagent; that is, the one which extracts the greatest amount of element. The calculation of the percentage in relation to the total of each single-extraction procedure is presented in Figure 24.

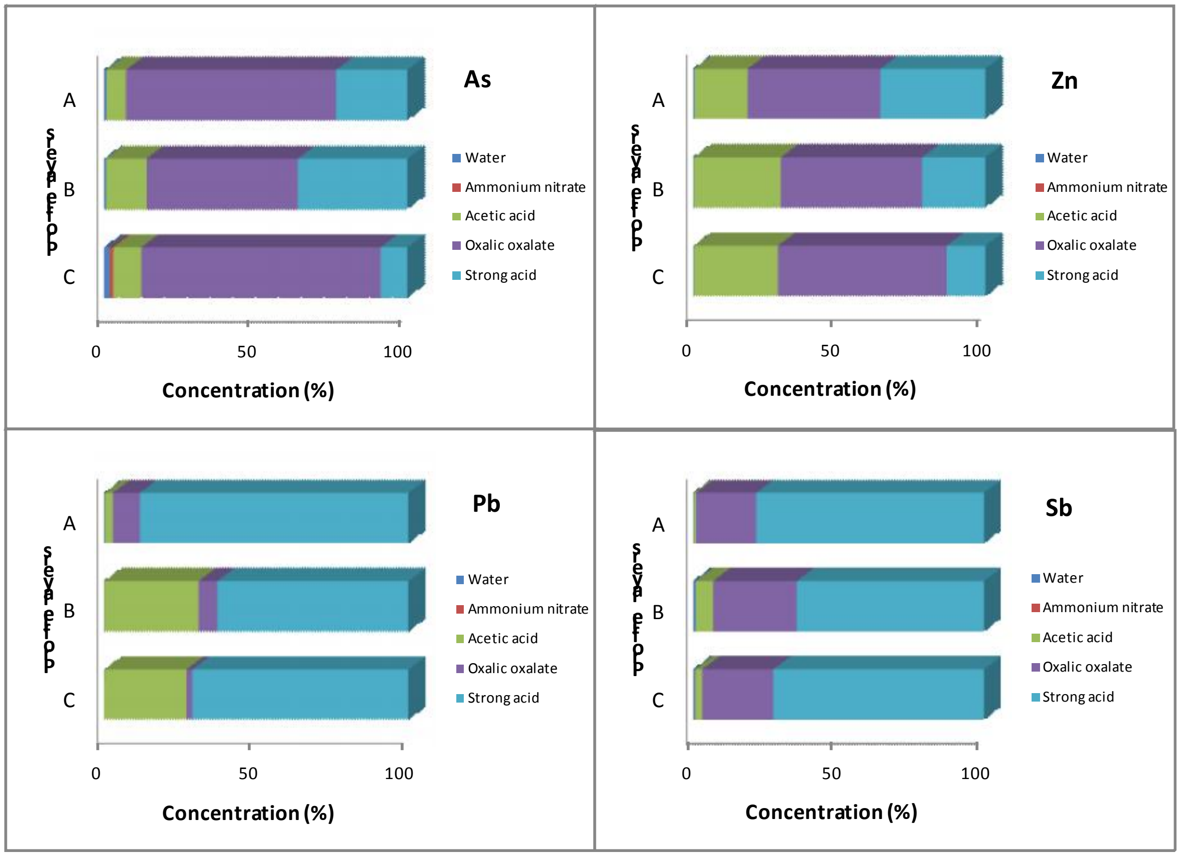

Figure 24. Percentage of extracted metal(loid)s (mean values) in the different layers of the tailing at the abandoned tailing dump.

According to this figure, most of the As (between 49.9 - 78.8% in relation to the total) was extracted by oxalic-oxalate buffer (As_{OX}) with the highest proportion in the C layer of the AbT profile. Oxalic-oxalate buffer is the reagent that extracts specifically the elements adsorbed and retained by the thus dissolved Fe-Mn oxides. The results are consistent with previous observations (Aguilar et al. 2006; Martín et al. 2011) which found that As in polluted soils is associated mainly with iron oxides. Iron oxide phases are therefore generally accepted as the primary sorption sites for arsenic in many soils and sediments (Adriano, 1986; Sadiq, 1997). Fe-Mn oxides are also important scavengers of heavy metals in soils, particularly in the high pH range (Li and Thornton, 2001). The residual fraction (extracted only with strong acids) is not as high (below 24% of the total) except in the B layer (mean 36% of the total), presumably associated with the presence of arsenopyrite in the tailings. Extractions determined that 6.5-13.3% of the total arsenic (AsT) was extractable with acetic acid (As_{AC}) without readsorption to other phases, whereas a negligible proportion (<2% of the total) was extracted by water (As_W) and ammonium nitrate (As_{AN}). Low solubility and exchangeable potential of As measured by these extractants agree with the soil pH and the presence of carbonates (Rodrigues et al., 2010), and can be related by the incorporation of As into the lattice structure of calcite as arsenite under alkaline pH (Di Benedetto et al., 2006; Alexandratos et al., 2007). Despite the low water-soluble ratios, concentrations of As_W (mean 4.34 mg soluble As per kg dry soil) far surpassed the critical level of 0.04 mg of soluble As per kg dry soil (Bohn et al., 1985), indicating a need for detailed ecotoxicological studies to prevent the risk of pollution to the environment and the nearby population.

As with As, the highest extraction of Zn was in C layer and associated with the Fe-Mn oxides (mean 45.4-57.7% in relation to the total Zn), while the residual fraction had a mean range between 13.2-35.8% with the highest amount in the A layer. These results agree with previous observations of Ashraf et al. (2012) and Li and Thornton (2001), who found that Zn was associated primarily with Fe/Mn oxides and the residual fraction. Álvarez-Ayuso et al., (2008) and García et al., (2009) also stated that Zn may co-precipitate with oxides and hydroxides at high pH values. The next most abundant Zn fraction was that extracted with acetic acid (Zn_{AC}), which accounted for a mean range of between 18.2-29.7% in relation to the total Zn; this fraction, also called the exchangeable fraction, registered the same percentage, according to Marguí et al. (2004), but in other studies even far higher percentages have been reported (Iavazzo et al., 2012; Rodríguez et al., 2009), depending on the soil properties such as the Fe/Mn content. The percentage of the water-soluble (Zn_W) and ammonium-nitrate-extracted (Zn_{AN}) fractions were negligible (mean <0.5% for Zn_W and below detection limit for Zn_{AN}). However, the mean value of water concentration of 0.6 mg soluble Zn per kg dry soil was within the toxic range (0.5 mg soluble Zn per kg dry soil) in soil solution reported by Ewers (1991), indicating a potential risk of environmental pollution for this element. The highest concentration of Sb was in the residual fraction (mean 64.3 - 78.2% in relation to the total Sb), indicating that Sb is contained chiefly in the crystalline lattice of the secondary minerals. Wilson et al. (2010) reported that the residual Sb was up to 98% in mine-contaminated soils, but the relative proportion of Sb in this phase depends on the source (Tighe and Lockwood, 2007). The proportion of antimony extracted with oxalic-oxalate buffer (Sb_{OX}) was below 30% of the total Sb, slightly below the values of the same extraction phase reported by Tighe and Lockwood (2007), where 30-47% of the total Sb was associated with non-crystalline Fe and Al hydroxides. The acetic-acid-soluble fraction (Sb_{AC}) was low in relation to the total concentration (mean 0.7 – 5.9%), which coincides with the studies of He (2007), Tighe and Lockwood (2007), and Hou et al. (2006). The percentage of water-soluble (Sb_{W}) and ammonium-nitrate-extracted (Sb_{AN}) in relation to the total Sb concentrations were very low (mean <1%). Although Sb is generally described as a geochemically immobile element, its solubility depends on soil properties (Evangelou et al., 2012) and the rise of soil pH can inhibit Sb sorption to soil Fe and Al oxy-hydroxides, increasing the Sb in soil-solution phase (Nakamaru et al., 2006).

Pb was also associated mainly with the residual fraction (mean 70.9-88.2% in relation to the total Pb), containing the highest amount in the A layer. This agrees with the observations of Ashraf et al. (2012) and Ramirez et al. (2005), who reported that Pb is associated mostly with the residual phase. Pb associated with acetic acid-soluble fraction (Pb_{AC}) accounted for mean 2.5-30.9% followed by a minor amount of oxalic-oxalate buffer-extractable fraction (mean 1.9-8.8% of the total). In this case, Pb is considered to be bound to carbonates and related to weathered (oxidized) precipitates from old tailing waste materials (Anju and Banerjee, 2010). The least abundant proportion of Pb was found in water-soluble (Pb_{W} mean <0.5%) and ammonium-nitrate-extracted (Pb_{AN} below the detection limit) fractions in relation to the total concentrations, with similar results as those observed by other authors (Ramos et al. 1994, Chlopecka et al. 1996, Maiz et al. 2000). In any case, the Pb_{W} concentrations did not exceed the toxic level in the soil solution (1 mg/kg^{-1}) reported by Ewers (1991).

4.3.2. Correlation between tailing properties and metal(loid)s

The Pearson correlation analysis between the main physico-chemical properties of the tailing at the abandoned tailing dump, the total concentrations of metal(loid)s and the forms that are water soluble, ammonium nitrate, acetic acid, and oxalic oxalate buffer extractable, is presented in Table 14.

Table 14. Pearson correlation between total (T), water soluble (W), ammonium nitrate (AN), acetic acid (AC) and oxalic oxalate (OX) extracted forms of As, Sb, Zn, Pb and tailing properties in the vertical profile of the abandoned tailing dump.

	AsT	As_{W}	As_{AN}	As_{AC}	As_{OX}	SbT	Sb_{W}	Sb_{AN}	Sb_{AC}	Sb_{OX}
pH	-0.567*			-0.893*	-0.903*	-0.650*				-0.900*
EC										
CEC										
$CaCO_3$										
OC	-0.550*			0.880*	0.899*	-0.688**				0.894*
Clay										
Silt			0.870*							
Sand			-0.903*							
	ZnT	Zn_{W}	Zn_{AN}	Zn_{AC}	Zn_{OX}	PbT	Pb_{W}	Pb_{AN}	Pb_{AC}	Pb_{OX}
pH						-0.595*				-0.952**
EC	0.575*									
CEC	-0.818**					-0.583*	0.724*			
$CaCO_3$									0.814*	
OC										0.881*
Clay	-0.602*					-0.601*				
Silt										
Sand										

EC: Electrical conductivity; CEC: Cation exchange capacity; OC: Organic carbon.
*** Correlation is significant at the 0.01 level (2-tailed).*
** Correlation is significant at the 0.05 level (2-tailed).*

The results for arsenic indicate that AsT together with As_{AC} and As_{OX} showed a significant ($p<0.05$) and negative correlation with pH, indicating that for this type of pollution involving the release of sulfide tailings, their oxidation and hence acidification processes are related to the increase in total pollution by the generation of acidic conditions that lead to a release of contaminants (Romero-Freire et al., 2015, Simón et al., 2001). Significant correlation of As_{AC} and As_{OX} was found with OC in our samples. The effect of organic carbon to arsenic mobility is controversial. In some studies the application of organic matter reduced the As mobility (Gadepalle et al., 2007), whereas in others As is mobilized after compost application and by phytoremediation due to the competing effect of organic matter with arsenate for adsorbing surface sites (Clemente et al. 2008, Martín et al. 2011). No correlation in relation to tailing properties was found for the As_{W}, whereas a significant positive correlation was found for As_{AN} with silt fraction and a significant negative correlation with sand. Simón et al. (2001) showed that there was a strong positive correlation between arsenic levels and the fine-silt fraction of the sludge due to the enhanced specific surface available for As exchange.

In relation to the tailing properties, total (SbT) and oxalic-oxalate buffer (Sb_{OX}) showed similar behaviour with As, presenting significant negative correlation with pH and OC. The oxyanion-forming metalloids As and Sb have comparable geochemical activity (Fu et al. 2016; Wilson et al., 2010; Casiot et al., 2007). However, the understanding of Sb toxicity and environmental activity is limited (Filella et al., 2002). The other extracted forms of the Sb did not present any correlation with tailing properties, suggesting that these parameters do not control the partitioning of this metalloid.

By contrast, the correlation of tailing properties and ZnT showed significant positive correlation with electrical conductivity, indicating that Zn is strongly related to the soluble salts produced after the oxidation reactions (Romero-Freire et al., 2015). On the other hand, ZnT negatively correlated with CEC and clay fraction, suggesting that these tailing properties also affect Zn activity. This is consistent with the data in the literature indicating also that clay and soil hydroxides can strongly adsorb to Zn especially under alkaline conditions (Vandana et al., 2011). No significant correlation was found for other Zn extractions.

Total concentrations of Pb were significantly and negatively correlated with pH, as well as with CEC and the clay fraction, indicating that alkaline pH, CEC, and the clay fraction were the main factors controlling the mobility of lead. As pH rises, Pb becomes less soluble under oxidizing conditions (Vandana et al., 2011) due to the formation of insoluble salts mainly under the presence of carbonates (Razo et al., 2004). The water-soluble form (Pb_{W}) was not related to any of the soil properties except for the CEC, with a significant and positive correlation, indicating the favorable effect of the adsorption processes for the retention of Pb. Acetic acid extractable Pb (Pb_{AC}) presented a significant correlation with $CaCO_3$ concentrations, while the proportion extracted by oxalic-oxalate buffer (Pb_{OX}) significantly correlated with OC, indicating also a major contribution of OC in retaining Pb.

Table 15. Principal component analysis among total concentration (T) of pollutant, soluble in water (W) and main physico-chemical properties in the tailing

	Component		
	1	2	3
ZnT	0.504	-0.785	
AsT	0.950		
SbT	0.953		
PbT	0.515	-0.738	
Zn_W		0.960	
As_W			0.940
Sb_W			-0.858
Pb_W		0.948	
pH	-0.862		
EC	0.751		
CEC		0.902	
$CaCO_3$	-0.849		
OC	0.951		
Clay		0.879	
Silt		-0.685	0.632
Sand			-0.754
% Cumulative Variance	35.4	70.7	91.6

EC: Electrical conductivity; CEC: Cation exchange capacity; OC: Organic carbon.

The mobility and potential toxicity were assessed in relation to physico-chemical properties of the tailings, using a principal-component analysis between total and soluble concentrations of the main pollutants and the tailing properties (Table 15). Three components explained 91.6% of the variance, with Component 1 being the one that included the total concentrations of metal(loid)s directly related to EC and inversely related to pH and $CaCO_3$, indicating that the pollution is controlled fundamentally by tailing oxidation processes involving acidification, weathering of $CaCO_3$, and increase in soluble salts (Simón et al., 2001). Component 2 includes the total concentrations of Zn and Pb inversely related to Zn_W and Pb_W forms, indicating that the soluble forms of these elements are not controlled by their total concentrations, but rather that the CEC and texture (clay fraction) were the main properties affecting the water concentration of these elements in the soil solution (Kumpiene et al., 2008). Component 3, explaining the 20.9% of the variance, includes As_W and Sb_W forms inversely related to each other, indicating a contrasting relation between the two elements (Mitsunobu et al., 2006) and a strong influence of carbonates usually found in the silt fraction on the activity of the soluble forms of these elements, as reported by Martínez-Lladó et al. (2011).

4.4. Conclusions

The geochemical fractionation, made from single-extraction procedure, of trace elements in the tailing of the abandoned tailing dump shows differences in the mobility and availability of the main potential pollutant analyzed. Soluble in water and ammonium nitrate extracted forms represent the readily soluble or available forms and are related the short-term mobility processes; in our study, the elements that presented higher mobility were As and Sb, with potential implications in the dispersion of the pollution to the surrounding areas. For the acetic acid extraction, the elements measured in greater concentrations were Zn, As and Pb, indicating that these elements could be partially uptaken by plants after slight acidification from the rhizosphere, or leached from the tailing by the acidification caused by the sulphide oxidation. This extraction allows an estimation of the potential fraction of metal(loid)s that could be remobilised after acidification of the tailings, so long-term potential problems related to this process could be deduced. For the oxalic-oxalate extraction, the element measures in higher concentration was As, followed by Zn and Sb. These values are related to the ability of amorphous or poorly crystallized iron forms to retain these elements, so this mechanism is considered as a positive response to the potential release of pollutants, preventing the dispersion of these elements in the environment.

The influence of physico-chemical properties is a key factor controlling the mobility and availability of potentially pollutant elements. In this sense, metal(loid)s behavior is directly related to EC and inversely related to pH and $CaCO_3$, indicating that the pollution is controlled fundamentally by tailing oxidation processes involving acidification, weathering of $CaCO_3$, and generating an increase in soluble salts. Moreover, the CEC and texture (clay fraction) were the main properties affecting the water concentration of these elements in the tailing solutions in the short-term;

while iron oxides are responsible of the retention in the long-term of the most potentially toxic elements (like As and Sb).

CHAPTER 5. EVALUATION OF THE POTENTIAL TOXICITY OF METAL(LOID)S BY THE USE OF TOXICITY BIOASSAYSS AND PHYTOEXTRACTION OF METAL(LOID)S BY THE WILD PLANTS OF THE AREA

5.1. Introduction

The development of mineral deposits and the operation of enrichment facilities are inevitably associated with environmental pollution. Every year, a large amount of ore is extracted from the mining industry, which, after enrichment, is stored in special storage facilities, the so-called tailing dumps, which remain a potential source of metal(loid) contamination of adjacent territories even after the end of the activity.

Soil is a key element in terrestrial ecosystems, while it is the medium that most frequently receives severe pollution (Bagur et al., 2010). Due to its role in the environment and its essential functions for the development of human life, it is vital to prevent its degradation, and with special emphasis on pollution problems (Simón et al., 2010). Thus, soil contamination has become an environmental problem of relevance to society and administration in the last decades (Galán and Romero, 2008).

When a pollutant occurs in concentrations above a certain threshold, it can generate adverse effects on the ecosystem and organisms. The toxicity of metal(loid)s is related to their total concentrations, but the study of mobility and bioavailability of these total values is the basis for environmental risk assessment, because these available forms can adversely affect biological functions in organisms. The bioavailability of an element depends on its chemical form, soil properties and the ability to absorb it by living organisms (Aguilar et al., 1999, Galán and Romero, 2008, Diez et al., 2010).

Frequently, only a small part of the total content of the potentially polluting elements in the soil is bioavailable and its effect may be different for each specific organism and for each type of soil. The bioavailability of the trace elements is a function of the chemical form in which it is found in the environment, the physical-chemical properties of the soil, and the capacity of the organisms to absorb or ingest it (Galán and Baena, 2008).

Ecotoxicity tests are key tools in the study of the fate and bioavailability of pollutants and to assess the potential ecotoxicological effects of metal(loid)s found in soils, sediments or waste deposits. These adverse effects are not only restricted to soil media, as they can be easily transferred to other compartments such as surface- or ground-waters, or even can be incorporated into the food chain. The use of biological tests is essential for determining the potential ecological risk of soil contamination to organisms and ecosystems, although the influence of long-term equilibration processes usually is not considered in such tests (Romero-Freire et al., 2015).There are many bioassays that can be applied to assess toxicity in potentially contaminated areas. They are divided mainly into two groups: those that use the liquid phase (the saturation extract of the soil) and those that use the solid phase (Farré and Barceló, 2003). There is a high correlation between bioassays that use both phases, although it is not always direct (Lors et al., 2011). The bioassays that use the soil extract seem to better reflect the behavior of the mobile phases, which allows to evaluate in the short term the risks of dispersion, solubilization and bioavailability of the contaminants in the soil (Romero-Freire et al., 2014).

The determination of the ecotoxicity of metal(loid)s using simple bioassays as the one applied in this study, allows to evaluate the toxicological risk of the analyzed samples and helps to take measures to evaluate the disturbance of the ecosystems and to promote alternatives for bioremediation (Shanker et al., 1996; Iannacone et al., 2000; Iannacone and Alvariño, 2005).

Bioavailable metal(loid)s can be accumulated in organisms up to several orders of magnitude higher than the concentration found in the environment where they live. Bioaccumulation may cause the persistence of pollutants for long periods promoting the potential danger on the ecosystem (Aguilar et al., 1999). Plants can adopt different strategies against the presence of metal(loid)s in the environment (Baker, 1981, Barceló et al., 2003). Some plants focus their resistance to pollutants by an efficient exclusion of the metal(loid)s, restricting their transport to the aerial parts. Others prefer to accumulate the metal(loid)s in the aerial part in a non-toxic way for the plant. Exclusion is more characteristic of sensitive and metal-tolerant species, while accumulation is more common for species that always appear in contaminated or mine soils. Some plants can tolerate and accumulate much higher concentrations of metal(loid)s; these plants are called hyperaccumulators and are used for phytoremediation or phytostabilization of contaminated soils (Salt et al., 1995). There are different criteria for considering a plant as hyperaccumulator, although in general terms it can be defined as plants that not retain pollutants in the roots but are translocated to the shoot and accumulated in above-ground organs, especially leaves, at concentrations 100–1000-fold higher than those found in non-hyperaccumulator species (Rascio and Navari-Izzo, 2011). There are numerous examples of plants capable of accumulate pollutants, among the most frequent elements to be accumulated we can mention Cu, As and Cd (Jiang et al., 2004, Yang et al., 2002, Yang et al., 2004). Moreover, there is a very extensive bibliography in relation to phytoremediation, being the reviews of Moosavi and Seghatoleslami (2013) and that of Wang et al. (2017) among the most complete and recent.

