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# **Impact of mining activities on the environment: Case studies from Greek mine sites**

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## **Abstract**

This dissertation was written as part of the MSc in MSc in Sustainable Agriculture and Business at the International Hellenic University.

In the present bibliographical study, data concerning the geological description, the mineralogy and the studies that have been carried out for the surface soils in 3 of the most important sites of mixed sulphide mines in Greece were summarized. What was attempted was, given the common characteristics between the sites at the mineralization level, to present and discuss data concerning the presence and characteristics of As, Pb and Ni which are heavy metal contaminants at all the sites discussed. The mines selected for inclusion were from the areas of Lavrio, Attica (one site) and Kassandra, Chalkidiki (2 sites). Finally, there is a brief reference to remediation techniques and strategies used in the literature for the management of heavy metal contaminated sites, with emphasis on the phytoremediation technique which is proposed as the most economically feasible and environmentally friendly solution.

Keywords: mining activity, soil, phytoremediation, heavy metals

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## Introduction

Mining activity in Greece, as in many countries around the world, has contributed to the economic development of society. Greece, compared to its size, is a country very rich in minerals. In its territory there is a variety of industrial, metallic and energy minerals which are of strategic importance for the development of European industry. Greece produces and exports bauxite and alumina, galena and sphalerite concentrates and ferronickel. For example, the bauxite deposits in the Parnassos-Giona zone are estimated at around 100 mt, while the alumina deposits are estimated at 2.5 mt. The potential reserves of lead and zinc from the Chalkidiki area are about 3.125 mt. Nickel is estimated about 1.392 mt. Copper from the Skouries mine site in Chalkidiki is about 1.943 mt. Gold from Chalkidiki and Evros area is estimated at about 19.37 million ounces and those of silver 131.6 million of ounces (Tsirambides and Filippidis, 2012). The total gross value of these deposits, as calculated at 2012 prices, reaches 79.4 billion euros.

Although mining activity is very beneficial to the socio-economic development of countries, the same is not true for the environment. The various phases of mining activity such as exploitation, processing, transportation, etc. cause adverse environmental impacts (Ainoo et al., 2009). In addition, significant problems to the environment are caused by the large amounts of waste resulting from the excavation of the deposits as this waste material is stored on the surface and can release significant amounts pollutants (Nieva et al. 2018) posing a risk to the surrounding soils and biota (Beniride et al., 2020). Pollutants from mining activity can affect large areas of the ecosystem even many years after mine closure (Gosar, 2004).

Heavy metals and metalloids released into the environment from mining activities pose a significant environmental risk. In recent years much attention has been paid to recording the concentrations of metals in the surrounding mining areas and studying their geochemical cycle. The collected information could help to reduce metal contamination of these sites and to minimize the environmental risk by appropriate restoration.

The purpose of this research is to discuss 1) the impact of the various stages and ways of mining activity on the environment, 2) the mining activity taking place in two very important deposits in Greece, such as those of Lavrion and Cassandra, which are of similar geochemical origin and are belong to mixed-sulfide deposits, 3) the possible pollutants from these giving emphasis mainly on heavy metal contamination of the soil in the surrounding mine area, considering the total metal concentrations and the soil fractions in which the metals appear. Finally, a reference is made to the restoration of mining areas contaminated with heavy metals using a low-cost technique such as phytoremediation.





## **Mining activity**

The term 'mining activities' refers to all those activities which include the exploitation of a deposit, beneficiation, metal processing, and transportation of the ore. They start with the mineral exploration and end with the closure of the mine and maybe with the reclamation of the area. Although mining activity contributes significantly to the national economic development and has many socio-economic benefits causes significant damage to the environment with adverse impacts on the quality of air, water, and soil as well as the loss of biodiversity (Matschullat and Gutzmer, 2012; Benidire et al., 2020)

### ***Phases of mining activity***

The operation of a mine is a large-scale project and divided into different stages which are outlined below.

#### **Exploration**

Exploration involves field studies, exploratory excavations, and drilling test boreholes to determine the grade and the volume of the deposit. At this phase, wide areas may be cleared of vegetation, and roads may be opened to allow access for heavy vehicles to carry out drilling. If this phase proves that the exploitation of the deposit is profitable, then the process of extracting the deposit begins.

#### **Site preparation**

Initially, roads are constructed to provide supplies and heavy equipment to the mine site and the transport of the mined ore. It is obvious that this type of work alters the natural landscape and causes significant impacts on the environment, especially when carried out in ecologically sensitive areas (Ainoo et al., 2009; Matschullat and Gutzmer, 2012). The impact is greater in the case where the ore is buried under a layer of soil or rock so this should be moved to gain access to the ore deposit. This layer of soil or rock is called "waste" or "overburden".

#### **Excavation**

There are several methods to extract and concentrate metallic ore: open-pit mining, underground mining, and placer mining. Each one has a particular environmental impact as indicated below.