Other important part in the environmental risk assessment is related to the implication for human health. Of particular concern in arid or semi-arid environment is the risk associated with the wind erosion of pollution practices coming from mining areas and the deposition over agricultural soils; this can lead to the direct ingestion of products grown in potentially contaminated soils.

Most of these assessments are based on soil guidelines according to total concentrations in soil and oral toxicity values are obtained from studies in which the potentially pollutant elements were spiked as soluble salts. Therefore, they may overestimate the risk associated with accidental soil ingestion since only a portion of the elements would be effectively absorbed by the human body (bioavailable). This fact has generated an increasing interest in incorporating bioavailability into risk assessments (Ge et al., 2002), which is estimated from *in vivo* tests using laboratory animals. However, due to bioethical considerations and to constraints in costs and time, during the last few years *in vitro* extraction tests are being developed to determine the oral bioaccessibility, defined as the fraction of a substance that is soluble in the gastrointestinal environment and is available for absorption (Ruby et al., 1999). The ingestion of dust coming from wastes or polluted soil is a route of exposure to environmental contaminants very important, especially in the case of children (IHOBE, 1994; Pierzynski et al., 2000). In the case of many metal(loid)s and other pollutants that have a low mobility in the soil, the ingestion of contaminated soil is one of the main routes of exposure to take into account in the evaluation of health risks (Oomen, 2003). The possible effects on health due to the ingestion of soils contaminated with potentially dangerous metal(loid)s should be evaluated with the incorporation of the measurement of their bioavailability in the calculations of exposure doses and not of the total content in the soil (Hamel et al., 1999, Martínez Sánchez and Pérez Sirvent, 2013) to be able to establish, based on the soil properties, the maximum permitted levels and to be able to carry out the cleaning operations of the site.

In this chapter we will present the results obtained when evaluating the degree of potential toxicity in the main materials founded in Chadak mining area. This evaluation will be carried out from three points of view: Firstly, we analyze the results obtained after the application of two toxicity bioassays (*Lactuca sativa* and *Vibrio fischeri* tests) in potentially contaminated samples of tailings from the abandoned tailing dump. Secondly, we analyze the results obtained in relation to the potential accumulation of heavy metal(loid)s in two of the most abundant plants in the area (*Artemisia absinthium* and *Phragmites australis*), to evaluate the degree of bioaccumulation and the potential of these plants to be used as hyperaccumulator species in the decontamination of contaminated areas by phytoextraction technique. Thirdly, the results obtained in a bioaccessibility study are evaluated from a standardized methodology for the evaluation of the risk of heavy metal(loid)s accumulation after human exposure through the ingestion of dust and its subsequent assimilation within the digestive system; this assessment was made to evaluate the risk in the active mining (industrial use) and in the surrounding areas close to the mine (urban and agricultural use).

5.2. Material and Methods

In this chapter, we correlate the obtained results from the different toxicity or bioaccumulation tests with the general properties and constituents of the samples (including physicochemical characteristics and metal(loid)s concentration). The methodologies used in relation to the physicochemical characterization of the studied samples, in addition to the analysis of the total concentrations (measured by PXRF) and extracted in the different procedures of selective extraction are detailed in Chapters 3 and 4.

5.2.1. Toxicity bioassays

The bioassays used in this study were made from the saturation extract of the samples. We used the soluble-in-water extractions because they better reflect the behavior of the mobile phases and assess the short-term risk of toxicity. In this case, a soil:water extract (1:5) using 10 grams of sample + 50 ml of distilled water were prepared, after 24 hours shaking the extracts were centrifuged and the liquid phase was used for the toxicity bioassays. The tests that were applied were i) *Lactuca sativa* bioassay, and ii) *Vibrio fischeri* bioassay; a detailed explanation of them is included below. The soluble concentration of potentially pollutant elements was also measured in this liquid phase in a ICP-MS spectrometer (PE SCIEX ELAN-5000A), at the Scientific Instrumentation Center (CIC) of the University of Granada.

5.2.1.1. *Lactuca sativa* bioassay

This test is adapted from the methodologies described by EPA (1996; OPPTS 850.4200). This bioassay was applied to assess the phytotoxic effects on seed germination and seedling growth (root elongation) in the first days of growth (Torres, 2003). For each sample, two replicates of 15 *Lactuca sativa* L. seeds were placed in 90-mm-diameter Petri dishes containing filter paper in the bottom as support. Five milliliters of saturation extract was then added, and the dishes were placed in a Memmert Din 40050-IP-20 incubator (Memmert, Bundesrespublik Deutschland, Germany) at 25±1°C.The number of seeds that had germinated and the length of the roots of the germinated seeds were measured after 120 h. Control samples were prepared in the same way, replacing the 5 ml of saturation extract with deionized water.

The variables analyzed were the number of germinated seeds and the elongation of the roots. The results for each sample were expressed as percentage of variation with respect to the control performed with distilled water, according to the following formula:

$$SG = [(Seed\_S \times 100) / Seed\_C]$$

Where *SG* is the Seed Germination percentage in each sample in relation to the control, *Seed_S* is the mean of the seeds germinated in the sample, and *Seed_C* is the mean of seed germinated in the control.

The root elongation of the seeds was calculated according to the percentage of reduction in the sample in relation to the control according to the following formula:

$$LsR = [100 - ((RE\_S \times 100) / RE\_C)]$$

Where *LsR* is the Root elongation reduction percentage in each sample in relation to the control, *RE_S* is the mean (cm) of the root elongation in the sample, and *RE_C* is the mean (cm) of the root elongation in the control.

In this case, values range from 0 for the samples that no presented toxicity, to 100 for the samples with the maximum toxicity. Values below 0 can occur when there stimulation of the study variable occurs (hormesis).

In all cases, 3 samples were prepared and 3 repetitions were performed for each sample; 6 controls with distilled water were also included.

5.2.1.2. *Vibrio fischeri* bioassay

This test is adapted from the Microtox® test (ASTM, 2004) and is based on the reduction of the light emitted by a non-pathogenic strain of luminescent marine bacterium *Vibrio fischeri* upon exposure to a toxic sample (Ribó and Kaiser 1987). The test was performed in a Microtox 500 analyser from Microbics Corporation, according to a modification of Microtox Basic Test for Aqueous Extracts Protocol (Martín et al. 2010; Azur Environmental 1998).

The protocol starts with the measurement of the luminescence in the regenerating solution with bacteria, before the mixture with the water extracts (0 minutes). Then, the mixture of the water extracts and the regenerating solution with bacteria was made, and the inhibition of bioluminescence was measured at 5 and 15 minutes after the mixture. The results for each sample were expressed as percentage of reduction (Red) with respect to the initial luminescence value. Afterwards, these values were used to calculate two toxicity indexes:

<u>Luminescence reduction at 5 minutes</u>:

$$VfR5 = 100 \times [(Red5\_S - Red5\_C) / (100 - Red5\_C)]$$

Where *VfR5* is the percentage of Luminescence reduction after 5 minutes in each sample in relation to the percentage of reduction in the control, *Red5_S* is the percentage of luminescence reduction in the sample at 5 minutes in relation to the luminescence at 0 minutes, and *Red5_C* is the percentage of luminescence reduction in the control at 5 minutes in relation to the luminescence at 0 minutes.

<u>Luminescence reduction at 15 minutes</u>:

$$VfR15 = 100 \times [(Red15\_S - Red15\_C) / (100 - Red15\_C)]$$

Where *VfR15* is the percentage of Luminescence reduction after 15 minutes in each sample in relation to the percentage of reduction in the control, *Red15_S* is the percentage of luminescence reduction in the sample at 15 minutes in relation to the luminescence at 0 minutes, and *Red15_C* is the percentage of luminescence reduction in the control at 15 minutes in relation to the luminescence at 0 minutes.

In this case, values range from 0 for the samples that no presented toxicity, to 100 for the samples with the maximum toxicity. Values below 0 can occur when there stimulation of the study variable occurs (hormesis). In all cases, 3 samples were prepared and 3 repetitions were performed for each sample; 6 controls with distilled water were also included.

5.2.2. Bioaccumulation of metal(loid)s in plants

Sampling of plants was carried out according to the existing protocols from Malyuga (1963) and Talipov (1988). From each sample point two replicates of composite plant samples were collected in the vicinity of Chadak mining area and in the tailing dumps which coincided with sampling points of soil and tailings samples, respectively. Two dominant plants growing in natural conditions (without fertilizers or artificial irrigation) were collected: *Artemisia absinthium* in soils surrounding of the active tailing dump and in the abandoned tailing dump (Fig.25), and *Phragmites australis* directly growing on the tailings of the active tailing dump (Fig.26). In all cases, the aboveground biomass of the plants was selected.

Figure 25. *Artemisia absinthium* collected from soils surrounding AcT and AbT.

Figure 26. *Phragmites australis* collected from the tailings of the AcT.

5.2.2.1. Preparation of plant samples and analyses

Collected plants were dried at 70ºC during 48 hours. The dry samples were placed in an aluminum dish and burned in the open air, and the charred mass was transferred to paper bags with the name of sample and sent to the laboratory for further analyses.

Dry ashes of plants were introduced in an electric muffle furnace at 450-500^{0}C. The ashing was performed until the complete removal of organics (constant weight). The resulting ash was prepared to microwave acid digestion in a CEM MARS 230/60 Microwave Accelerated Reaction System. To conduct acid digestion 0.3 grams of sample were dissolved in 5 ml of a combination of nitric-hydrochloric acids (HNO_3–HCl) in a ratio 1:3. The final solution was analyzed for V, Cr, Mn, Ni, Cu, Zn, As, Mo, Sn, Sb, Ba, and Pb by ICP-MS spectrometer (PE SCIEX ELAN-5000A), at the Scientific Instrumentation Center (CIC) of the University of Granada.

Results were presented as concentration (mg/kg dry weight) of pollutant in plants. Moreover, to estimate the degree of enrichment/transfer capacity of plants in relation to soil concentration, the bioaccumulation factor was calculated according to the following formula:

$$BF = [X\_p] / [X\_s]$$

Where *BF* is the bioaccumulation factor of the plant sample, [X_p] is the concentration (mg/kg) of the element "X" in plant, and [X_s] is the concentration (mg/kg) of the same element "X" in soil.

BF is a dimensionless value, representing the accumulation of a certain element in plant, where values below 1 indicate no accumulation and values above 1 indicate accumulation.

5.2.3. Bioaccessibility and human exposure assessment of metal(loid)s

A physiologically-based extraction test simulating was made for the analysis of metal bioaccessibility. A standard operating procedure for an *in vitro* bioaccessibility assay for lead and arsenic in soil (Ruby et al., 1996; EPA, 2017) was used to assess the potential hazard to human being from ingestion after the gastric phase of potentially toxic elements. After drying and sieving to 150 µm, 1 gram of sample is rotated with 100 ml (0.1 L) of 0.4 M glycine buffered extraction fluid with hydrochloric acid (pH 1.50). Samples were extracted by rotating at 30 ± 2 rpm for 1 hour. The time that ingested material is present in the stomach (stomach emptying time) is about 1 hour for a child, so this time was considered as standard (EPA, 2007). The temperature of 37°C is used as standard because this is the approximate temperature of gastric fluid *in vivo* in humans; for this purpose, samples were placed in a water bath at this temperature (±2ºC). A pH of 1.5 was selected because the highest amounts of lead and arsenic are extracted at this value compared with higher pHs (Brattin et al., 2013). The supernatant is separated from the sample by filtration with a 0.45-µm cellulose acetate disk filter and analyzed for metal(loid)s by a ICP-MS spectrometer (PE SCIEX ELAN-5000A), at the Scientific Instrumentation Center (CIC) of the University of Granada. A control blank was also measured, including the extraction fluid only. All samples were measured in triplicate.

Results were expressed as concentration (mg/kg) of element in soil potentially bioaccesible after gastric digestion. The reference sample used was CRM025-050, a sandy loam soil polluted with trace metals (Sigma-Aldrich RTC, 2011). Moreover, metal(loid)s bioaccessibility (BA) was calculated as the percentage of extractable element (after the gastric phase) to total concentration in sample, accoding to the following formula (Oomen et al., 2002):

$$\text{BA (\%)} = (C_g \times 100) / C_s$$

Where BA is the percentage of bioaccessibility of the element; C_g is the extractable concentration after the gastric digestion; and C_s is the total concentration in sample.

To assess the associated human health risk, average daily intake of metal(loid)s via ingestion route (ADI_{ing}) was calculated using the following formula (EPA, 1989):

$$\text{ADI}_{\text{ing}} = C_g \times (\text{IR} \times \text{EF} \times \text{ED}) / (\text{BW} \times \text{AT})$$

Where C_g is the extractable concentration after the gastric digestion; IR is the ingestion rate; EF is the exposure frequency; ED is the exposure duration; BW is the average body weight; and AT is the average exposure time.

The human health risk was calculated according to the via of ingestion route for three different soil uses: 1) Industrial soil use (mining activity); 2) Urban use (separating between children and adults); and 3) Agricultural soil use. Exposure parameters used in this work (RD 9/2005; EPA, 2001) are presented in Table 16. Human health risk of metal(loid)s were determined by the hazard quotient (HQ) in a dose-response model according to the following formula (EPA, 1989):

$$\text{HQ} = \text{ADI}_{\text{ing}} / \text{RfD}$$

Where HQ is the hazard quotient of potentially pollutant metal(loid)s; ADI_{ing} is the average daily intake via ingestion route; and RfD is the oral reference dose that is unlikely to pose appreciable risks of deleterious effect during lifetime (Table 17).

When HQ < 1.0, the health risk is negligible; and when HQ > 1.0 some degree of risk exists.

Table 16. Parameters values for calculation of associated human health risk for ingestion route in the three soils uses considered.

Parameter		Industrial	Urban children/adult	Agricultural
Ingestion rate (g/day)	IR*	0.02	0.05 / 0.02	0.05
Exposure frequency (day/year)	EF	250	350	350
Exposure duration (year)	ED	25	6 / 30	30
Average body weight (kg)	BW	70	15 / 70	70
Average exposure time (day)	AT	ED x 365	ED x 365	ED x 365

** According to EPA (2017a).*

Table 17: Oral reference dose (RfD) in mg/kg according to EPA (2001).

Element	Cu	Zn	As	Sb	Pb
RfD (mg/kg)	0.14	0.30	3×10^{-4}	4×10^{-4}	0.0036

5.2.4. Statistical analysis

In all cases, the normality of the samples was first checked with the Kolmogorov-Smirnov test, and the homogeneity of the variance with the Levene test. In the cases in which the requirements of normality or homogeneity of variance were not met, the data was transformed logarithmically and checked again. If the requirements of normality and homocedasticity were met, a one-way analysis of variance (ANOVA) was carried out taking into account the requirements of the test, in order to study the differences between treatments. As a method of multiple comparisons, the Tukey's test was applied. In the case of not meeting the requirements, nonparametric tests were applied, specifically the Kruscal-Wallis analysis. Pearson or Spearman correlation analysis was performed (for parametric and non-parametric data, respectively) to analyze the relationships of physicochemical properties on toxicity variables. An analysis of the main components rotated by the standardization method of Varimax with Kaiser was carried out to establish the relationship between sample properties, contaminants and their ecotoxicological effects. All analyzes were performed at a confidence level of 95%. For the statistical analyzes the statistical package SPSS 20.0 (SPSS Inc., Chicago, USA) was used.

5.3. Results and discussion

In this section the results related to the potential ecotoxicity in the main materials analyzed in Chadak mining area were presented. This assessment was carried out from three points of view: 1) Toxicity bioassays according to *Lactuca sativa* and *Vibrio fischeri* tests; 2) Potential accumulation of heavy metal(loid)s in plants; and 3) Bioaccessibility and human exposure assessment of potentially pollutant elements.

5.3.1. Toxicity bioassays

For the study of potential toxicity in the area according to the bioassays response, tailings from the abandoned tailing dump were selected because of the high concentration of metal(loid)s detected, which could be related to a high risk of pollution to the surrounding areas. The total concentration of metal(loid)s in these samples and their physicochemical properties are summarized in Table 18. According to this data, a first assessment of the potential pollution in these samples could be made by the comparison with regulatory levels. In this case, there is no published official regulatory levels for metal(loid)s in Uzbekistan, so we made a comparison with the regulatory levels in two countries of reference: Spain (Decree 18/2015 for polluted soils in Andalucía) and Holland (VROM, 2000).

According to these reference levels (Table 18), the studied samples exceed the intervention levels for some metal(loid)s. In the case of As, the concentration in tailings is very high and all samples exceed these levels, with maximum concentrations increasing more than 30-folds the value in Holland and 47-folds the value in Andalucía, which could indicate a high potential risk of toxicity according to the total concentrations. In the case of Sb, the concentration in tailings is also very high and many samples, with maximum concentrations increasing more than 100-folds the value in Holland and 17-folds the value in Andalucía, which could also indicate a high potential risk of toxicity according to these total concentrations. The Pb concentrations were not exceeded the intervention values in Holland in any sample, and slightly exceeded these values in some cases, indicating a very low potential risk of toxicity for this element. Zn was not exceeded the intervention values used as reference in this work in any case, so there is no potential risk of toxicity for this element in the studied samples.

Table 18. Total concentration of main metal(loid)s and physicochemical properties in tailings from the abandoned tailing dump.

	ZnT	AsT	SbT	PbT	pH	EC	CEC	$CaCO_3$	OC	Clay	Silt	Sand
Sample	(mg/kg)					(dS/m)	($cmol_+$/kg)			(%)		
Chd IV1a	143	376	341	106	8,3	0,129	7,2	7,0	0,3	12,0	23,4	64,6
Chd IV2a	273	1689	1507	386	7,0	0,922	5,0	4,0	0,5	8,4	28,1	63,5
Chd IV3a	223	672	544	188	8,0	0,958	5,0	5,0	0,2	10,0	34,5	55,5
Chd IV4a	181	98	180	195	8,0	0,405	4,8	10,0	0,1	8,3	28,7	63,0
Chd IV5a	257	450	55	366	8,0	0,407	3,9	14,0	0,2	9,1	42,2	48,8
Chd IV6a	202	245	81	220	8,0	0,165	3,5	14,0	0,1	7,6	35,5	56,9
R. Spain-And.	10000	36	90	275								
R. Holland	720	55	15	530								

R. Spain-And.: Intervention levels in Andalucía, Spain (Decree 18/2015); R. Holland: Intervention levels in Holland (VROM, 2000. Dutch list). EC: Electric conductivity; OC: Organic carbon.

5.3.1.1. *Lactuca sativa* bioassay

The results of the toxicity bioassay according to *Lactuca sativa* L. response in the tailing samples at the abandoned tailing dump are presented below. In the case of Seed germination (SG), the reliability indices established by the test protocol (> 90% of germination in the control samples) (OECD, 2006), determined that the control carried out with distilled water presented a value of 96.7%, indicating that this index was met. In the case of the studied samples, the pH and EC values are considered in the range for the growth of lettuce seeds (Valadez, 1997).

The results of the studied samples (Fig. 27) indicate high seed germination in all cases, with no significant differences ($p>0.05$) among samples. The similarity of these values with the control samples shows that no toxicity was detected according to SG. Anyway, a low degree of discrimination of this variable could be related with the low availability of pollutant elements in relation to the soil properties. These relationships will be discussed below, but previous studies (Martín et al., 2012) reported that SG is a variable with a low degree of sensitivity under medium to low potentially toxic conditions.

Figure 27. Seed germination (SG) in tailing samples and in control (distilled water) showing no significant differences among samples and control.

In relation to the *Lactuca sativa* L. reduction of root elongation (LsR), the results are presented in Figure 28. Toxicity will be shown at positive values, indicating a reduction of the root elongation in relation to the control (distilled water). In the case of studied samples, no toxicity was detected in any tailing sample, and negative values (hormesis) were found in all cases, indicating a positive response in the root elongation in relation to the control.

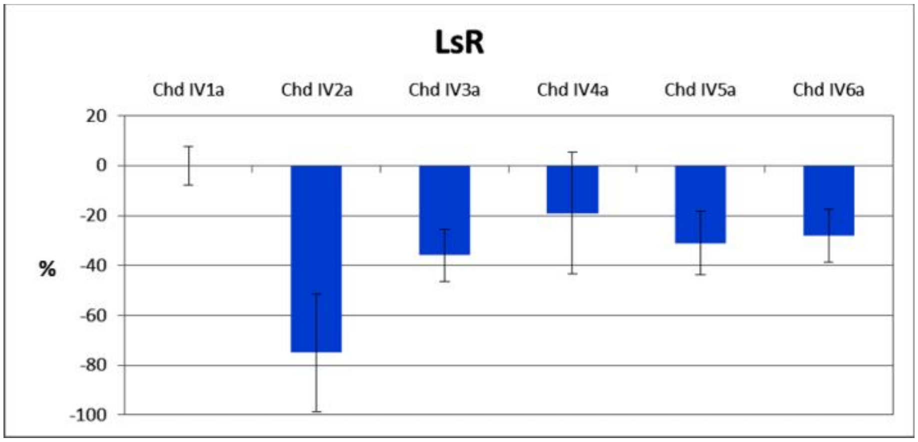

Figure 28. Root elongation reduction (LsR) in tailing samples and in control (distilled water) showing negative values (no toxicity) in all cases.

In general, the low degree of toxicity detected in these samples, despite the high concentrations of potentially contaminating elements measured, is related to the low concentrations of soluble elements detected (see Chapter 4). In semi-arid environments, it is common that the total concentrations of metals do not correlate with those of their soluble fractions, differences that can be explained by the influence of soil properties (Romero-Freire et al., 2016). In this sense, As and Sb are metalloids that tend to accumulate in soils due to their low mobility (Yang et al., 2012; Nakamaru and Martín, 2017), and their solubility is more controlled by soil properties than for the total concentration detected (Martín et al., 2012; Romero-Freire et al., 2015).The properties studied with greater influence on the availability of As and Sb are pH, OC, iron oxides, clay content, calcium carbonate and CEC (Martín et al., 2012; Romero-Freire et al., 2014; Song et al., 2006; Nakamaru and Martín, 2017). Special is the case of pH in As, in which the presence of basic pH or a high content of calcium carbonate, could cause an increase in the solubility of some forms of As (Fleming et al., 2013; Simón et al., 2010), although in our study, the absence of toxicity observed in the two tests carried out, seems to indicate a low degree of solubility of As under these conditions.

5.3.1.2. ***Vibrio fischeri*** **bioassay**

The results of the toxicity bioassay with *Vibrio fischeri* in the tailing samples are similar to that obtained in the bioassay with *Lactuca sativa* in relation to the root elongation reduction (LsR). In the *Vibrio fischeri* bioassay, the influence of pH and EC should be tested, and according to our samples (pH: 7.90 ± 0.40; and EC: 0.50 ± 0.36) these values are within the recommended range for this toxicity bioassay (Onorati y Mecozzi, 2004). According to the toxicity bioassay with *Vibrio fischeri*, all samples showed a decrease in the luminescence in relation to the initial value, even in the control samples (distilled water), because this bacterium is from a marine environment, for this reason, the luminescence reduction was normalized according to the percentage of reduction in relation to the control (Martín et al. 2010).

The reduction of luminescence at 5 minutes indicated a slight reduction in relation to the control in two samples (Chd IV1a and Chd IV6a), but the differences were not statistically significant ($p>0.05$)in relation to the control sample (distilled water). For the other samples, a positive response indicated that the soil solution of these samples stimulated bacterial activity (hormesis), and no toxicity was observed (Fig. 29).

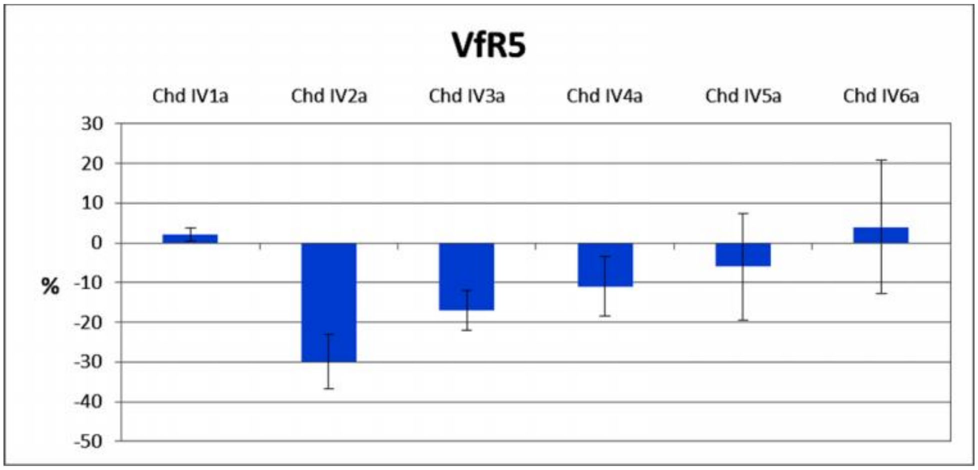

Figure 29. *Vibrio fischeri* reduction at 5 minutes (LsR) in relation to the control (distilled water) in tailing samples showing no toxicity (hormesis) in all cases.

The reduction of luminescence at 15 minutes indicated no reduction in relation to the control in any sample and the differences were not statistically significant ($p>0.05$) in relation to the control sample (distilled water) (Fig. 30). Therefore, the luminescence after 15 minutes showed no toxicity and even an increase in the values over time was observed; this evolution is normal when no toxicity occurs and is reflected by an rise in the negative values in relation to the luminescence detected at 5 minutes.

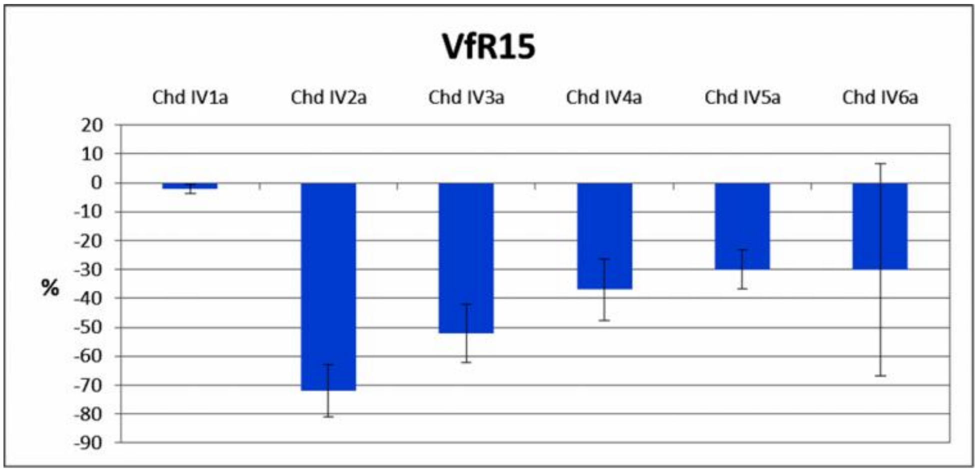

Figure 30. *Vibrio fischeri* reduction at 15 minutes (LsR) in relation to the control (distilled water) in tailing samples showing no toxicity (hormesis) in all cases.

5.3.1.3. Influence of physicochemical properties and total concentration of metal(loid)s on toxicity bioassays

Finally, to obtain information about the relationships between the variables obtained in the toxicity bioassays, a factorial analyses was applied using all bioassays results, on one hand, and the total concentration of metal(loid)s and physicochemical properties, on the other hand. In this case the factorization type used was a principal component (PCA) which supposes that all of the variability of the data corresponds exclusively to common factors. We applied an orthogonal rotation of the axis (Varimax rotation) and obtained new groups of variables called components, which usually group the studied variables in accordance with common features and a percentage of variance explained (Pérez-López, 2002). The results of the PCA are shown in Figure 31. This analysis grouped the variables in two main Components explaining the 70.7% of the variance: Component 1 explaining the 47.8%, and Component 2 explaining the remaining 22.9% of the variance.

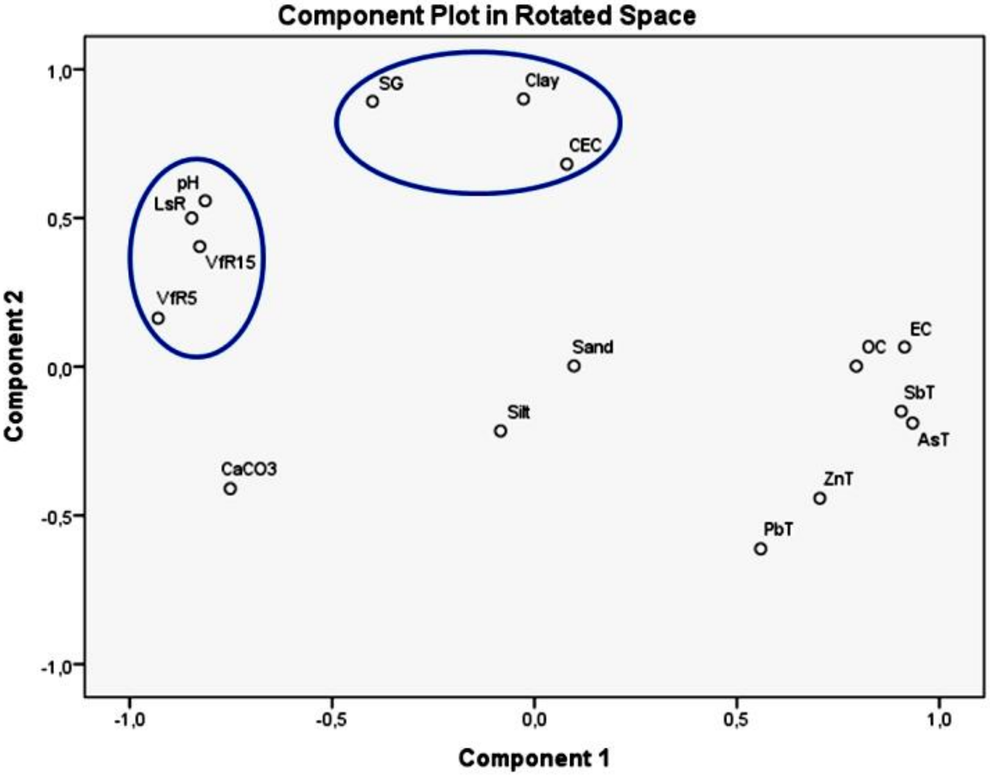

Figure 31. Principal component analysis (PCA), using Varimax rotation, among the variables in toxicity bioassays, total metal(loid)s concentration and physicochemical properties of the tailings.

According to these results, we can conclude that the absence of toxicity in the studied samples is directly related to some physicochemical properties that prevent and control the influence of metal(loid)s. In this way, seed germination (SG) of *Lactuca sativa* is closely grouped with clay content and cation exchange capacity (CEC), indicating the positive effect of these two variables in the reduction of the solubility of potentially polluted elements. The influence of these two variables in the mobility of metal(loid)s has been extensively studied (Kabata-Pendias, 2011; Romero-Freire, 2015a) and our results are in the line of these findings. Otherwise, pH is strongly grouped with the variables from the *Vibrio fischeri* bioassay (VfR5 and VfR15) and the *Lactuca sativa* root elongation reduction (LsR). The role of high pH conditions on the reduction of metal(loid)s toxicity has been extensively studied (Kabata-Pendias, 2011), although the presence of basic pH could cause an increase in the solubility of As (Fleming et al., 2013; Simón et al., 2010). In this way, despite of the high concentration of some elements (mainly As and Sb) our results indicate the absence of toxicity under these conditions.

5.3.2. Bioaccumulation of metal(loid)s in plants

In this section, the results of bioaccumulation of two dominant plants growing in the area are presented: *Artemisia absinthium* dominant in soils surrounding of the active tailing dump and in the abandoned tailing dump, and *Phragmites australis* directly growing on the tailings of the active tailing dump.The concentrations of the main micronutrients in plants are shown in Table 19, indicating a high range of variability between species and among the values measured for the same species.

The concentrations of micronutrients measured in plants showed significant differences ($p<0.05$) between both species. *A. absinthium* presented significant lower concentrations in Mn and significant higher concentrations in Ni than *P. australis*. The other micronutrients (Cu, Zn and Mo) did not presented significant differences between both species. Otherwise, *A. absinthium* showed significant differences among the different locations sampled, with significantly lower concentrations of Mn and Ni in the soil cover at the abandoned tailing dump (AbT).

Table 19. Mean concentration and range (mg/kg d.w.) of main micronutrients in plants collected in different sites of the study area (letters in brackets indicate statistically significant differences between samples; Tukey's test: p<0.05).

		Plant species		**Mn**	**Ni**	**Cu**	**Zn**	**Mo**
AcT	Soil	*Artemisia absinthium*	Mean ± SD	1051±343 (bc)	29.6±7.3 (a)	214±62.9 (a)	528±347 (a)	14.2±7.9 (a)
			Range	593-2142	11-49	110-332	262-1798	6-40
	Tailing	*Phragmites australis*	Mean ± SD	2214±543 (a)	7.7±1.2 (d)	149±240 (ab)	644±243 (a)	25.8±17.1 (b)
			Range	1641-2969	6-9	37-639	376-1005	9-49
AbT	Soil Cover	*Artemisia absinthium*	Mean ± SD	673±265 (c)	14.8±4.9 (c)	109±39.9 (b)	465±299 (a)	16.2±10.8 (ab)
			Range	361-1162	10-27	48-192	174-1217	3-44
Open pit wastes area	Soil	*Artemisia absinthium*	Mean ± SD	1311±488 (b)	21.9±2.5 (b)	149±45.0 (ab)	431±140 (a)	17.3±8.6 (ab)
			Range	717-2556	17-27	68-211	269-892	5-41
Backgr. Conc.				390	31	37	135	3
Excessive or toxic values in plants *				400-1000	10-100	20-100	100-400	10-50

** Kabata-Pendias (2011); Backgr. Conc.: Background concentration in unpolluted soils in the area.*

The concentrations of micronutrients measured in plants showed significant differences (p<0.05) between both species. *A. absinthium* presented significant lower concentrations in Mn and significant higher concentrations in Ni than *P. australis*. The other micronutrients (Cu, Zn and Mo) did not presented significant differences between both species. Otherwise, *A. absinthium* showed significant differences among the different locations sampled, with significantly lower concentrations of Mn and Ni in the soil cover at the abandoned tailing dump (AbT). The comparison of these concentrations with the reported as "toxic values in plants" reported in Kabata-Pendias (2011), indicate that these plants are able to accumulate some metals in their aboveground biomass. In the case of *A. absinthium*, Mn is concentrated up to 2-fold, Cu 3-fold and Zn 4-fold in relation to the maximum toxic value for other plants; meanwhile in the case of *P. australis*, Mn is concentrated up to 3-fold, Cu 6-fold and Zn 2.5-fold in relation to the maximum toxic value for other plants.

The concentration of potentially toxic metal(loid)s in plants is presented in Table 20. These values showed significant differences (p<0.05) between both species and among the different location for the same specie (*A. absinthium*), with a high range of concentrations in all cases.

Table 20. Mean concentration and range (mg/kg d.w.) of non-essential elements in plants collected in different sites of the study area (letters in brackets indicate statistically significant differences between samples; Tukey’s test: $p<0.05$).

		Plant species		**V**	**Cr**	**As**	**Sb**	**Pb**
AcT	Soil	*Artemisia absinthium*	Mean ± SD	33.7±13.6 (a)	21.5±7.5 (a)	7.2±3.1 (ab)	9.4±3.9 (a)	62.7±50.5 (a)
			Range	3-57	7-35	2-15	3-17	25-228
	Tailing	*Phragmites australis*	Mean ± SD	3.5±1.9 (c)	7.5±2.5 (b)	3.3±1.0 (a)	5.7±1.6 (a)	52.5±112 (a)
			Range	2-7	5-11	2-5	4-8	4-282
AbT	Soil Cover	*Artemisia absinthium*	Mean ± SD	15.1±7.9 (b)	8.7±3.3 (b)	54.2±89.9 (b)	21.8±30.3 (a)	22.3±10.0 (a)
			Range	6-30	4-14	5-341	7-121	14-51
Open pit wastes area	Soil	*Artemisia absinthium*	Mean ± SD	18.4±8.1 (b)	10.3±2.6 (b)	7.9±6.1 (ab)	12.9±2.4 (a)	26.7±9.4 (a)
			Range	10-35	7-17	3-26	10-18	15-43
Backgr. Conc.				131	51	15	4	48
Excessive or toxic values in plants *				5-10	5-30	5-20	150	30-300

** Kabata-Pendias (2011); Backgr. Conc.: Background concentration in unpolluted soils in the area.*

A. absinthium presented significant ($p<0.05$) higher concentrations in V than *P. australis*. The other potentially pollutant elements(Cr, As, Sb and Pb) did not presented significant differences between both species. Otherwise, *A. absinthium* showed significant differences among the different locations sampled, with significantly higher concentrations of V and Cr in the soil surrounding the active tailing dump (AcT). The comparison of these concentrations with the reported as “toxic values in plants” reported in Kabata-Pendias (2011), indicate that these plants do not to accumulate high amounts of metal(loid)s in their aboveground biomass. In the case of *P. australis*, none of the metal(loid)s analysed are accumulated above the maximum toxic value for other plants. In the case of *A. absinthium*, the mean values of some elements slightly exceed the maximum toxic value for other plants, although in some individual plants, concentrations measured were up to 5.7-fold in the case of V, 1.2-fold for Cr and 17-fold for As, indicating a potential of this plant to accumulate As in its aboveground biomass. It is important to point out that the maximum concentration of As in *A. absinthium* was found in plants growing over the soil cover of the abandoned tailing dump (AbT), which could mean a potential risk of dispersion of this contaminant to the food chain, if appropriate preventive measures are not adopted.

The bioaccumulation factor (BF) of the plants is presented in Table 21, and was calculated from the ratio between the concentration (mg/kg) of the element in plant, and the concentration (mg/kg) of the same element in soil. According to these results, we found a different behavior between the two plant species studied. *P. australis* showed a BF<1 for Ni, V, Cr, As, Sb and Pb, which indicates a low transfer of these elements from the soil to the aboveground biomass. The other elements were bioaccumulated in low ratio for Zn and Mn (BF~2.5), moderate for Mo (BF~5.5) and high for Cu (BF~11). The comparison of our values with the BF reported by Bragato et al (2009) in degraded areas of North Italy, indicates that bioaccumulation of these elements are in the same range. *P. australis* is an invasive species frequently found in disturbed areas (Ye et al., 1997), and although is not considered as hyperaccumulator, it has a fast growing and high-biomass production, with a deep root system that can tolerate and/or accumulate a range of heavy metals in their aerial portion (Bragato et al., 2009). Otherwise, *P. australis* has also a very low (<<1) translocation factor (ratio of metal in aerial biomass in relation to roots) for most metals (Deng et al., 2004), which could indicate that trend to accumulate the metal pool into belowground biomass (Weis and Weis, 2004). In our case, this plant may be efficiently utilized for metal removal (mainly Cu) and, in any case, can also be used for phytostabilization of contaminated sites.

Table 21. Bioaccumulation factor (BF) of metal(loid)s in plant of the study area.

			Mn	Ni	Cu	Zn	Mo	V	Cr	As	Sb	Pb
AcT	Soil	*Artemisia absinthium*	1.43	1.20	37.82	4.80	7.83	0.42	0.73	0.66	3.54	0.05
	Tailing	*Phragmites australis*	2.42	0.80	11.06	2.54	5.56	0.07	0.87	0.07	0.71	0.67
AbT	Soil Cover	*Artemisia absinthium*	1.34	1.03	3.74	4.27	9.55	0.19	0.30	1.07	2.53	0.55
Open pit wastes area	Soil	*Artemisia absinthium*	1.77	1.66	4.24	4.78	10.29	0.17	0.43	0.34	7.88	0.74

On the other hand, *A. absinthium* showed a BF<1 for Pb, V and Cr; and a BF~1 for Ni, As and Mn, which indicates a low transfer of these elements from the soil to the aboveground biomass. Other elements like Zn, Sb and Mo were bioaccumulated in a moderate to high ratio (BF between 5 and 10); and Cu was the element with the highest bioaccumulation (BF~38). The total concentration of metal(loid)s in aboveground biomass of *A. absinthium* and the BF for most elements are in the range of values reported by Massa et al. (2010) in a polluted site in Italy. The potential use of this plant as possible agent in recovery of heavy metal contaminated soils was previously reported (Samkayeva et al., 2001; Lyubun and Tychinin, 2007), although little specific affinity between the potentially polluting elements has been reported. According to our results, *A. absinthium* can be considered as a suitable plant for phytoextraction of Cu, Zn and Sb in polluted areas. Moreover, the ability to accumulate potentially toxic elements in shoots or root of this plant, along with its tolerance to the contamination and good adaptation to the local environmental conditions (Massa et al., 2010), make this plant can be regarded as bioindicator of terrestrial ecosystem pollution (Samkayeva et al., 2001), as well as phytostabilizator in polluted areas.

5.3.3. Bioaccessibility and human exposure assessment

The bioaccessibility (BA) of metal(loid)s after gastric phase extraction strongly change depending on the element. According to results in Figure 32, bioaccessible metal(loid)s concentrations in tailings in descending order were as follows: Pb > Zn > Ni ≈ Cu ≈ As ≈ Co > Sb. The comparison of this sequence with the obtained in the standard reference material (CRM) indicates that the BA (%) of the potentially pollutant elements is completely different, although there were statistically significant differences in relation to the percentage of elements extracted only in the case of Zn, As and Sb; in these cases, the amount extracted was significantly lower in the tailings in relation to the reference polluted soil, indicating that these metal(loid)s are in less bioaccessible forms in relation to the soil.