#### **OPEN-PIT MINING**

The open-pit method is used in cases where the deposit extends to a great depth, and it is necessary to move the overlying soil layers. In many cases, it is necessary to log off the trees and burn the existing vegetation to remove the overburden usually with bulldozers and trucks. Often requires the transfer of settlements and the resettlement

of residents. Because the deposit is extracted from a great depth, usually exceeding the underground aquifer, groundwater pumping is required. The result is a change in the landscape the movement of the dominant features and the creation of dumps (Singh et al. 2016), as well as the formation of water areas that causes microclimatic changes, irreversible in many cases (Hüttl and Bradshaw, 2001).

#### UNDERGROUND MINING

In the underground mining method, smaller quantities of overburden need to be removed to access the deposit. Access to the deposit is by means of tunnels or underground galleries. This method is less harmful to the environment, but is more costly, and involves greater risk to workers. Atypical landscape features like conical dumps are created from the material extracted for tunneling, (Vivanco, 2013). Fertile land may be disturbed and reclaimed hardly, depending on the dimensions and the shape of the dump (Sahu, 2015).

#### PLACER MINING

The placer mining method is used when the precious metal of interest is found in the sediments of a river basin. Mining is carried out using bulldozers and dredges. This method destructs the environment as changes the topography of the mined area as large amounts of sediments moved, modifies the route of the streams and introduce large amounts of materials (sediments) into the stream system which may affect the quality of surface water over a long distance from the mine (Madison, 1981).

#### Reclamation

When mining activities cease, the reclamation of the area should begin. Reclamation is the process by which any negative impact on the environment caused by the operation of the mine is remedied. The goal is to return the site to the stable pre-mining condition or to improve the landscape to an ecologically functional state. The site restoration plan is a necessary condition for the authorization of the commencement of mining operations on the deposit. During the last decades, scientists have developed theoretically and practically new insights for restoration actions along with reconstruction of natural ecosystems (Clewel and Aronson, 2007; Falk et al., 2006).

## **Impacts of mining activity**

Although mining has many social and economic benefits, its negative impact on the environment and public health cannot be ignored (Ainoo et al. 2009; Matschullat and Gutzmer, 2012).

It is obvious from what has referred above that mining activities cause a considerable impact on the environment as they modify the landscape and disrupt the soil, water, and air of the surrounding areas. The image of a mining site is composed of open pits, underground galleries, tailings, ore enrichment, processing plants, railway tracks, abandonment settlements, etc. The adverse effects of mining activities both in the environment as well as in all living organisms and especially in human health, have been reported in many countries (Boularbah et al. 2006; Lim et al. 2008; Kelepertzis et al. 2006; Antoniadis et al. 2022).

### ***Acid mine drainage***

One of the most adverse effects of mining activities on the environment is the acid mine drainage which may pose a significant risk to the environment, human health, and agriculture (Karaca et al. 2018; Osonimi et al. 2019). The problems caused by acid mine drainage are groundwater pollution and surface run-off from waste dumps. When sulfide mined materials are excavated and exposed to the water and the oxygen of the atmosphere, they form sulfuric acid which has a low pH value and can dissolve metals from the surrounding materials promoting high metal concentrations (Anawar, 2015; Kefeni et al. 2017). Once acid drainage has occurred, controlling the release of metals is a difficult and costly problem to be solved. Hence prediction is becoming an important tool for operators and regulators. If acid mine drainage is not controlled may leach into streams and underground aquifer and affects water quality. Alkaline substances could be added (like crushed limestone to the overburden) to reduce the acid drainage (Keita and Traore, 2020). The chemical reactions that cause the pollution of the underground aquifer begin when the mine starts operating, as water is pumped continuously to keep the mine dry. Minerals such as iron pyrite, when exposed to air, release soluble metal sulphate ions. Pumping stops after the mine closure and the groundwater table begins to rise. The rise can take several months or even years. As the level rises, the oxidation of the sulfide minerals appears to stop, but water dissolves the metal ions and sulfuric acid is formed. If the adjacent rocks contain carbonate minerals, then the acidic nature of the groundwater can be neutralized, and the metal ions can be immobilized. Usually, water solubilizes large concentrations of iron, copper, zinc, aluminum, cadmium, manganese, and lead. In general, mining activity reduces the level and quality of water in the area's rivers, wells, and boreholes, forcing residents to bring water from other areas. Waters impacted by acid mine drainage may have a pH value lower than 4, toxic levels for most aquatic life (Hill, 1974).