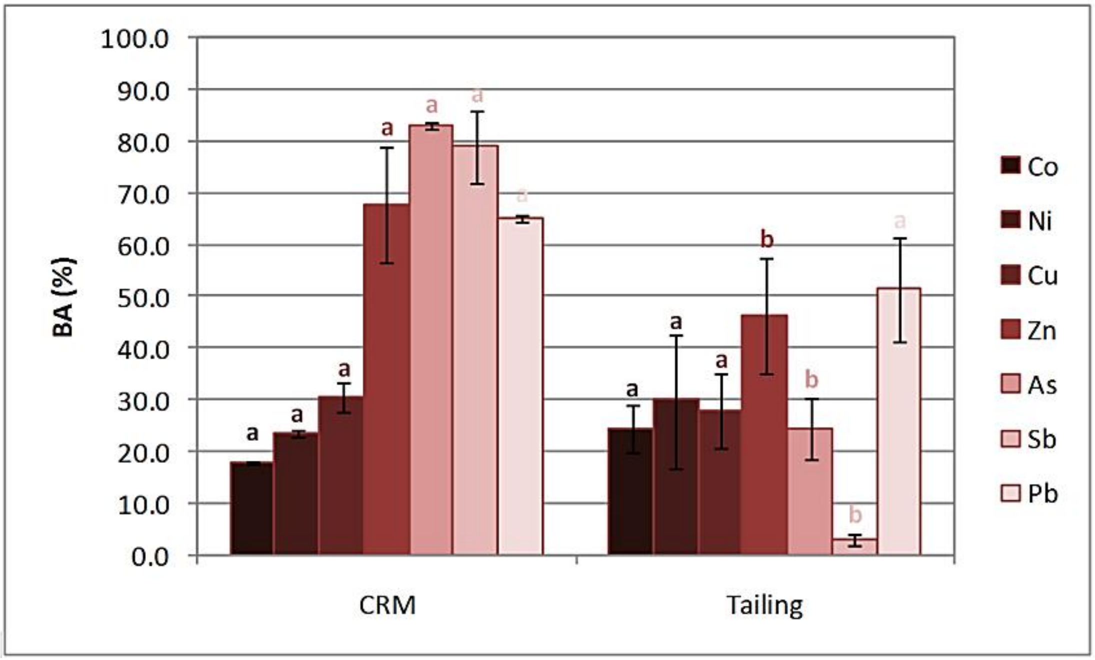

Figure 32. Mean metal(loid)s bioaccessibility after gastric phase extraction in tailings and in reference material (CRM)

According to the total concentrations of metal(loid)s measured in tailings, the potentially pollutant elements considered for the assessment of human health risk were Cu, Zn, As, Sb and Pb. In the case of these elements, we calculated the average daily intake (ADI_{ing}) via ingestion route for three soil uses (Industrial, Urban and Agricultural), and the hazard quotient (HQ) by the ration between ADI_{ing} and the oral reference dose (RfD) that is unlikely to pose appreciable risks of deleterious effect during lifetime (Table 22).

The assessment of human health risk according to the hazard quotient indicate that the risk is negligible for Cu and Zn (HQ<1), but a high risk for human health occurs for As, Sb and Pb. The element with highest values of HQ was As, followed by Pb and Sb. Special high risk is detected in the case of urban soils exposed to children (gardens or parks) and in agricultural soils located close to the mining areas. The exposure of dust particles coming from the tailing dump could deposit variable amounts of potentially pollutant elements increasing the human health risk to the population living in nearby areas.

Table 22. Average daily intake (ADI_{ing}) via ingestion route and hazard quotient (HQ) for the potentially pollutant metalloids in three different soil uses.

		Cu	Zn	As	Sb	Pb
Industrial	**ADI_{ing}**	0.0055	0.0091	0.0048	0.0006	0.0101
	HQ	0.04	0.03	15.94	1.60	2.80
Urban	**ADI_{ing}**	0.0897	0.1483	0.0781	0.0105	0.1644
(children)	**HQ**	0.64	0.49	260.27	26.13	45.68
Urban	**ADI_{ing}**	0.0077	0.0127	0.0067	0.0009	0.0141
(adults)	**HQ**	0.05	0.04	22.31	2.24	3.92
Agricultural	**ADI_{ing}**	0.0192	0.0318	0.0167	0.0022	0.0352
	HQ	0.14	0.11	55.77	5.60	9.79

In toxicological studies, calculations of exposure to soils contaminated with heavy metals assume that 100% of the elements in the soil is absorbed after the accidental ingestion of contaminated soil (Ruby et al., 1999) and based on this, the contaminant concentrations that must be reached in recovery work is fixed. Numerous studies carried out with materials from the mining activity and soils affected by it with high concentrations of lead and arsenic (Ruby et al., 1996, Kelley et al., 2002, Mercier et al., 2002, Oomen et al., 2002), show that contaminants in soil have lower solubility than in the environments in which toxicological studies are normally carried out, such as water or food, and therefore, the risk associated with the presence of the contaminant in the soil is overestimated (IHOBE, 1998; Oomen, 2003). Therefore, in the evaluation of exposure to a metal, it is necessary to take into account the matrix in which it is found.

In our study area, the most common minerals bearing metal(loid)s are sulphides. In this case, the elemental form and sulphides are usually less soluble in biological fluids (Ruby et al., 1999) and therefore, less bioavailable than oxides, hydroxides or carbonates of the same metal. In acidic soils (pH<5), products are formed that will be more stable in the acidic conditions of the stomach and therefore, less bioavailable (Juhasz, 2003); while the products that form in alkaline soils (pH>8) tend to have greater bioavailability. Under acidic conditions (pH<3), adsorption within the organic matter of arsenic can reduce its mobility in mining waste, while mobility can increase under alkaline conditions (pH>7) (Wang and Mulligan, 2009). Many metals, including cadmium, lead, mercury and nickel, are usually associated with carbonates in alkaline soils, these being more bioavailable in the oral exposure route (Kientz et al., 2003). Soils with high concentrations of iron and manganese (> 3-5%) tend to have low bioavailability, due to adsorption processes on the surfaces of soil particles, especially in the case of arsenic. However, when we consider oral ingestion of fine dust the risk associated with As in mine wastes is different. Meunier et al. (2010) based on tailings samples from several abandoned gold mines in Nova Scotia, showed that As bioaccessibility depends on As mineralogy. In particular, relatively low As bioaccessibility exhibited by scorodite ($FeAsO_4 \cdot 2H_2O$) and arsenopyrite (FeAsS), whereas samples containing Ca-Fe arsenate minerals, such as yukonite [$Ca_7Fe_{12}(AsO_4)_{10}(OH)_{20} \cdot 15H_2O$] have relatively high bioaccessibility. Higher As bioaccessibility associated with Ca-Fe arsenate could be related to the residual carbonate and the As-hosting Ca-bearing minerals present in tailings that dissolve more readily in the gastric fluid (Jamieson, 2011). Due to the fact, that yukonite like phases are observed in samples at the AbT in Chadak mine might therefore be considered the riskiest material.

5.4. Conclucion

The toxicity assessment in the Chadak mining area was made according to three approaches: Toxicity bioassays, Plant accumulation and Human health risk. The toxicity bioassay showed no risk of toxicity in the short-term, in this case, the test was made with the soluble-in-water phase, indicating that the metal(loid)s in tailings are mainly associated to secondary phases related to carbonates and iron/manganese forms that reduce the mobility and toxicity of these soluble phases. The plant accumulation results indicated that *Artemisia absinthium* can be considered as a suitable plant for phytoextraction of Cu, Zn and Sb in polluted areas, and *Phragmites australis* may be efficiently utilized for metal removal (mainly Cu) and, in any case, can also both be used for phytostabilization of contaminated sites. Finally, the human health risk assessment indicate a high potential of toxicity by accidental ingestion route for As, Sb and Pb. Special high risk was detected in the case of urban soils exposed to children (gardens or parks) and in agricultural soils. Therefore, the exposure of dust particles coming from the tailing dump could deposit variable amounts of potentially pollutant elements, increasing the human health risk to the population living in nearby areas. The main implication of this study is the recommendation of remediation actions to mitigate or prevent the risk of toxicity to the population close to the mining area.

Part III

Conclusions

CHAPTER 6. CONCLUSIONS

Chadak ore field is one of the main gold-producing sites in Uzbekistan. Abandoned and active tailing dumps with wastes enriched with metal(loid)s poses a potential pollution risk for this mining area and for populations living in the vicinity. As a result of this work following conclusions have been obtained:

1. The total concentrations of As, Sb, Zn, and Pb exceeded the background concentrations in wastes at the active tailing (AcT) dump and in soils at abandoned tailings dump (AbT). Waste deposits at AbT have very high concentrations of As (mean > 1030 mg/kg) and Sb (mean > 920 mg/kg), exceeding intervention threshold values by 20- and 62-fold, respectively.

2. Physico-chemical properties of soils and tailing samples showed a moderate critical load of pollutants related to the alkaline pH and calcium carbonate, low EC, CEC and OC. Due to the moderate presence of calcium carbonate in the tailings, the net neutralization potential indicates that the active tailing dump is potentially acid generating, while the abandoned tailing dump is not. This is directly related to a higher amount of sulfide minerals with high acid potential in the AcT in relation to the AbT dump.

   Mineralogical composition from selected soil and tailings materials obtained by XRD presented that samples were dominated by quartz, feldspars, calcite, micas and chlorite, and gives useful information in relation to the amount of neutralizing minerals (like calcite), although minerals bearing potentially pollutant elements are not detected by this technique. Otherwise, the results of the SEM-EDS analysis made on the tailings and open pit waste materials identified primary and secondary minerals consisting of sulfides, silicates and secondary precipitations of Fe and Mn oxyhydroxides. The presence of yukonite-like precipitation of Ca–Fe–As phases were also detected and could be related to potentially available forms of As.

3. The geochemical fractionation, made from single-extraction procedure, of trace elements in the tailing of the abandoned tailing dump shows differences in the mobility and availability of the main pollutants analyzed. Readily soluble or available forms were found for As and Sb, indicating a potential short-term dispersion of these pollutants to the surrounding areas. Otherwise, Zn, As and Pb presented a potential fraction that could be remobilised after acidification of the tailings, so long-term potential problems related to this process could be deduced.

   The influence of physico-chemical properties is a key factor controlling the mobility and availability of potentially pollutant elements. In this sense, metal(loid)s behavior is directly related to tailing oxidation processes involving acidification and weathering of $CaCO_3$. Moreover, the CEC and texture (clay fraction) were the main properties controlling the soluble-in- water concentration of pollutants in the tailing in the short-term; while iron oxides are responsible of the retention in the long-term of the most potentially toxic elements (like As and Sb).

4. The plant accumulation results indicated that *Artemisia absinthium* can be considered as a suitable plant for phytoextraction of Cu, Zn and Sb in polluted areas, and *Phragmites australis* may be efficiently utilized for metal removal (mainly Cu) and, in any case, can also both be used for phytostabilization of contaminated sites.

5. The toxicity bioassay using *Lactuca sativa* and *Vibrio fischeri* showed no risk of toxicity in the short-term. In this case, the tests were made with the soluble-in-water phase, indicating that the metal(loid)s in tailings are mainly associated to secondary phases related to carbonates and iron/manganese forms that reduce the mobility and toxicity of these soluble phases.

6. Finally, the human health risk assessment indicate a high potential of toxicity by accidental ingestion route for As, Sb and Pb. Special high risk was detected in the case of urban soils exposed to children (gardens or parks) and in agricultural soils. Therefore, the exposure of dust particles coming from the tailing dump

could deposit variable amounts of potentially pollutant elements, increasing the human health risk to the population living in nearby areas. The main implication of this study is the recommendation of remediation actions to mitigate or prevent the risk of toxicity to the population close to the mining area.

Part IV

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Trace metal(loid) mobility in waste deposits and soils around Chadak mining area, Uzbekistan

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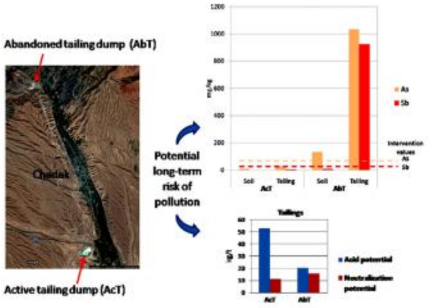
HIGHLIGHTS

- Total concentrations of As and Sb strongly exceed the intervention values in abandoned wastes.
- Selective extractions showed As and Sb with relatively high potential mobility.
- Zn and Pb mobility was controlled by cation exchange capacity of clay particles.
- Precipitation of Ca–Fe(III)–AsO_4 phases was first observed in Chadak mine wastes.
- Long-term pollution will be mainly controlled by tailing oxidations processes.

GRAPHICAL ABSTRACT



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ABSTRACT

The assessment of potential trace metal(loid) contamination in tailing dumps and soils was characterized in the Chadak mining area (Uzbekistan). Concentrations of trace elements (V, Cr, Co, Ni, Cu, Zn, As, Cd, Sb, Pb) were determined by X-ray fluorescence analysis and compared with background and intervention values (IV). The concentrations of As, Zn, Sb, and Pb were higher in the abandoned than in the active tailing dump, ranging from 42–1689 mg/kg for As, 73–332 mg/kg for Zn, 14–1507 mg/kg for Sb, and 27–386 mg/kg for Pb. Selective extractions were applied in order to assess the mobility and availability of trace metal(loid)s in samples. Oxyanion-forming elements such as As and Sb were immobilized by Fe oxides, although to some extent also extractable with acetic acid and soluble-in-water forms were detected, indicating potential bioavailability that can impose a potential toxicity risk for the environment. Selective extractions data also showed that Zn and Pb were relatively immobile, although in higher contamination sites significant amounts of these elements were also extractable with acetic acid. In tailing materials Zn and Pb mobility were negatively correlated by the cation-exchange capacity (CEC) and clay content, indicating the importance of these factors in the reduction of the potential toxicity for these elements. Total concentration of As, Sb, and Pb were also negatively correlated with soil pH, indicating that the oxidation process of sulphide tailings and thus the generation of acidic conditions may lead to release of contaminants over time. However, due to the calcium carbonate content, the acid neutralization capacity of the tailings is not yet exhausted and contaminant concentrations in soil-pore water are still relatively low. The results of our investigation suggest that environmental risk associated with these wastes in semi-arid climate is therefore not a short-term problem but rather requires constant monitoring and additional ecotoxicological studies.

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1. Introduction

The increase in mining activities in recent decades inevitably exerts a negative influence on the environment. The exploitation of mineral resources results in the production of large volumes of mining wastes containing metals or metalloids at elevated concentrations (Lottermoser, 2010). In particular, opencast mining activities may therefore have a negative environmental impact on soils and watersheds. Sulphide-rich minerals represent a major ore deposit for extracting metal(loid)s worldwide, generating millions of tonnes of tailings and acid mine drainage (Dudka and Adriano, 1997). The major concern of contamination of soil, sediments, and waters by trace metals is their toxicity and threat to human life and the environment (Nriagu et al., 2007).

Acid mine drainage (AMD) is one of the most serious environmental problems in sulphide mineralized areas, causing the solubilization and dispersion through the environment of trace metals and related toxic elements (Astrom, 1998). Most of the environmental-impact assessment and remediation efforts related to AMD generation have been focused on temperate climates, and few on mine sites exposed to semi-arid climates where AMD is not an immediate problem (Razo et al., 2004; Hayes et al., 2012). In these areas, the presence of soils with high buffering capacity is common, and when the AMD infiltrates the soil, the acidity is neutralized and most of the pollutants precipitate (Simón et al., 2005). In any case, although AMD generation in a semi-arid climate is not a short-term problem, the pollution can persist for thousands of years due to the slow time course of the processes related to oxidation, hydrolysis and acidification (Kempton and Atkins, 2000), which poses a long-term risk and even a chemical time-bomb for environment and human health.

Metal(loid)s are transferred to the environment via fly ash, dust, and leachates coming from point-source pollution such as mine quarries, dumps, and tailings (Shukurov et al., 2014; Martín et al., 2007), and may become a problem of diffuse pollution due to the widespread partitioning of these elements through the ecosystem (Martín et al., 2010). It is now widely recognized that the mobility and bioavailability of trace metals in soils depend not only on the total concentration, but also on their specific chemical form or binding state in relation to soil properties and constituents (Dang et al., 2002; Sauve et al., 2000; Nyamangara, 1998; Romero-Freire et al., 2014). However, changes in environmental conditions such as acidification, changes in the redox-potential conditions or increases in organic-ligand concentrations can result in trace-element mobilization from the solid to the liquid phase and cause contamination of surrounding waters (Gleyzes et al., 2002).

To assess the mobility and bioavailability of potentially polluting elements, several extraction schemes have been developed and described in the literature (Rauret et al., 1989; Kersten, 2001; Gleyzes et al., 2002; Quevauviller, 2002). These extraction schemes are based on operationally defined fractions that allow the assessment of distinct reagent-extractable forms (distilled water, single salts, acetic acid, complexing agents, etc.), which are usually defined as pool-extractable forms (soluble, exchangeable, carbonate associated, Fe/Mn oxide-associated, organics associated, residual, etc.). The most insoluble forms (extracted only by strong acids) are usually defined as residual forms (Beckett, 1989). In this way, a set of selective extraction techniques are used to determine the most leachable and thus potentially the most bioavailable compounds, while the total abundance of potentially harmful elements was determined by strong acid digestion (Anju and Banerjee, 2010). Despite the uncertainties associated with non-selectivity of the extractants, readsorption, and redistribution problems, extraction schemes remain widely used as an essential tool in element fractionation in soil and sediments (Kersten, 2001; Gleyzes et al., 2002).

The present study is focused on the Chadak mining area, one of the main gold-producing sites in Uzbekistan. The Chadak ore area has been known since antiquity and was in use up to the 12th century, with mining traces (abandoned open-pit mines and placer fields) preserved in the lower Chadak village and other surrounding areas. However, in the 12th and 13th centuries the mining activity declined and was revived only in the 20th century (Kuldashev and Abdurahmanov, 2009). In this study, the total concentration and distribution of metal(loid)s are determined in soils and waste deposits in and around the tailing dumps of Chadak mining area, and the mobility and potential bioavailability of the main contaminants by selective chemical extractions are assessed, with the aim of evaluating the potential risk of pollution as the first step in an environmental risk assessment of the area.

2. Materials and methods

2.1. Study area

Samples were collected from the vicinity of the Chadak ore field located in the Pap district of Namangan region at the southern slopes of the Kurama ridge in Chadak basin (eastern Uzbekistan, Fig. 1). Chadak ore field includes gold silver deposits (Pirmirab and Guzaksay) and a number of other exploitable minerals. The gold silver veins of the Chadak deposits are of low sulphidation type hosted by Carboniferous andesite volcanites and are associated with quartz-sericite-pyrite type alteration. The main gangue minerals are quartz (SiO_2), calcite ($CaCO_3$), adularia ($KAlSi_3O_8$), sericite ($KAl_2(AlSi_3O_{10})(OH)_2$), wollastonite ($CaSiO_3$), and tremolite ($Ca_2(Mg,Fe)_5Si_8O_{22}(OH)_2$). The main ore minerals are pyrite (FeS_2) and hematite (Fe_2O_3), but galena (PbS), chalcopyrite ($CuFeS_2$), and sphalerite (ZnS) are also common (Smirnova et al., 2009).

The area is characterized by a relatively well-developed mining industry, operated since 1970 by the Chadak gold-extracting plant (GEP) with the capacity of 180,000 t/y. The plant treats gold-bearing ore from the Pirmirab and Guzaksai deposits. Mining is conducted by both an underground and open-pit method, and two tailing dumps were established to store the waste from the mineral-extraction procedures. The first tailing dump, which operated from 1970 to 1979, is now abandoned (AbT), while a new tailing dump has been operating since 1979 and is still active (AcT). According to Filimonov (2009), the wastes stored in tailing dumps amount to as much as 3 Mt. The technological ore-extracting scheme includes: three-stage crushing, one-stage milling in a closed cycle with a two-stage ore classification and hydrocyclone overflow thickening; cyanidation of thickened product; filtration of gold-bearing solutions; precipitation of precious metals (Au and Ag) onto zinc dust; and drying of the zinc precipitates. The tailing waste products, after sterilization with liquid chlorine, are delivered to a dump for storage (Smirnova and Shamaev, 2012).

Production facilities of the mining group includes: mines, beneficiation plant, tailing dumps, and administrative-domestic premises. Two villages, Oltinkon and Chadak, are located on the banks of the Chadak-Sai river (Fig. 2A). Oltinkon is located close to the Chadak GEP and upstream from the abandoned tailing dump, while Chadak is located between the two tailing dumps. The river Chadak-Sai is the only source of water for mining processes, but also for residents of the villages on its banks.

2.2. Soil sampling and sample preparation

Samples were taken in a systematic pattern (100 × 100 m grid) from the upper soil layer (0–10 cm) around the two tailing dumps, and from the surface layer of both the abandoned (AbT, Fig. 2B) and active (AcT, Fig. 2C) tailing dumps. A vertical profile of 1.5 m deep was also sampled in the abandoned tailing dump (A: 0–30, B: 30–80, C: 80–150 cm). A total of 40 samples were collected from both areas. Samples were placed in polyethylene bags and transported to the laboratory for physico-chemical analyses. Samples were air-dried at room temperature, sieved through 2-mm mesh, ground, and homogenized in an agate mortar. Powder pellets for X-ray fluorescence analysis were prepared under a

Fig. 1. Location map of the study area.

pressure of 7 t with an epoxy-resin admixture in 30-mm dies by a hydraulic press (Herzog, Germany).

2.3. Chemical and mineralogical analysis

The main physico-chemical properties of the samples were measured by standard soil-analysis techniques (MAPA, 1994): the pH was measured by a pH-meter (CRISON digit 501) in a 1:2.5 (w/v) soil-water suspension; electrical conductivity (EC) was measured using a EUTECH XS Con 700 m in extracts prepared by filtering 1:10 soil-water suspensions through 0.45-μm cellulose acetate membrane filter; organic carbon (OC) was determined by wet oxidation method; cation-exchange capacity (CEC) was determined by 1 N sodium acetate solution at pH 8.2 measured by atomic absorption spectroscopy using a VARIAN SpectrAA 220FS instrument; particle-size distribution was determined by the pipette method; and calcium carbonate content was determined manometrically upon HCl digestion. The neutralization potential (NP) of tailing samples were evaluated with the modified Sobek acid-base accounting (ABA) method (Lawrence and Scheske, 1997). The acid potential (AP) and net neutralization potential (NNP) was calculated according to SRK (1989).

The total concentration of trace elements (V, Cr, Co, Ni, Cu, Zn, As, Cd, Pb, Sb) was measured using X-ray fluorescence (XRF) analysis of the powder pellets (MagiX Pro XRF with rhodium anode X-ray tube). The total concentration of major elements was determined by XRF using glass pellets of subsamples melted with lithium tetraborate fluxer (0.6:5.5). QA/QC criteria were fulfilled by the use of geochemical standard reference materials GSS-2 and GSS-4 (Table S1, Supporting Information); the experimental average values ranged within the certified reference values in both cases.

Selective extractions were applied to assess trace metal(loid) mobility in sieved samples (<2 mm) at the abandoned tailing dumpsite (AbT) with the following reagents: 1) distilled water (Sposito et al., 1982), 2) ammonium nitrate 1 M (DIN 19730, 1995), 3) acetic acid 0.43 M (Ure et al., 1993), and 4) oxalate buffer pH 3 (Schwertmann and Taylor, 1977). The total concentration of trace metal(loid)s was determined additionally by strong acid digestion (HNO_3/HF/HCl). All extracted fractions were analysed by inductively coupled plasma–mass spectrometry (ICP–MS) in a Perkin-Elmer Sciex-Elan 5000 instrument equipped with quartz torch, nickel sampler, and skimmer cones. Standard solutions were prepared from ICP single-element standard (Merck, Darmstadt, Germany) after appropriate dilution with 10% HNO_3. The accuracy of the method was evaluated by six replicate analyses of the certified reference material SRM 2711, average recoveries of the certified reference values ranged between 91% and 105% for the main pollutant elements (Martín Peinado et al., 2015).

Selected subsamples were prepared for scanning electron microscopy (SEM SUPRA40VP, ZEISS, Germany). The imaging was performed at an acceleration voltage of 30 kV in both conventional secondary electron and backscattered electron mode. For the elemental microanalysis of mineral particles, an energy-dispersive X-ray (EDX) spectrometer (model AZTEC 2.4, Oxford instruments, UK) was used in pinpoint

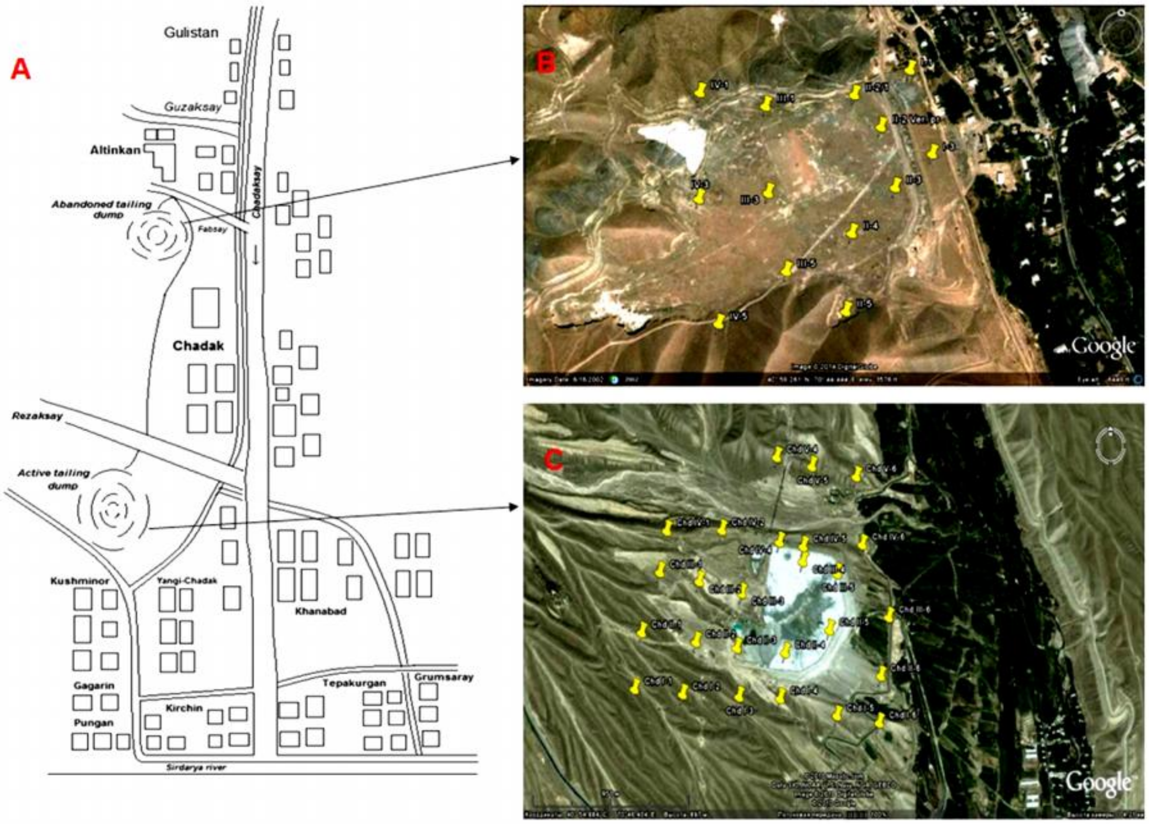

Fig. 2. Location of the samples collected. A: General view; B: abandoned tailing dump (AbT); C: active tailing dump (AcT).

mode (diameter 1 μm), resolution of 10 eV/channel, and a full-spectrum collection time of 100 s.

2.4. Statistical analyses

Geochemical background values of trace metal(loid)s for the study area were calculated from surrounding soil samples collected near the tailing dumps using mean (Mf) ± twice the standard deviation (σ) of the calculated distribution functions (Matschullat et al., 2000).

Statistical analyses of the data were carried out after evaluating the data set for normal distribution by a Kolmogorov-Smirnov test. Mean comparison study was made by one-way analysis of variance (ANOVA) and Tukey's test, where significant differences were considered when $p < 0.05$. The relationship between normally distributed variables was investigated using Varimax-rotation principal-component analysis (PCA). All statistical treatments were made using SPSS v.20.0 software.

3. Results and discussion

3.1. Soil properties

The general physico-chemical properties of soils and tailing samples are summarized in Table 1, and the properties of the vertical profile collected on AbT in Table 2. The pH values of soil samples collected in the vicinity of AcT and soils covering AbT showed mean values of 8.2 and 8.4, respectively. The moderately alkaline conditions are presumably related to the presence of carbonate minerals calcite, ankerite, and dolomite (Iavazzo et al., 2012), and can be also related to the arid climate in the study area. In any case, calcium carbonate content in soil and tailings was moderately low (mean values <15%), with minimum concentrations in tailings ranging from 2.9 to 4.2%. The presence of S was also detected in tailing samples, with values ranging from 1.70 to 0.45%. Therefore, the tailings possess a neutralization potential (NP) which can balanced with the acid potential (AP) assessed for a worst case from the total S content (neglecting the minor sulphate mineral content as a product of previous oxidation). The acid-base accounting (ABA) of tailings and concentrates are shown, respectively, in Tables 1 and 2. The acid potential (AP) of tailings for AbT is equal to 20.3 ± 4.6 kg $CaCO_3$/t, while for AcT it is 53.1 ± 7.8 kg $CaCO_3$/t; meanwhile the mean neutralization potential (NP) of the tailings amount to 15.5 ± 2.9 and 11.1 ± 2.7 kg $CaCO_3$/t, respectively. Thus, the net neutralization potential (NNP = NP - AP) indicates that the active tailing dump is potentially acid generating (NNP = −42.0 ± 6.5 kg/t), while the abandoned tailing dump is not (NNP = −4.8 ± 1.2 kg/t), according to the criteria defined by SRK (1989: NNP < −20 kg $CaCO_3$/t). In this sense, the acidification by sulphide oxidation in carbonate soils was previously reported in other semi-arid areas (García et al., 2009; Sánchez-Marañon et al., 2015), where soils with similar range in $CaCO_3$ (3.2–7.6%) and S (0.2–0.8%) showed a sharp decrease in pH from 7.4 to 3.1 after 10 years of continuous oxidation under natural conditions.

Soil samples from both areas showed very low EC values (SSDS, 1993), very low CEC (Marañes et al., 1998), sparse OC content, and a sandy-loam texture, with no significant differences between active and abandoned tailing dumps. Tailings at AcT, registered similar values to soil samples for pH, EC, and OC, but significant lower values for CEC

Table 1

Mean and standard deviations ($n = 3$) of general physicochemical properties of surface samples (0–10 cm) in the active (AcT) and abandoned (AbT) tailing dumps. Letters (a, b) indicate significant differences between samples ($p < 0.05$). EC: electrical conductivity; CEC: cation-exchange capacity; OC: organic carbon; AP: acid potential; NP: neutralization potential; NNP: net neutralization potential.

Area	Subarea	pH	EC	CEC	$CaCO_3$	OC	Clay	Silt	Sand	AP	NP	NNP
			(dS/m)	(cmol/kg)	(%)	(%)	(%)	(%)	(%)	kg/t		
AcT	Soil	8.2 ± 0.2 (a)	0.17 ± 0.04 (a)	10.4 ± 2.7 (a)	4.8 ± 2.6 (a)	1.07 ± 0.90 (a)	12.0 ± 1.6 (ab)	33.4 ± 0.3 (a)	53.1 ± 0.8 (a)			
	Tailing	8.3 ± 0.1 (a)	0.53 ± 0.05 (a)	2.6 ± 1.0 (b)	5.4 ± 1.7 (a)	0.83 ± 0.24 (a)	5.8 ± 0.6 (b)	22.9 ± 5.8 (a)	71.3 ± 6.4 (a)	53.1 (±7.8)	11.1 (±2.7)	−42.0 (±6.5)
AbT	Soil (cover)	8.4 ± 0.2 (a)	0.30 ± 0.44 (a)	7.9 ± 2.3 (ab)	10 ± 1.4 (ab)	0.66 ± 0.30 (a)	13.8 ± 2.9 (a)	35.9 ± 30.2 (a)	50.3 ± 28.6 (a)			

and clay content (Table 1), indicating a selection in the particle size towards the sand fraction and concomitant reduction in clay content that is directly related to the reduction in the CEC (Jung, 2008).

The comparison between tailings from vertical profile in AbT and active tailing dump (AcT) showed similar properties, with no significant differences in any of the main variables studied except $CaCO_3$, which showed significantly lower values from the A to C layers (Table 2).

3.2. Total trace metal(loid) concentrations

The mean total concentration of trace metal(loid)s in soils and tailings determined by XRF is shown in Table 3. The results were compared with the calculated background concentration (BC) of the soils in the area, and the intervention values (IV) reported by the Ministry of Environment of the Regional Government in Andalusia (Spain), based on a review of the intervention values in many countries worldwide (Aguilar et al., 1999) and the Dutch Target and Intervention Values (RIVM, 2000).

The mean concentrations of V, Cr, Co, Ni, Cu, and Cd in all surface samples (soils and tailings) were in the range of the background concentrations (BC) in the area. On the other hand, Zn, As, Sb, and Pb showed significantly higher mean concentrations (Table 3) both in tailings of AcT (exceeding 1.7-, 1.8-, 0.8-, and 2.8-fold the BC values, respectively), and in the covering soils of AbT (exceeding 1.5-, 8.8-, 1.8-, and 2.6- fold the BC values, respectively).

In the vertical profile of AbT, trace metals V, Cr, Co, and Ni presented significant differences although these values were in the range of BC (Table 3). Layer A had the highest concentrations of these elements, which decreased in the next two layers. On the other hand, concentrations of Cu, Zn, and Cd were slightly above the BC but below the intervention values (IV) and presented no significant differences along the vertical profile. The Pb concentrations in the vertical profile were higher than the BC (between 3.9- and 6.1-fold), but also below the IV. However, the mean values of Zn and Pb revealed an inverse trend in vertical distribution, showing the highest mean concentrations in the deepest C layer. High values of these elements in tailings could be attributed not only to the presence of sulphide and suphosalt minerals (pyrite, sphalerite, arsenopyrite, galena, and tetrahedrite) in ores of the Chadak deposits but also to the concentration related to the metal-extraction procedure in the mining activity of the Chadak ore field. The two elements with the highest concentrations in all three layers were As and Sb, with mean values strongly exceeding the IV (up to 20-fold for As, and 62-fold for Sb), with the highest concentrations in the surface A layer (1030 and 920 mg/kg, respectively). A comparison of these concentrations with the ecotoxicological threshold levels reported of 55 mg/kg for As (Van den Berg et al., 1993) and 60 mg/kg for Sb (Sheppard et al., 2005) indicate a high risk of pollution in the area. The problem is exacerbated by the fact that these wastes are located upstream of the main population area (Chadak city), which poses a serious potential pollution risk over time.

3.3. Chemical metal(loid) fractionation

Due to the elevated concentrations of As and Sb, and the relatively high concentrations of Zn and Pb in the samples analysed from the vertical profile in the abandoned tailing dump (AbT), mobility and availability were assessed by selective extractions (water, ammonium nitrate salt solution, acetic acid, and oxalic-oxalate bugger). The results of the selective extraction procedure are shown in Fig. 3. Generally, the water-extractable forms (Xx_w) constitute the readily soluble fraction (Sposito et al., 1982), forms extracted with ammonium nitrate salt solution (Xx_{am}) are associated with the easily exchangeable and potentially bioavailable fraction (DIN 19730, 1995), the acetic acid extracts (Xx_{ac}) represent the forms associated with carbonates and also cations specifically adsorbed by oxides as well as organic matter (Beckett, 1989), and the reducing oxalic-oxalate buffer form (Xx_{ox}) represents the metal(-loid) fraction adsorbed to amorphous or poorly crystallized iron or manganese oxides (Schwertmann and Taylor, 1977).

Statistically significant differences ($p < 0.05$) were found between the different selective extractions in the case of As, following the sequence $As_{ox} \geq As_T > As_{ac} > As_{am} = As_w$. Accordingly, most of the As (between 49.9–78.8% in relation to the total) was extracted by oxalic-oxalate buffer (As_{ox}) with the highest proportion in the C layer of the AbT profile. Oxalic-oxalate buffer is the reagent that extracts specifically the elements adsorbed and retained by the thus dissolved Fe-Mn oxides. The results are consistent with previous observations (Aguilar et al., 2006; Martín et al., 2011) which found that As in polluted soils is associated mainly with iron oxides. Iron oxide phases are therefore generally accepted as the primary sorption sites for arsenic in many soils and sediments (Sadiq, 1997). Fe-Mn oxides are also important scavengers of heavy metals in soils, particularly in the high pH range (Li and Thornton, 2001). The residual fraction (extracted only with strong acids) is not as high (below 24% of the total) except in the B layer (mean 36% of the total), presumably associated with the presence of arsenopyrite in the tailings. Extractions determined that 6.5–13.3% of the total arsenic (As_T) was extractable with acetic acid (As_{ac}) without

Table 2

Mean and standard deviations ($n = 3$) of general physicochemical properties of samples collected from vertical profile in the abandoned tailing dump (AbT). Letters (a, b) indicate significant differences between layers ($p < 0.05$). EC: electrical conductivity; CEC: cation-exchange capacity; OC: organic carbon; AP: acid potential; NP: neutralization potential; NNP: net neutralization potential.

Area	Profile	pH	EC	CEC	$CaCO_3$	OC	Clay	Silt	Sand	AP	NP	NNP
			(dS/m)	(cmol/kg)	(%)	(%)	(%)	(%)	(%)	kg/t		
AbT	A (0–30 cm)	8.1 ± 0.3 (a)	0.52 ± 0.57 (a)	6.1 ± 1.6 (a)	6.0 ± 2.5 (a)	0.37 ± 0.13 (a)	10.2 ± 2.5 (a)	25.7 ± 3.3 (a)	64.0 ± 0.8 (a)	20.3 (±4.6)	15.5 (±2.9)	−4.8 (±1.2)
	B (30–80 cm)	8.2 ± 0.1 (a)	0.68 ± 0.39 (a)	4.9 ± 0.1 (a)	8.2 ± 3.2 (ab)	0.15 ± 0.06 (a)	9.2 ± 1.2 (a)	31.6 ± 4.1 (a)	59.3 ± 5.3 (a)			
	C (80–150 cm)	8.6 ± 0.1 (a)	0.29 ± 0.17 (a)	3.7 ± 0.3 (a)	14.4 ± 0.6 (b)	0.12 ± 0.05 (a)	8.3 ± 1.1 (a)	38.8 ± 4.7 (a)	52.8 ± 5.8 (a)			

Table 3
Total element concentrations in mg/kg^{-1} (mean ± SD; $n = 3$) in the surface sampling (0–10 cm) at active (AcT) and abandoned (AbT) tailing dumps and in the vertical profile (AbT). Letters (a, b) indicate significant differences ($p < 0.05$); nd: not determined.

Area	Subarea	V	Cr	Co	Ni	Cu	Zn	As	Cd	Sb	Pb
AcT	Soil	85.0 ± 12.7 (a)	46.5 ± 2.1 (a)	10.5 ± 2.1 (ab)	25.0 ± 2.8 (ab)	24.5 ± 0.7 (a)	84.0 ± 1.4 (a)	10.5 ± 2.1 (a)	1.3 ± 0.7 (a)	0.0 ± 0.0 (a)	36.0 ± 0.0 (a)
	Tailing	62.7 ± 2.5 (abc)	13.6 ± 1.5 (b)	9.0 ± 3.0 (ab)	5.7 ± 1.5 (a)	37.0 ± 9.8 (a)	233.7 ± 98.6 (a)	27.5 ± 5.0 (a)	1.0 ± 1.8 (a)	3.3 ± 0.6 (a)	137.3 ± 68.6 (a)
AbT	Soil (cover)	81.7 ± 4.9 (ab)	30.8 ± 13.5 (ab)	12.2 ± 1.5 (a)	15.0 ± 6.4 (ab)	29.5 ± 9.4 (a)	215.7 ± 109.4 (a)	132.2 ± 71.1 (a)	1.1 ± 1.0 (a)	7.5 ± 5.8 (a)	126.5 ± 123.3 (a)
Profile (AbT)	A	89.7 ± 14.5 (a)	35.9 ± 13.9 (ab)	11.1 ± 0.3 (a)	26.3 ± 12.1 (b)	23.97 ± 0.1 (a)	207.8 ± 91.6 (a)	1032.6 ± 928.8 (a)	2.4 ± 1.9 (a)	924.0 ± 824.7 (a)	246.3 ± 198.2 (a)
	B	47.5 ± 26.2 (bc)	29.3 ± 1.4 (ab)	7.0 ± 1.0 (ab)	16.2 ± 5.4 (ab)	42.4 ± 27.6 (a)	201.9 ± 29.4 (a)	385.3 ± 405.7 (a)	1.5 ± 0.7 (a)	362.1 ± 257.2 (a)	191.5 ± 5.5 (a)
	C	27.6 ± 1.0 (c)	15.3 ± 0.4 (b)	4.7 ± 0.6 (b)	11.8 ± 1.0 (ab)	38.4 ± 3.4 (a)	229.7 ± 38.9 (a)	347.2 ± 144.8 (a)	1.5 ± 0.3 (a)	68.1 ± 18.2 (a)	293.1 ± 103.3 (a)
Background		131	51	19	31	37	135	15	1	4	48
Interv. value (S)[a]		–	450	300	300	500	1000	50	10	–	500
Interv. value (D)[b]		250	380	240	210	190	720	55	12	15	530

[a] Intervention value according to Ministry of Environment of the Board of Andalusia (Spain).

[b] Dutch Target and Intervention Values (The New Dutch List, 2000).

readsorption to other phases, whereas a negligible proportion (<2% of the total) was extracted by water (As_w) and ammonium nitrate (As_{am}). Low solubility and exchangeable potential of As measured by these extractants agree with the soil pH and the presence of carbonates (Rodrigues et al., 2010), and can be related by the incorporation of As into the lattice structure of calcite as arsenite under alkaline pH (Di Benedetto et al., 2006; Alexandratos et al., 2007). In our case, the precipitation of Ca–Fe(III)–AsO_4 phases was detected by SEM imaging (Fig. 4), indicating the possible presence of yukonite-like phases previously reported in oxidized As-bearing ores (Gomez et al., 2010) and in tailings of a gold-mining operation in Nova Scotia, Canada (Walker et al., 2009). Despite the low water-soluble ratios, concentrations of As_w (mean 4.34 mg soluble As per kg dry soil) far surpassed the critical level of 0.04 mg of soluble As per kg dry soil (Bohn et al., 1985), indicating a need for detailed ecotoxicological studies to prevent the risk of pollution to the environment and the nearby population.

As with As, statistically significant differences ($p < 0.05$) were found between the different selective extractions in the case of Zn, following the sequence $Zn_{ox} = Zn_T > Zn_{ac} > Zn_{am} = Zn_w$. The highest extraction of Zn was in C layer and associated with the Fe-Mn oxides (mean 45.4–57.7% in relation to the total Zn), while the residual fraction had a mean range between 13.2–35.8% with the highest amount in the A

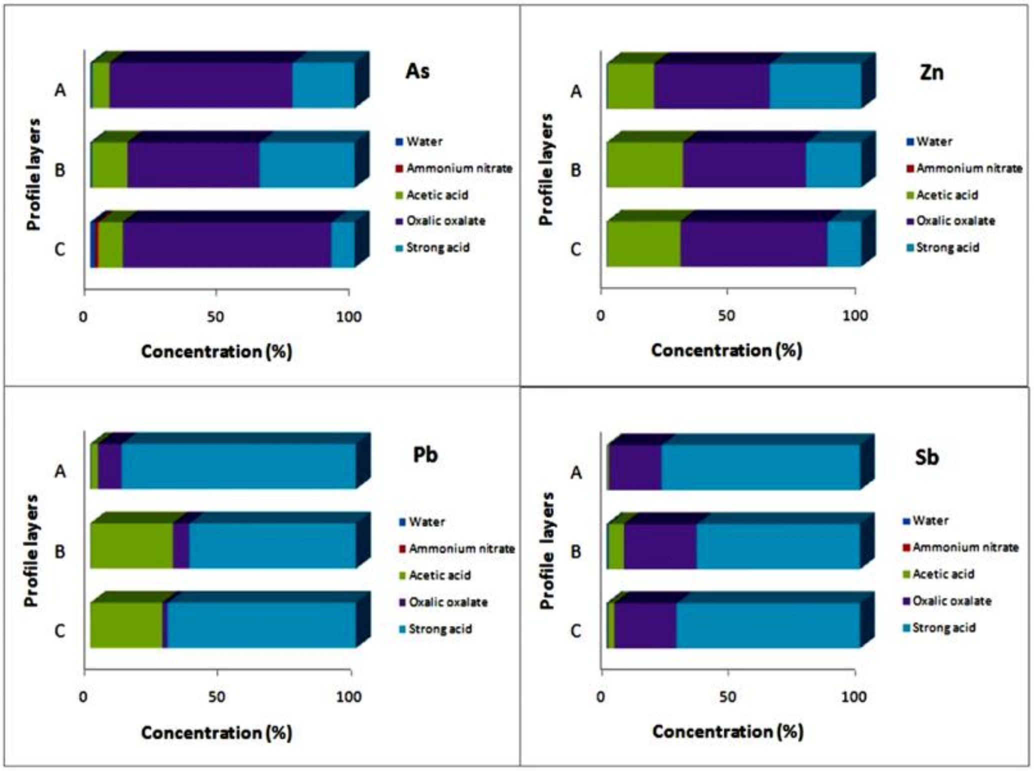

Fig. 3. Percentage of extracted metal(loid)s (mean values; $n = 3$) in relation to the total concentration in the different layers at the abandoned tailing dump.

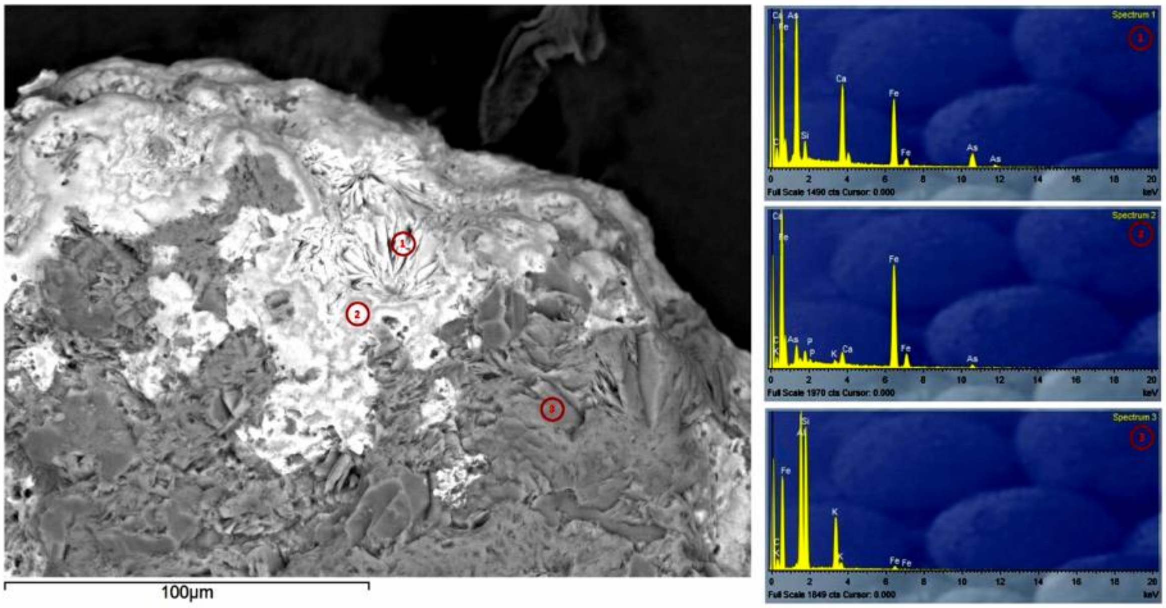

Fig. 4. Secondary precipitation of Ca–Fe(III)–AsO_4 phases (point 1) and amorphous Fe phases (point 2) on the surface of a grain of K-Fe alumino-silicate (point 3).

layer. These results agree with previous observations of Ashraf et al. (2012) and Li and Thornton (2001), who found that Zn was associated primarily with Fe/Mn oxides and the residual fraction. García et al. (2009) also stated that Zn may co-precipitate with oxides and hydroxides at high pH values. The next most abundant Zn fraction was that extracted with acetic acid (Zn_{ac}), which accounted for a mean range of between 18.2–29.7% in relation to the total Zn; this fraction, also called the exchangeable fraction, registered the same percentage, according to Marguí et al. (2004), but in other studies even far higher percentages have been reported (Iavazzo et al., 2012), depending on the soil properties such as the Fe/Mn content. The percentage of the water-soluble (Zn_w) and ammonium-nitrate-extracted (Zn_{am}) fractions were negligible (mean < 0.5% for Zn_w and below detection limit for Zn_{am}). However, the mean value of water concentration of 0.6 mg soluble Zn per kg dry soil was within the toxic range (0.5 mg soluble Zn per kg dry soil) in soil solution reported by Ewers (1991), indicating a potential risk of environmental pollution for this element.

In the case of Sb, statistically significant differences ($p < 0.05$) were found between the different selective extractions, following the sequence $Sb_T \geq Sb_{ox} > Sb_{ac} > Sb_{am} = Sb_w$. The highest concentration of Sb was in the residual fraction (mean 64.3–78.2% in relation to the total Sb), indicating that Sb is contained chiefly in the crystalline lattice of the secondary minerals. Wilson et al. (2010) reported that the residual Sb was up to 98% in mine-contaminated soils, but the relative proportion of Sb in this phase depends on the source (Tighe and Lockwood, 2007). The proportion of antimony extracted with oxalic-oxalate buffer (Sb_{ox}) was below 30% of the total Sb, slightly below the values of the same extraction phase reported by Tighe and Lockwood (2007), where 30–47% of the total Sb was associated with non-crystalline Fe and Al hydroxides. The acetic-acid-soluble fraction (Sb_{ac}) was low in relation to the total concentration (mean 0.7–5.9%), which coincides with the studies of He (2007) and Tighe and Lockwood (2007). The percentage of water-soluble (Sb_w) and ammonium-nitrate-extracted (Sb_{am}) in relation to the total Sb concentrations were very low (mean < 1%). Although Sb is generally described as a geochemically immobile element, its solubility depends on soil properties (Evangelou et al., 2012) and the rise of soil pH can inhibit Sb sorption to soil Fe and Al oxy-hydroxides, increasing the Sb in soil-solution phase (Nakamaru et al., 2006).

Pb also presented statistically significant differences ($p < 0.05$) between the different selective extractions, following the sequence $Pb_T > Pb_{ac} = Pb_{ox} > As_{am} = As_w$, indicating that this element was also associated mainly with the residual fraction (mean 70.9–88.2% in relation to the total Pb), containing the highest amount in the A layer. This agrees with the observations of Ashraf et al. (2012) and Ramirez et al. (2005), who reported that Pb is associated mostly with the residual phase. Pb associated with acetic acid-soluble fraction (Pb_{ac}) accounted for mean 2.5–30.9% followed by a minor amount of oxalic-oxalate buffer-extractable fraction (mean 1.9–8.8% of the total). In this case, Pb is considered to be bound to carbonates and related to weathered (oxidized) precipitates from old tailing waste materials (Anju and Banerjee, 2010). The least abundant proportion of Pb was found in water-soluble (Pb_w mean < 0.5%) and ammonium-nitrate-extracted (Pb_{am} below the detection limit) fractions in relation to the total concentrations, with similar results as those observed by other authors (Ramos et al., 1994; Maiz et al., 2000). In any case, the Pb_w concentrations did not exceed the toxic level in the soil solution (1 mg/kg) reported by Ewers (1991).

3.4. Correlation between tailing properties and metal(loid)s

Table 4 presents the correlation between the tailing properties and the total forms of metal(loid)s and forms that are water soluble and extractable by ammonium nitrate, acetic acid, and oxalic oxalate buffer. The results for arsenic indicate that As_T together with As_{ac} and As_{ox} showed a significant ($p < 0.05$) negative correlation with pH, indicating that for this type of pollution involving the release of sulphide tailings, their oxidation and hence acidification processes are related to the increase in total pollution by the generation of acidic conditions that lead to a release of contaminants (Romero-Freire et al., 2015; Simón et al., 2001). Significant correlation of As_{ac} and As_{ox} was found with OC in our samples. The effect of organic carbon to arsenic mobility is controversial. In some studies the application of organic matter reduced the As mobility (Gadepalle et al., 2007), whereas in others As is

Table 4

Pearson correlation between total (T), water soluble (w), ammonium nitrate (am), acetic acid (ac) and oxalic oxalate (ox) extracted forms of As, Sb, Zn, Pb and tailing properties in the vertical profile of the abandoned tailing dump.

	AsT	As w	As am	As ac	As ox	SbT	Sb w	Sb am	Sb ac	Sb ox	ZnT	Zn w	Zn am	Zn ac	Zn ox	PbT	Pb w	Pb am	Pb ac	Pb ox
pH	−0.567^{a}			−0.893^{a}	−0.903^{a}	−0.650^{a}				−0.900^{a}						−0.595^{a}				−0.952^{b}
EC											0.575^{a}									
CEC											−0.818^{b}					−0.583^{a}	0.724^{a}			
$CaCO_3$																			0.814^{a}	
OC	−0.550^{a}			0.880^{a}	0.899^{a}	−0.688^{b}				0.894^{a}										0.881^{a}
Clay											−0.602^{a}					−0.601^{a}				
Silt			0.870^{a}																	
Sand			−0.903^{a}																	

[a] Correlation is significant at the 0.05 level (2-tailed).

[b] Correlation is significant at the 0.01 level (2-tailed).

mobilized after compost application and by phytoremediation due to the competing effect of organic matter with arsenate for adsorbing surface sites (Clemente et al., 2008; Martín et al., 2011). No correlation in relation to tailing properties was found for the As_w, whereas a significant positive correlation was found for As_{am} with silt fraction and a significant negative correlation with sand. Simón et al. (2001) showed that there was a strong positive correlation between arsenic levels and the fine-silt fraction of the sludge due to the enhanced specific surface available for As exchange.

In relation to the tailing properties, total (Sb_T) and oxalic-oxalate buffer (Sb_{ox}) showed similar behavior with As, presenting significant negative correlation with pH and OC. The oxyanion-forming metalloids As and Sb have comparable geochemical activity (Fu et al., 2016; Wilson et al., 2010). However, the understanding of Sb toxicity and environmental activity is limited (Filella et al., 2002). The other extracted forms of the Sb did not present any correlation with tailing properties, suggesting that these parameters do not control the partitioning of this metalloid.

By contrast, the correlation of tailing properties and Zn_T showed significant positive correlation with electrical conductivity, indicating that Zn is strongly related to the soluble salts produced after the oxidation reactions (Romero-Freire et al., 2015). On the other hand, Zn_T negatively correlated with CEC and clay fraction, suggesting that these tailing properties also affect Zn activity. This is consistent with the data in the literature indicating also that clay and soil hydroxides can strongly adsorb Zn especially under alkaline conditions (Vandana et al., 2011). No significant correlation was found for other Zn extractions.

Total concentrations of Pb were significantly and negatively correlated with pH, as well as with CEC and the clay fraction, indicating that alkaline pH, CEC, and the clay fraction were the main factors controlling the mobility of lead. As pH rises, Pb becomes less soluble under oxidizing conditions (Vandana et al., 2011) due to the formation of insoluble salts mainly under the presence of carbonates (Razo et al., 2004). The water-soluble form (Pb_w) was not related to any of the soil properties except for the CEC, with a significant and positive correlation, indicating the favourable effect of the adsorption processes for the retention of Pb. Acetic acid extractable Pb (Pb_{ac}) presented a significant correlation with $CaCO_3$ concentrations, while the proportion extracted by oxalic-oxalate buffer (Pb_{ox}) significantly correlated with OC, indicating also a major contribution of OC in retaining Pb.

The mobility and potential toxicity were assessed in relation to physico-chemical properties of the tailings, using a principal-component analysis between total and soluble concentrations of the main pollutants and the tailing properties (Table 5). Three components explained 91.6% of the variance, with Component 1 being the one that included the total concentrations of metal(loid)s directly related to EC and inversely related to pH and $CaCO_3$, indicating that the pollution is controlled fundamentally by tailing oxidation processes involving acidification, weathering of $CaCO_3$, and increase in soluble salts (Simón et al., 2001). Component 2 includes the total concentrations of Zn and Pb inversely related to Zn_w and Pb_w forms, indicating that the soluble forms of these elements are not controlled by their total concentrations, but rather that the CEC and texture (clay fraction) were the main properties affecting the water concentration of these elements in the soil solution (Kumpiene et al., 2008). Component 3, explaining the 20.9% of the variance, includes As_w and Sb_w forms inversely related to each other, indicating a contrasting relation between the two elements (Mitsunobu et al., 2006) and a strong influence of carbonates usually found in the silt fraction on the activity of the soluble forms of these elements, as reported by Martínez-Lladó et al. (2011).

The mobilization of pollutants in soils and tailings is strongly controlled by the presence of calcium carbonate and sulphide minerals. Our results indicate that the net neutralization potential (NNP) for the active tailing dump (AcT) potentially generates acid, so that long-term oxidation processes pose a potential hazard to the environment. In this sense, soils contaminated by heavy metals after sulfur oxidation are usually amended with calcium carbonate, but in some cases the amount of $CaCO_3$ required to neutralize acidity is underestimated. Long-term acidification over time was described after the liming of a soil polluted with heavy metals and small amounts of S ($\approx$0.5%) (McTee et al., 2017), the formation of coatings around calcium carbonate grains being one of the main processes responsible for this underestimation and for the progress of acidification over time (Simón et al., 2005). Moreover, the transfer of heavy metals to plants in carbonate soils contaminated by mine tailings with high concentrations in heavy metals were reported in relation to local acidification and/or oxidation processes occurring in the rhizosphere (Boussen et al., 2013). Our data indicate that there is a potential risk of acidification and, therefore, of

Table 5

Principal-component analysis between total (XxT) and soluble in water (Xx_W) pollutant concentrations and main properties of the tailings.

	Rotated component		
	1	2	3
ZnT	0.504	−0.785	
AsT	0.950		
SbT	0.953		
PbT	0.515	−0.738	
Zn_w		0.960	
As_w			0.940
Sb_W			−0.858
Pb_W		0.948	
pH	−0.862		
EC	0.751		
CEC		0.902	
$CaCO_3$	−0.849		
OC	0.951		
Clay		0.879	
Silt		−0.685	0.632
Sand			−0.754
% cum. var.	35.4	70.7	91.6

Rotation method: Varimax with Kaiser Normalization. % cum. var.: Percentage of cumulative variance.

pollutant dispersion over time in the Chadak mining area that should be monitored and assessed with additional studies.

4. Conclusion

Chadak ore field is one of the main gold-producing sites in Uzbekistan. Abandoned and active tailing dumps with wastes enriched with metal(loid)s poses a potential pollution risk for this mining area and for populations living in the vicinity. Our data indicate that the total concentrations of As, Sb, Zn, and Pb exceeded the background concentrations in wastes at the active tailing (AcT) dump and in soils at abandoned tailings dump (AbT). Waste deposits at AbT have very high concentrations of As (mean > 1030 mg/kg) and Sb (mean > 920 mg/kg), exceeding intervention threshold values by 20- and 62-fold, respectively. Selective extractions were made to assess the potential mobility and bioavailability of the pollutants both in wastes and in soils. Selective extraction results showed that As and Sb were strongly retained by iron oxides, but still with increased potential bioavailability (extractable with acetic acid); higher water-soluble and ammonium nitrate concentrations were also measured for both elements, indicating a potential toxicity risk for the environment. On the other hand, the selective extraction data showed that Zn and Pb were relatively immobile in the tailings, although in some cases large amounts of these elements were extracted with acetic acid, indicating a potential bioavailability once the neutralization potential is exceeded. However, a balance between the acid potential of the tailings and the neutralization potential indicate that the active tailing dump (AcT) is potentially acid generating, constituting a long-term hazard to the environment. Thus, more studies are required in the area for toxicity assessments using bioassays and for evaluations of the potential long-term risk of pollution in this area.

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Annexes

Annex A. Total concentration of trace elements in soils and tailing material

Area	Subarea	Sc	V	Cr	Co	Ni	Cu	Zn	Ga	Rb	Sr	Y	Zr	Nb	Cs	Ba	W	As	Mo	Cd	Sb	Pb	Bi	Th	U
Active tailing dump	natural soil	9	94	48	12	27	24	85	16	146	228	25	192	17	5	830	2	12	1.5	1.8	0	36	2	15.2	3.4
		9	76	45	9	23	25	83	16	147	222	24	181	14	6	827	0	9	0.5	0.8	0	36	1	16.3	4.9
	tailing material	8	60	14	9	4	48	347	10	134	148	9	87	6	10	688	15	27	5.2	3.1	3	212	4	5.4	3.2
		8	63	12	6	6	29	168	10	147	162	12	87	6	3	831	6	22	2.8	0	4	123	2	4.4	2.3
		7	65	15	12	7	34	186	11	138	150	10	85	5	5	776	14	32	2.6	0	3	77	2	4.8	2.7
Old tailing dump	tailing surface soil	9	75	29	10	14	20	200	15	159	179	22	159	16	11	957	8	179	2.6	0	8	54	3	13.9	4.6
		10	85	25	13	13	31	258	17	160	177	20	153	14	10	1097	11	198	6.9	1.5	14	301	8	9.3	4.6
		10	86	50	13	24	32	73	17	148	192	24	157	16	7	784	5	42	1.3	0.6	0	27	2	14.6	4.9
		10	81	19	13	9	49	332	14	165	163	13	85	7	14	795	15	110	8.9	2.5	8	124	4	6.7	4
Vertical profile in old tailing dump 1.5m depth	tailing material	11	128	44	12	34	25	318	20	143	213	31	228	29	2	2462	26	2524	4.1	4.3	177	287	31	11.4	5.6
		11	136	45	12	40	23	343	19	134	203	33	244	37	6	3149	34	3371	5.4	4.8	217	319	42	10.5	4.8
		8	52	19	9	10	30	369	11	144	178	13	98	10	6	1085	16	518	3.5	1.8	43	295	11	8.8	3.2
		5	32	13	7	6	70	202	9	131	140	9	75	6	7	761	0	144	2.3	0	28	234	7	6.5	3.3
		7	39	23	8	10	50	310	10	126	190	11	81	8	3	878	7	575	2	0.8	4	409	13	3.2	3.4
		8	57	27	7	12	43	221	11	136	201	13	89	8	6	914	13	544	3.4	0.2	14	247	10	8.2	3.9

Annex B. Total concentration of trace elements in Guzaksay open pit area and chadaksay river sediments

Area		Sc	V	Cr	Co	Ni	Cu	Zn	Ga	Rb	Sr	Y	Zr	Nb	Cs	Ba	W	As	Mo	Cd	Sb	Pb	Bi	Th	U
Open pit area	natural soil	18	187	35	35	26	59	117	21	225	176	27	148	12	25	1040	5	24	1	2.1	3	55	1	11.5	5.1
		19	187	48	30	30	54	138	22	216	250	30	164	13	14	1135	6	16	1.9	0.6	0	46	1	9.5	3
		10	96	25	13	15	24	94	18	158	168	23	185	16	14	1086	3	15	1.4	0.9	0	34	1	12.9	4.4
		12	137	30	12	16	37	92	23	117	287	19	179	14	9	1580	1	8	1.5	1.9	0	18	0	8.5	2.9
		12	122	23	20	11	31	115	17	204	166	18	131	10	21	965	5	141	3.9	0.1	3	65	3	11.2	4.5
		10	91	27	16	14	28	94	17	180	153	25	181	14	14	958	2	26	1.6	0	1	40	1	13.1	4.4
	Open pit dump	23	223	28	46	20	34	107	23	165	163	25	139	10	17	1223	5	11	1.3	0.7	1	33	2	6.4	2.7
		6	41	10	9	7	22	34	15	219	71	17	124	13	24	1404	4	12	1.4	0.4	5	36	1	34.7	10.9
		13	125	23	24	13	26	99	18	197	162	18	129	9	18	925	7	117	3.3	1.3	0	49	2	10.2	5.2
		11	119	36	23	17	188	131	15	184	307	18	145	9	11	1391	122	35	7	1.2	0	40	2	11.5	4.3
		11	124	24	13	14	33	195	21	262	131	21	135	11	29	1121	7	44	2.5	1.2	3	67	2	15.4	4.5
		13	120	22	21	11	144	66	16	214	238	17	136	9	14	1141	9	93	11.4	1.3	1	61	8	13.5	5.4
River sediment	Sediment	6	45	12	6	5	25	66	15	174	262	15	116	12	10	888	2	6	1.4	0.5	0	34	2	19.4	4.7
		9	70	22	11	12	47	101	17	185	225	22	207	16	10	774	6	9	3.6	0	1	56	3	26.9	7.5
		5	48	12	8	5	27	73	14	177	259	16	139	13	5	929	4	7	2.2	0	0	45		19.7	5.1
		7	60	20	7	9	33	94	16	177	237	19	221	15	12	866	3	9	2.1	0	0	59		24.5	6.8

Annex C. SEM-EDS imaging made on the tailings and open pit waste materials (Figures: 14-23).

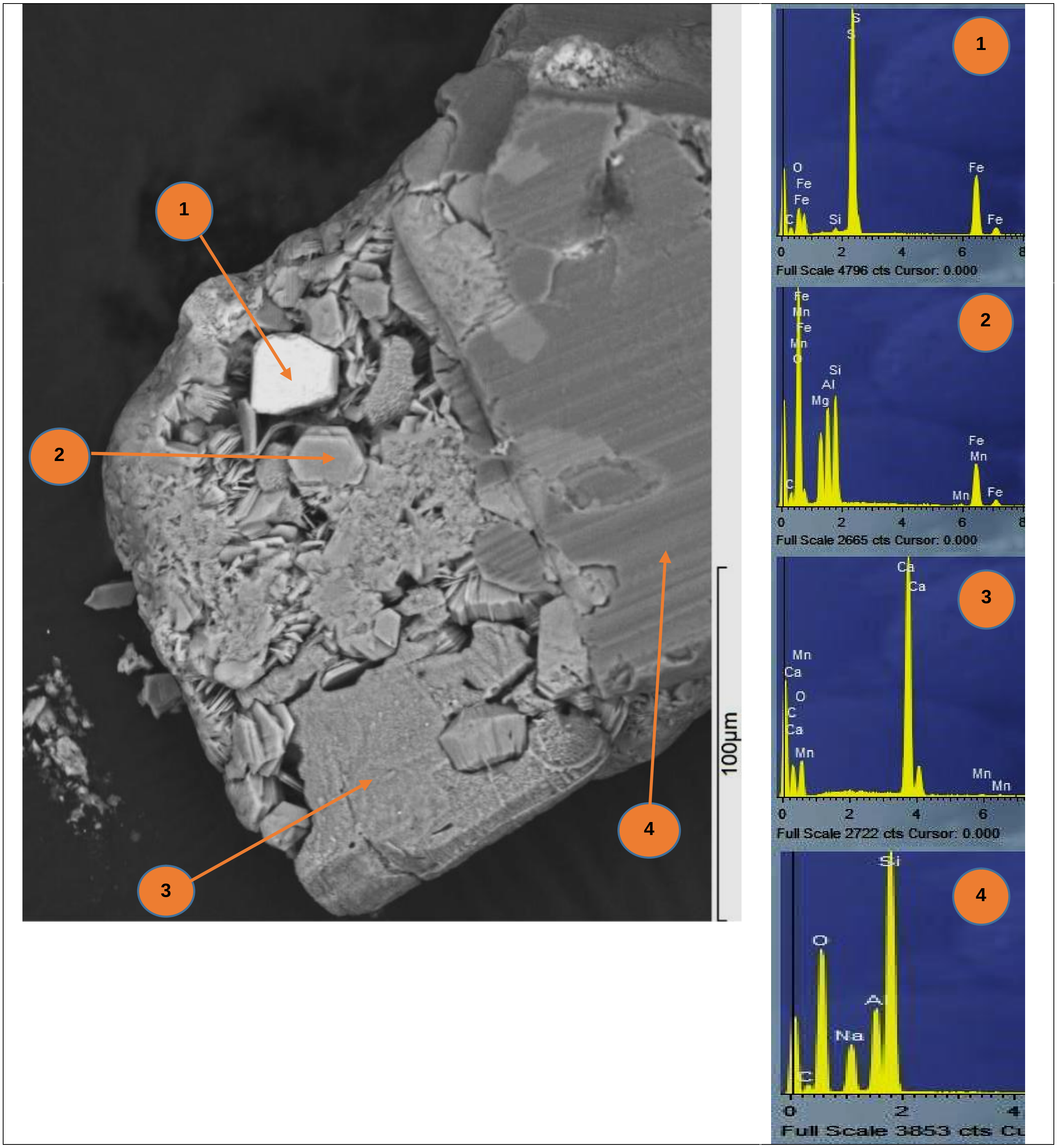

Figure 14. Microphotography by SEM of tailing material from AcT: 1 – pyrite; 2 – clinochlore; 3 – calcite; 4 - albite

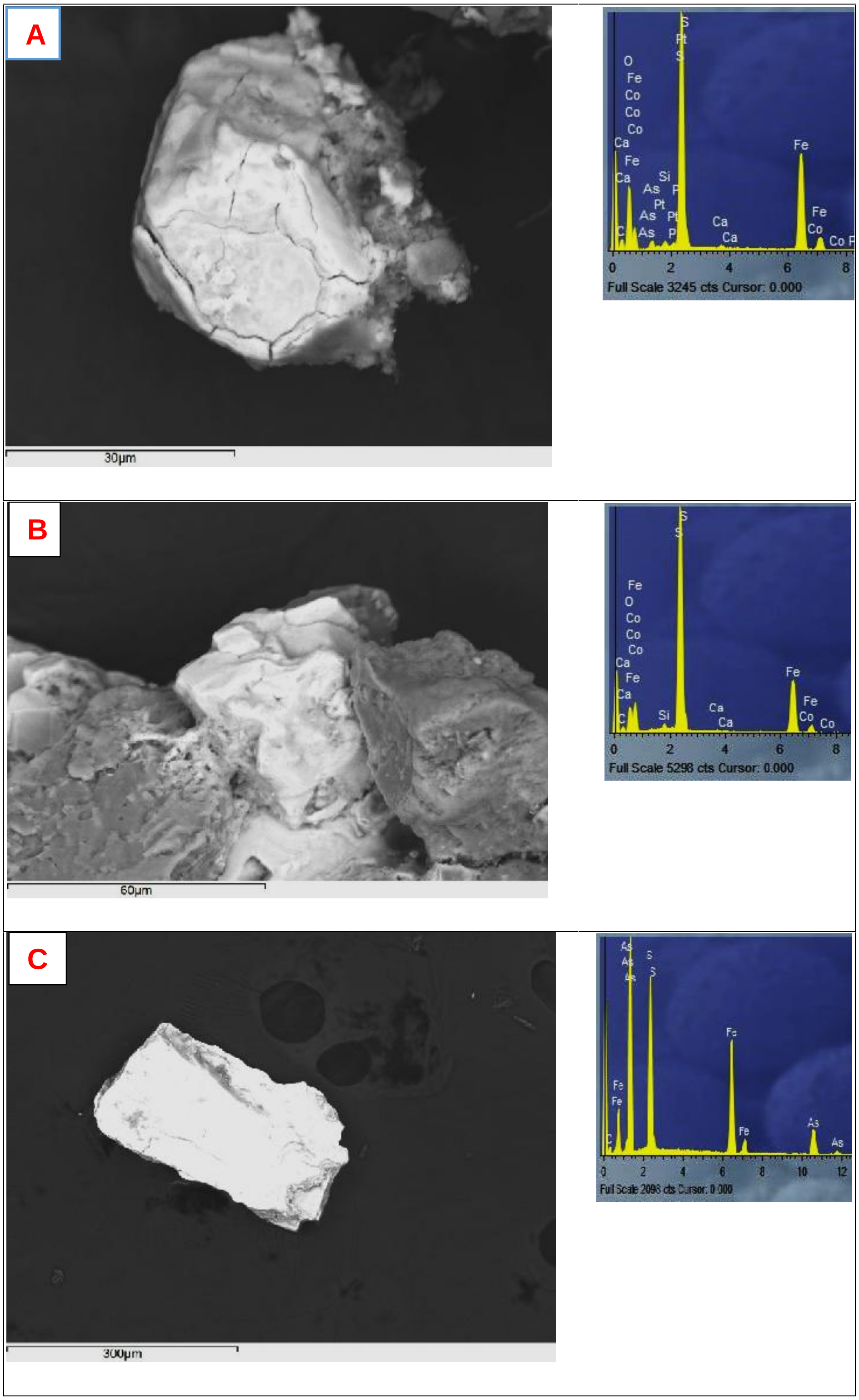

Figure 15. Microphotography by SEM of tailing material from vertical profile of AbT: A – oxidized pyrite; B – oxidized pyrite; C - arsenopyrite

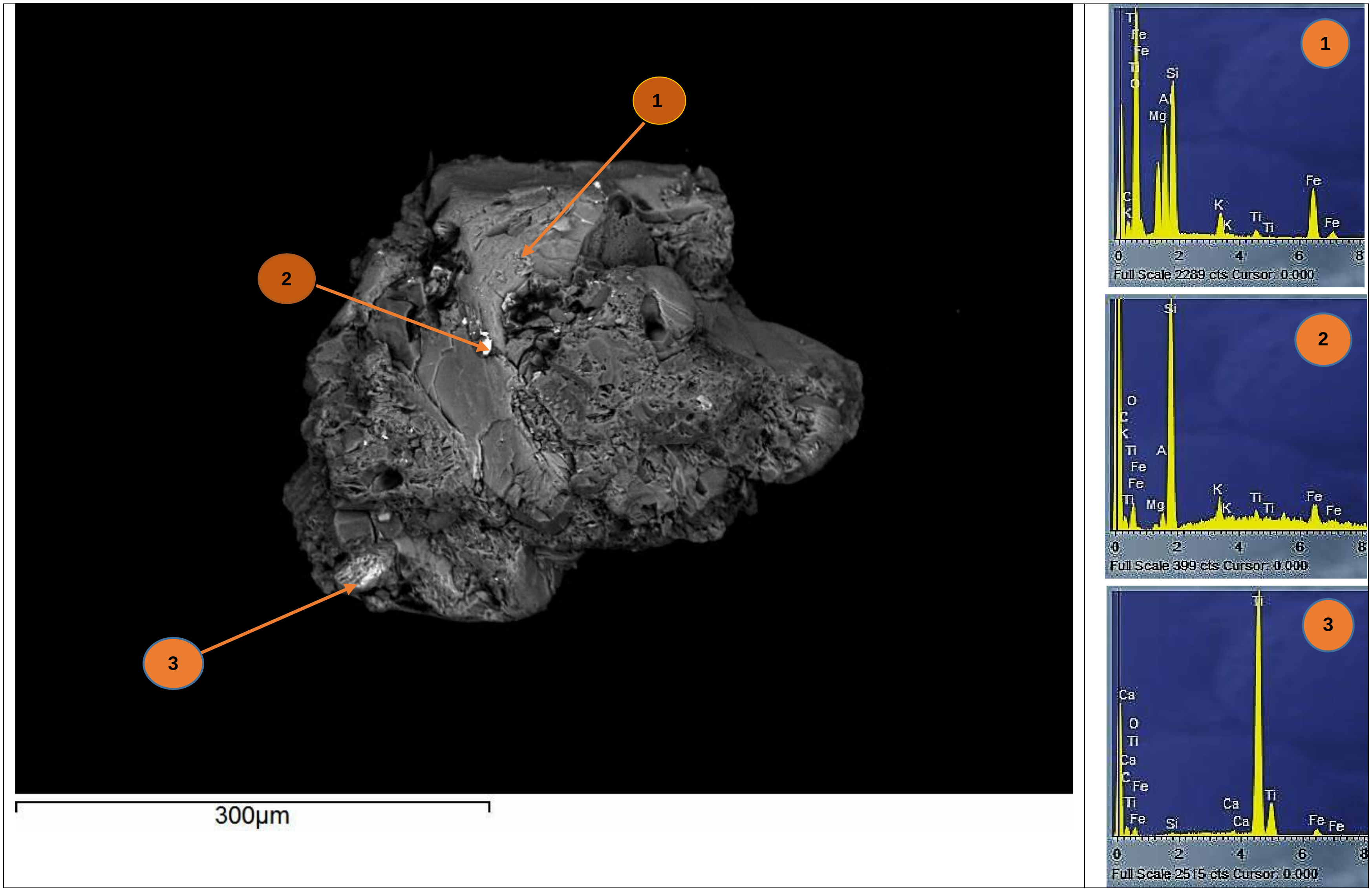

Figure 16. Microphotography by SEM of tailing material from vertical profile of AbT: 1 – mica, 2 – quartz, 3 – rutile

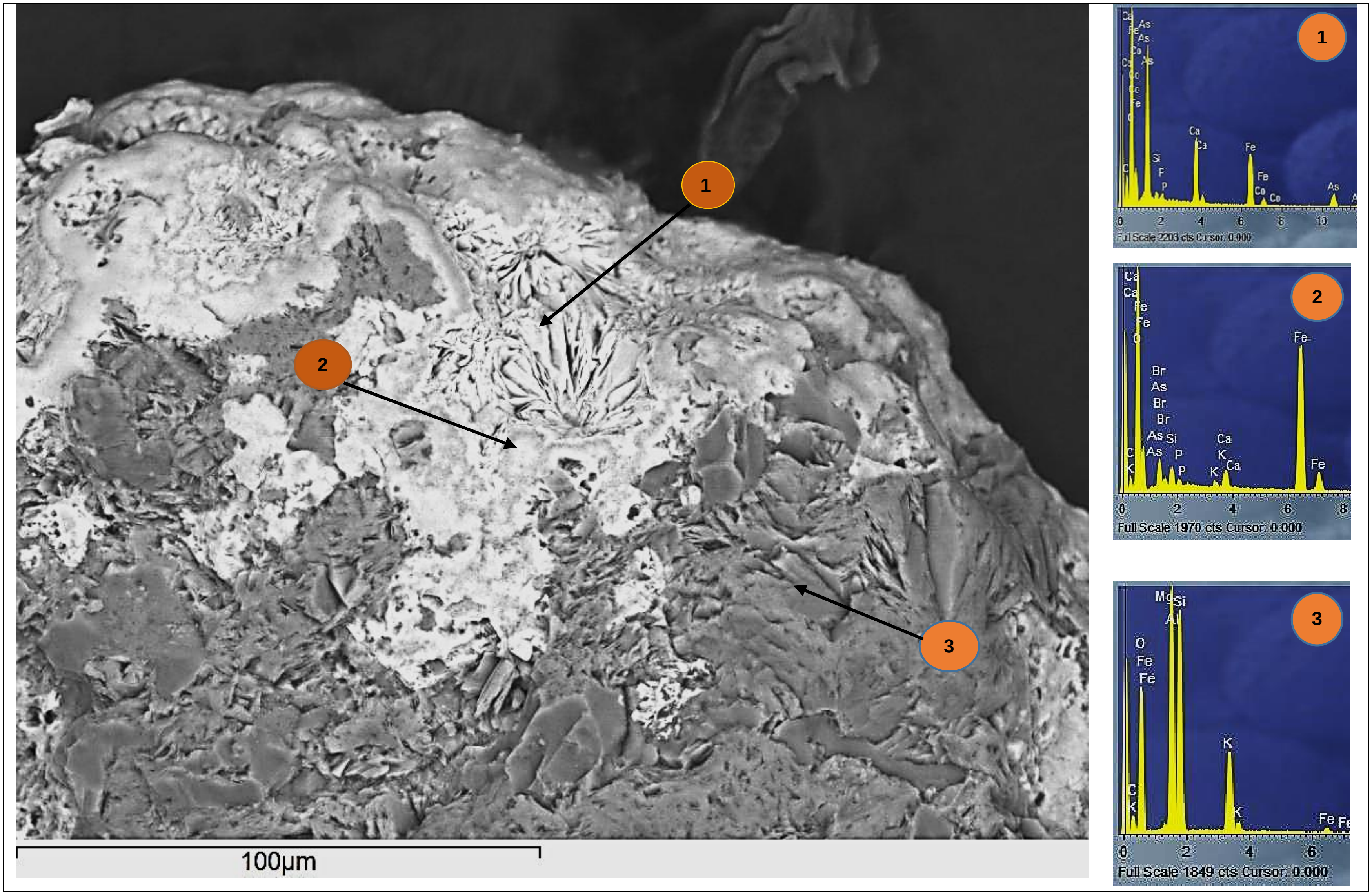

Figure 17. Microphotography by SEM of tailing material from vertical profile of AbT: 1 – yukonite like phases; 2 – secondary precipitation of Fe with accompanying Ca, K and P; 3 – biotite

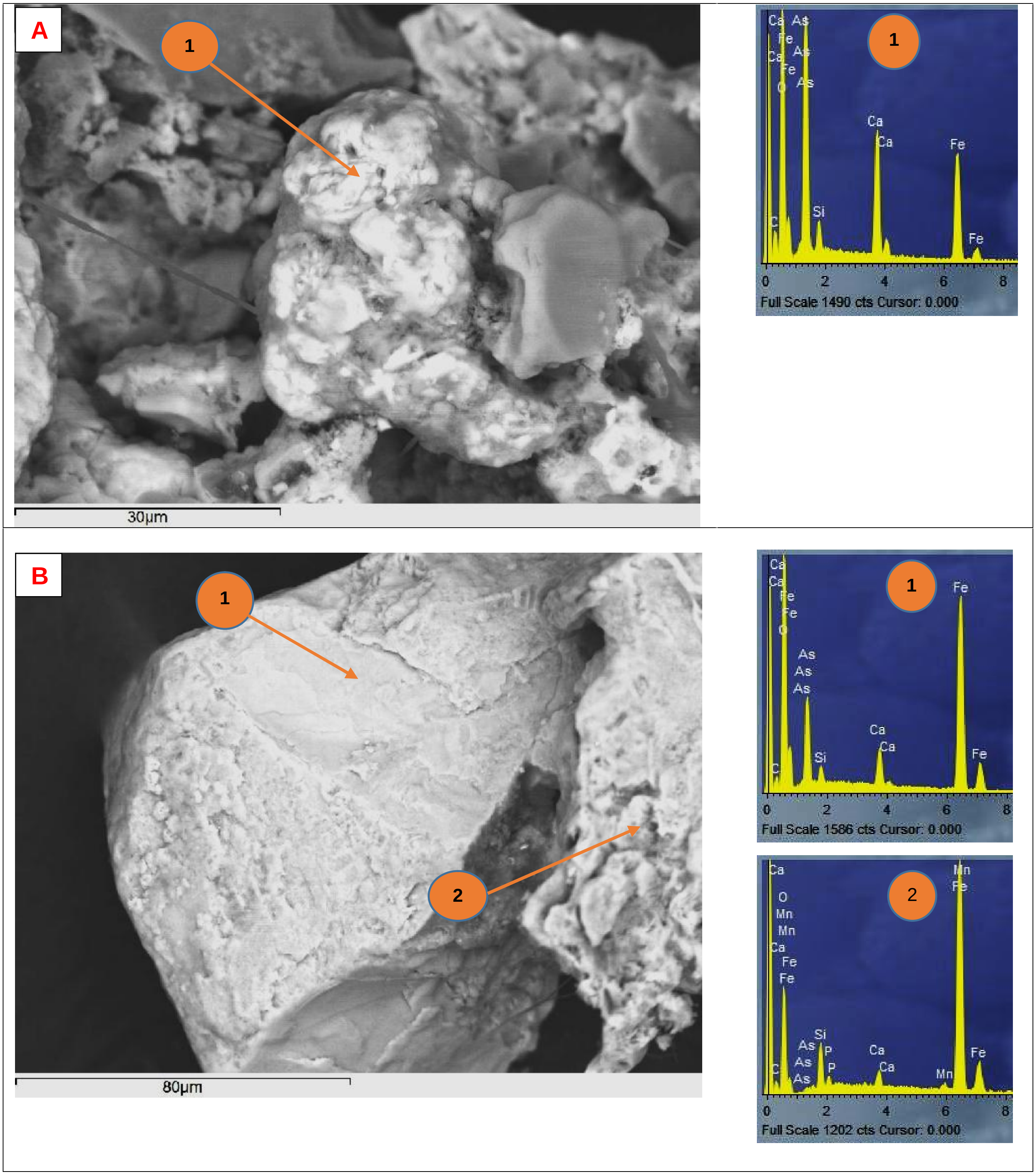

Figure 18. Microphotography by SEM of tailing material from vertical profile of AbT: A (1 – yukonite like phases; B (1- arsenosiderite like mineral, 2- secondary precipitation of Fe and Mn with accompanying Si, Ca, P and As)

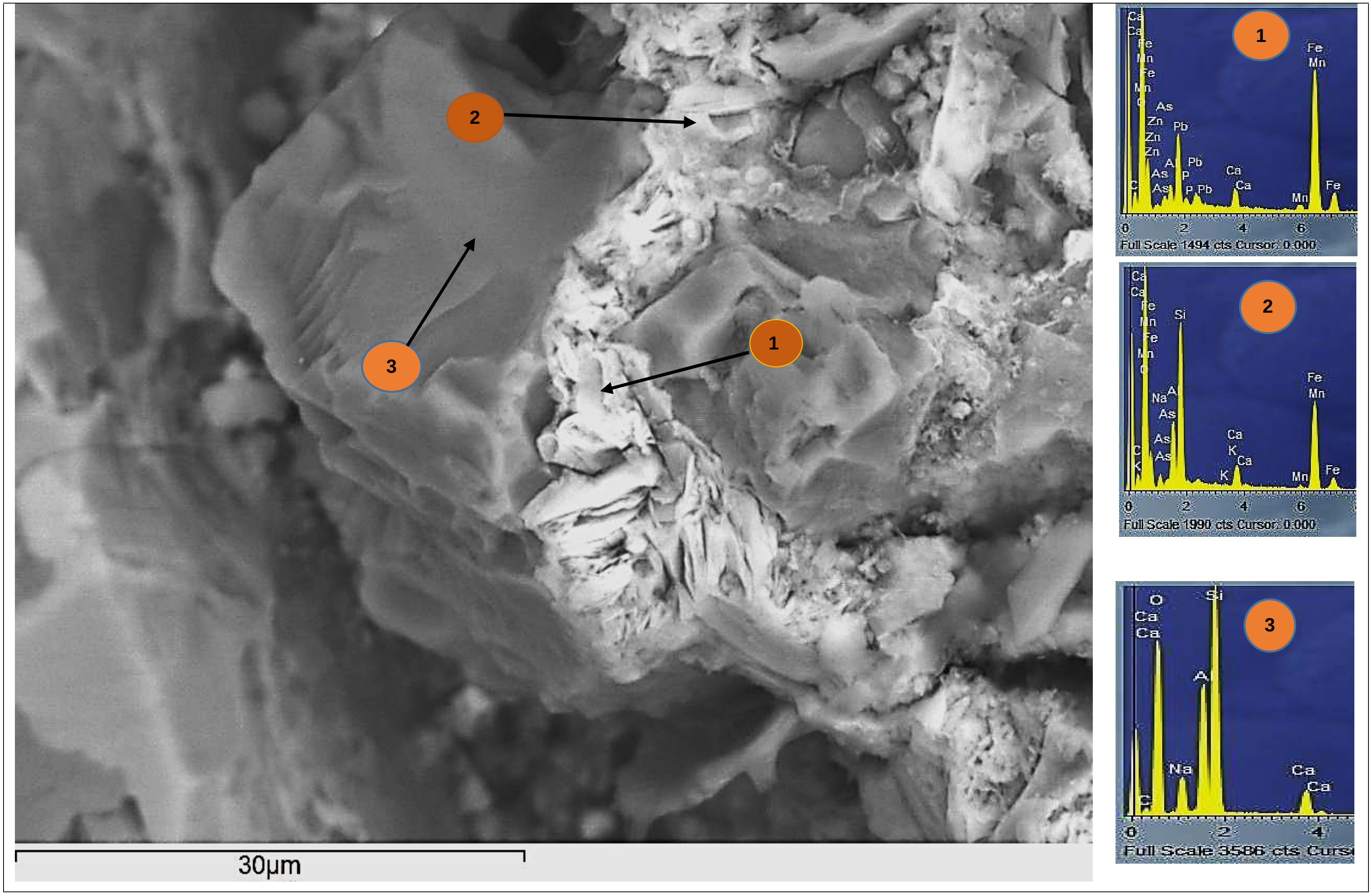

Figure 19. Microphotography by SEM of tailing material from vertical profile of AbT: 1 – magnetoplumbite; 2 – secondary precipitation of Si, Fe and Mn with accompanying of Ca, K Na and As; 3 – plagioclase

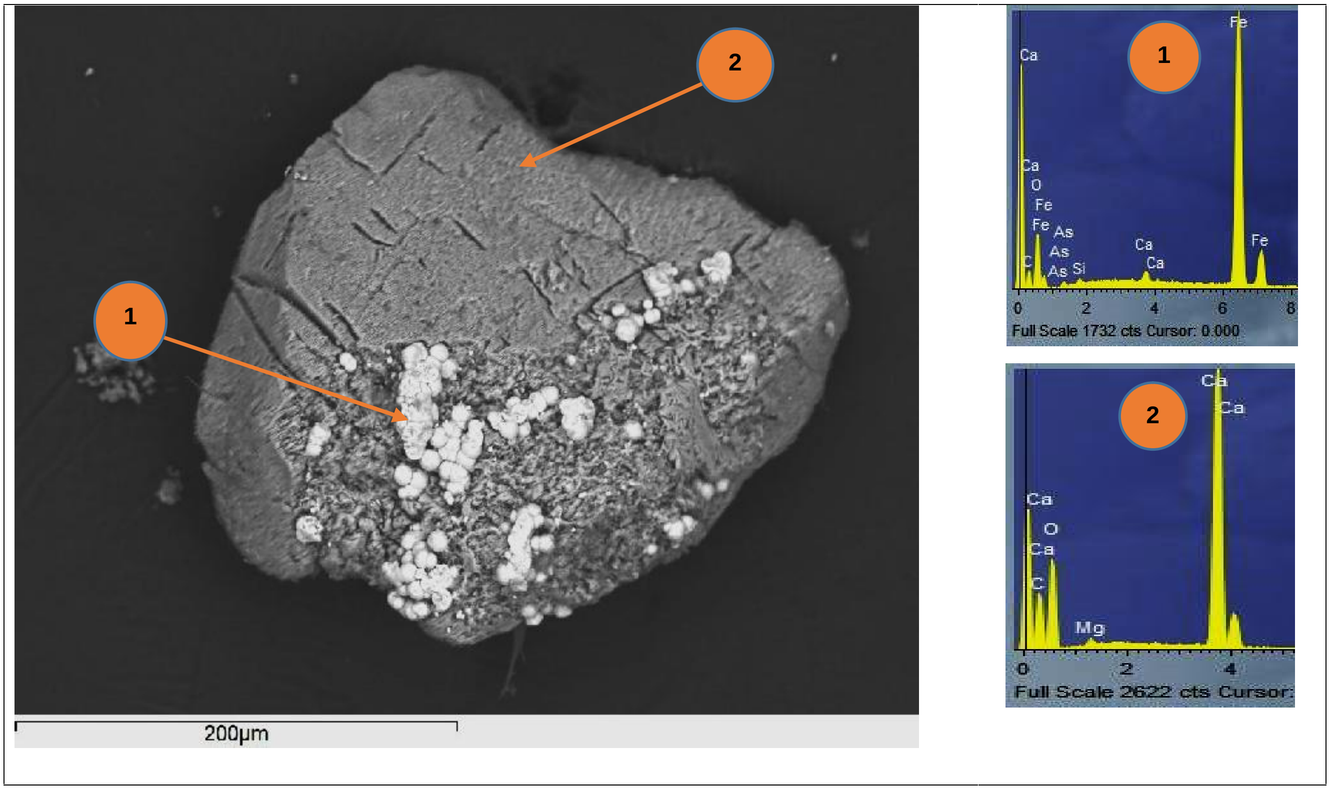

Figure 20. Microphotography by SEM of tailing material from vertical profile of AbT: 1 – Fe precipitates with accompanying Ca, Si and As; 2 – calcite

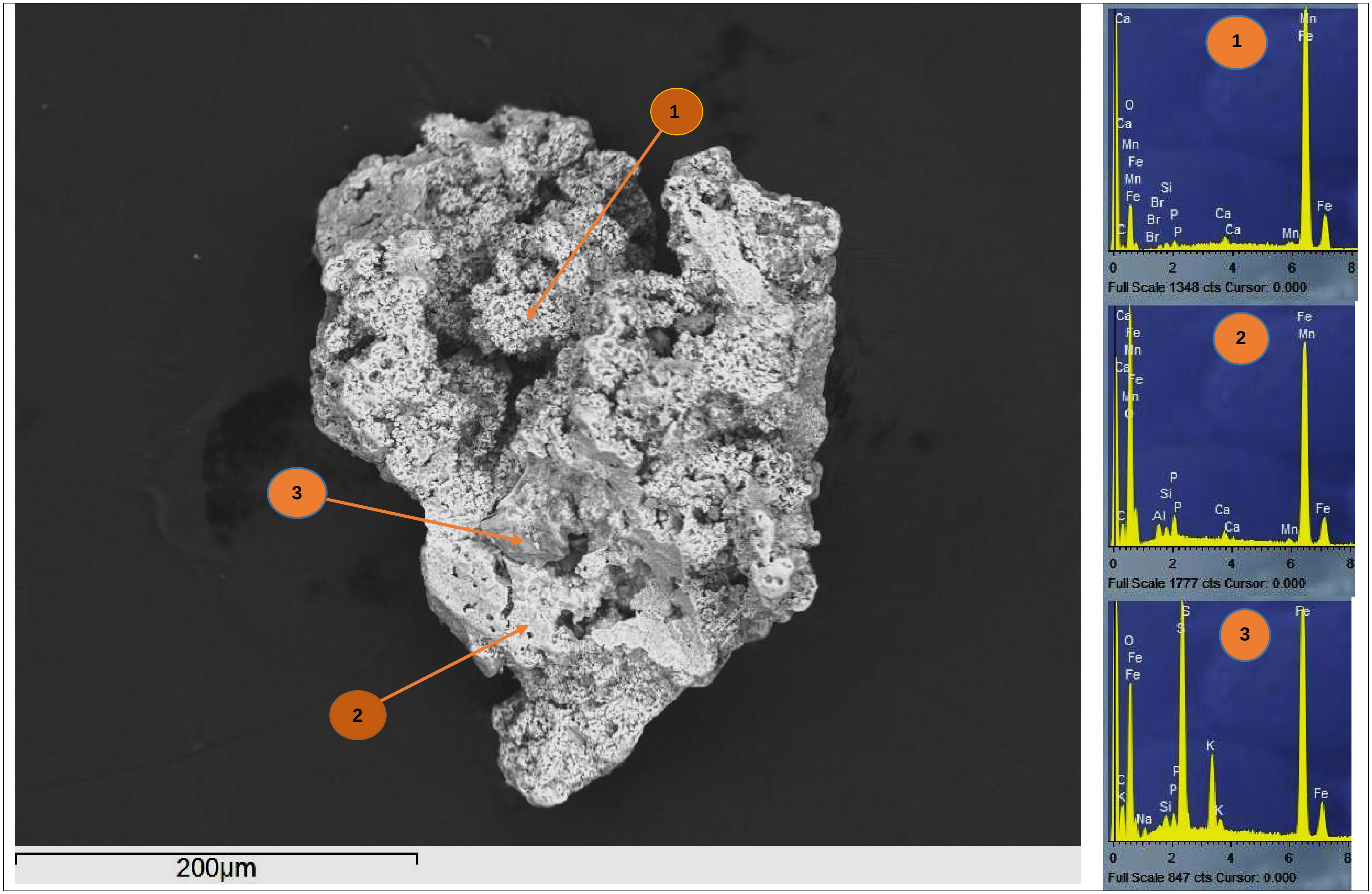

Figure 21. Microphotography by SEM of open pit waste material: 1 – Mn and Fe precipitates with accompanying Ca, P and Si; 2 – Fe and Mn precipitates with accompanying P, Al, Si and Ca; 3 - jarosite

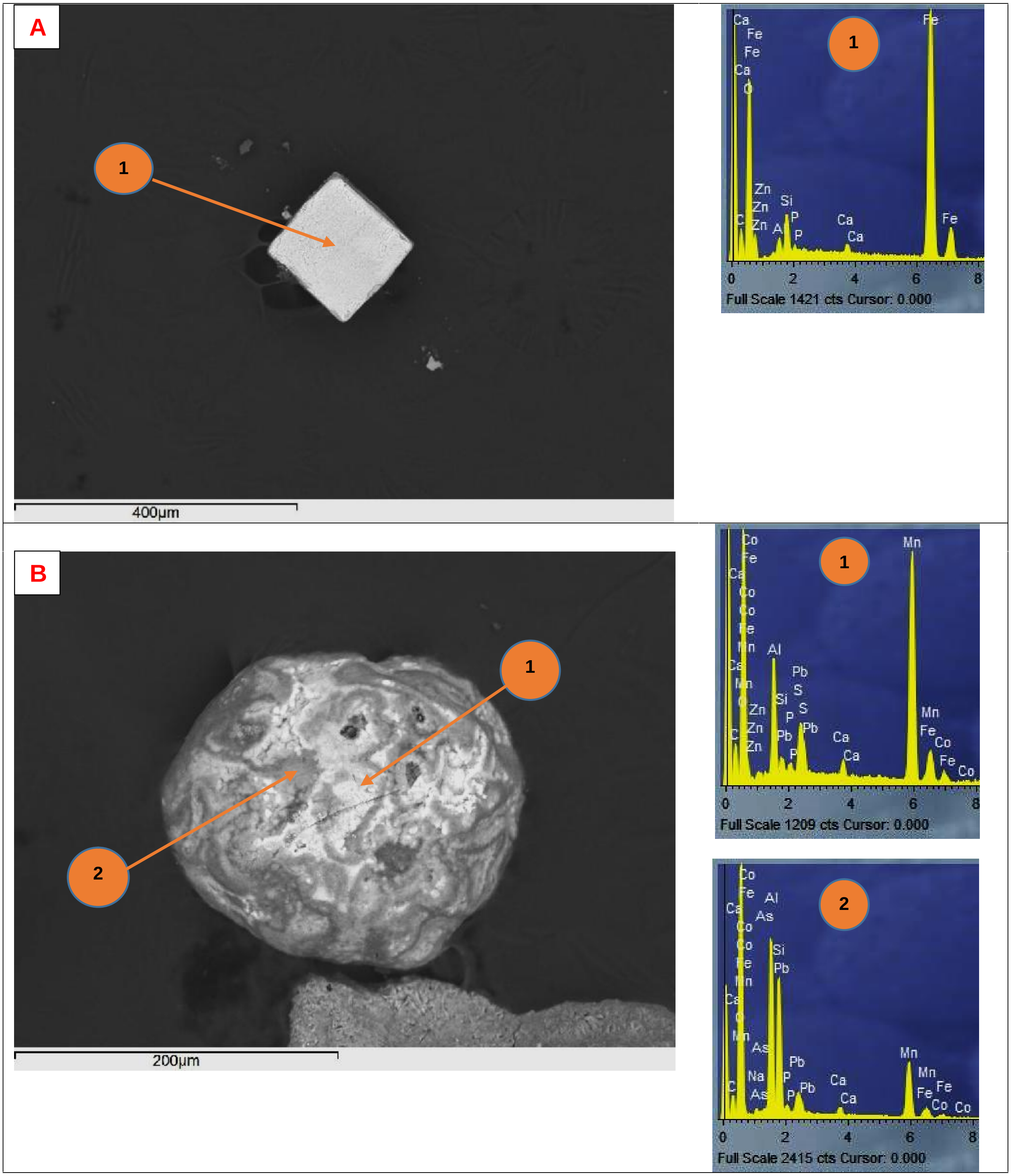

Figure 22. Microphotography by SEM of open pit waste material: A – magnetite; B (1 – Mn and Al precipitates with inclusions of S, Fe, Co, Pb and Ca; 2 – Si, Pb and Mn precipitates with inclusions of As, Ca and Co.

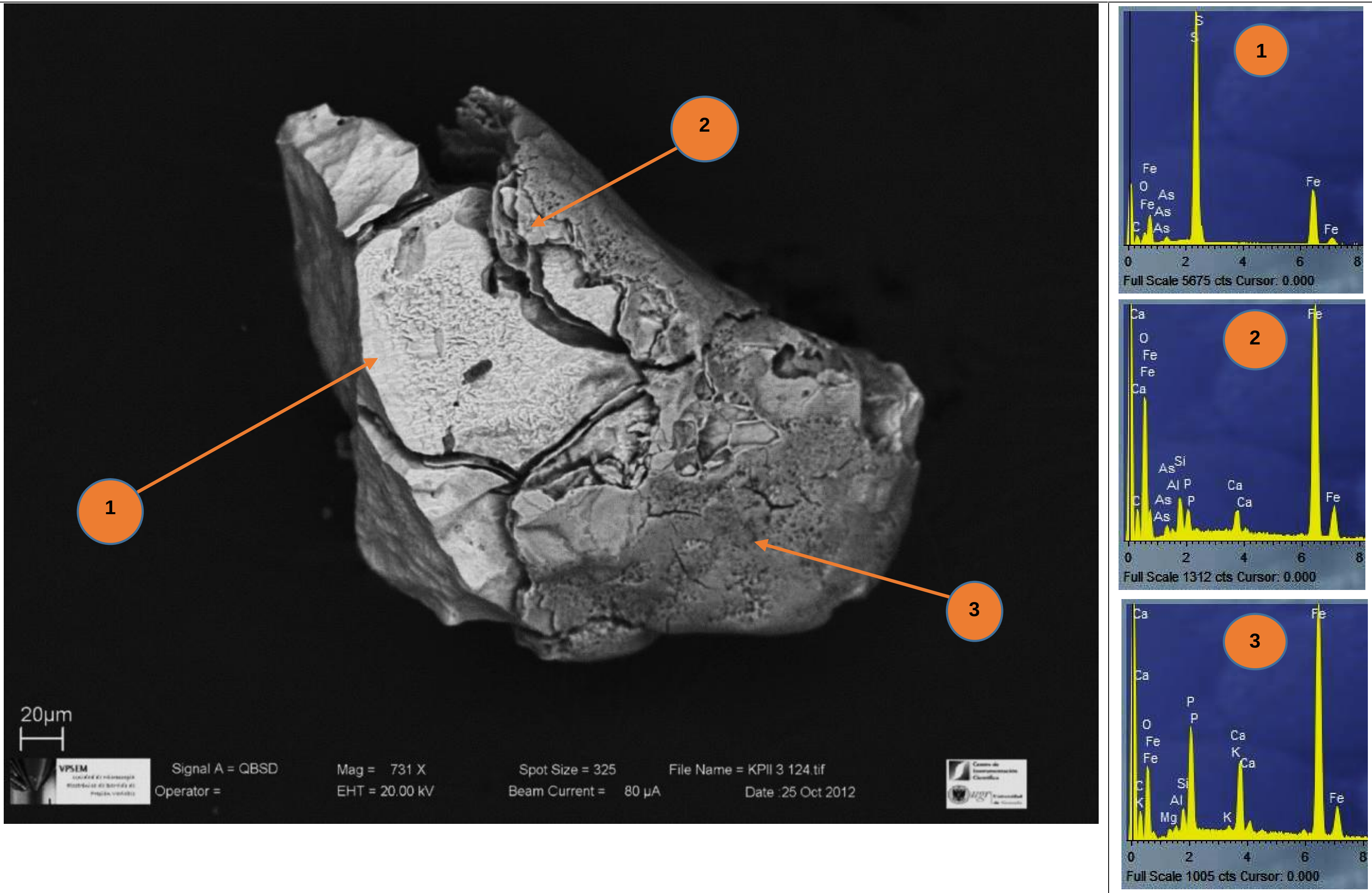

Figure 23. Microphotography by SEM of open pit waste material: 1 – pyrite; 2 – Fe precipitates with inclusions of Ca, Al, As and P; 3 - Fe precipitates with inclusions of P, Ca, K Si, Al and Mg.