### ***Soil loss and erosion***

Mining activities can lead to the physical destruction of the landscape by the removal of large quantities of rocks and sediments, formed external dumps, particularly in the case of open-pit mining. This results in the alteration of the topographic relief, creating different slopes from the existing ones, changing the topography, and eliminating the vegetation. Steep slopes and the restriction of vegetation lead to an increase surface runoff (Zhao et al. 2013). The fine soil particle fractions, such as humus and clay, both of which are stabilizing agents and nutrient carriers improving soil physicochemical properties, are lost. The magnitude of erosion depends on the annual precipitation and characteristics, topography, and soil characteristics (Puigdefabregas et al., 1999). As a result, soil becomes more depleted in nutrients and less fertile over time.

### ***Heavy metal pollution***

Mining activity is considered one of the main anthropogenic sources of pollution with heavy metals and metalloids in various ecosystems. Mining areas are characterized by excessive concentrations of potentially toxic elements in soils which can be related both to the weathering of parent rocks and pedogenesis as well as to the anthropogenic activities associated with the exploitation of the deposit. Heavy metals and metalloids have received special attention from scientists around the world because of their effect on all living organisms. Even if present at low concentrations in the soil, can be taken up by plants and enter the food chain (Donkor et al. 2005). Unlike organic chemicals, metals are not chemically or biologically degradable into non-toxic and environmentally neutral constituents. Thus, contaminated sites with toxic metals have received exceptional interest and their remediation is a grade challenge for the scientists.

Heavy metals and metalloids are constituents of soils (Lasat, 2002). Heavy metals are generally defined as metals with relatively high (>5 g/cm<sup>3</sup>) atomic weight, higher than sodium (>22.98), and an atomic number greater than calcium (>20). Metalloids are considered elements that sometimes behave as metals and sometimes as non-metals. Arsenic is a commonly recognized metalloid. Many scientists are referred to as heavy metals as in the case of this work.

Some heavy metals like mercury (Hg), lead (Pb), and arsenic (As), do not participate in the physiological functions of plants and thus they are not considered essential for plant growth. Other metals like nickel (Ni), manganese (Mn), cobalt (Co), zinc (Zn), iron (Fe), copper (Cu), etc. are essential for plant growth as they participate in metabolic processes, but they could be toxic when they overcome critical concentrations (Carrido et al. 2002). Since metals are accumulated in the soil and are not bio-degradable, soil contamination of heavy metals is a constant danger. Especially in the case of gold mining sites, the waste constitutes over 99% of the extracted deposit (Adler, 2007) and is disposed of in elemental, organic, and inorganic forms (Krishna et al. 2013). Such waste is deposited in artificial lakes or dams and causes harmful effects on the environment hundreds of years after the cessation of mining activities (Navarro et al, 2008). The toxicity of this waste is due to the increased concentration of heavy metals

and metalloids in the extracted deposit but also the toxic reagents used for ore beneficiation by chemical methods.

The high concentration of heavy metals also affects the population of soil microbes resulting in the disappearance of many species that manage the cycle of nutrients in the soil and impacts negatively all the functions of the ecosystem (Fashola et al. 2016). In addition to high concentrations of heavy metals in mining areas, other issues like extremely low soil pH, low organic matter content, high electrical conductivity, and high salinity, adversely affect soil quality.

### ***Noise pollution***

Noise pollution associated with blasting, drilling, shoveling, crushing, transport, and movement of large vehicles is another concern in mining areas. Depending on their placement the mining noise varies in quality and level. In opencast mines the levels of noise generated is in the range of 90-115 dBA. Exposure to this level of noise over long time can result in noise induced hearing loss and other non-auditory health effects in the miners (Ghatak 1997).

### ***Aeolian dispersion***

Another source of pollution in the areas surrounding the mine sites is the particulate matter that results from the movements of overburden, heavy equipment operation, blasting, and wind erosion of mine tailings which affects air quality and human health (Saviour, 2012; Wang et al., 2021). This dust is the finest particle of the deposit and so is as toxic as this and sometimes may be radioactive. It affects initially mining workers but also the communities located near mining areas. The aeolian transport and dispersion of this contaminated dust impacts large areas many kilometers down-wind the mine site (Conko et al., 2013). Researchers who studied the transport of contaminated particulate matter ( $< 2\mu\text{m}$ ), found that this travels great distances from the main source (Davis & White, 1981).

### ***Landscape change***

Mining activity impacts landscape in various ways. In open-pit mines surface soil is stripped off and replaced, resulting in the degradation of surface structure and vegetation. The replacement surface soil is piled up on dumps, which are characterized of steep slopes, debris flow and instability. The artificial hills created by the deposition of tailings and slag affect the natural environment not only morphologically but also ecologically. The vegetation growing on the hills is different from the rest of the area because different biological factors prevail. In underground mining areas, the main effects include crown holes, cracks and subsidence. Surface subsidence may cause the changes of surface configuration, structure, and vegetation, affecting surface land use and landscapes (Zhang et al. 2008).

### ***Loss of biodiversity***

Mining and related activities are one of the major causes of environmental degradation of flora and fauna. Mining activities affects biodiversity through direct and indirect processes. Most research focuses on the direct habitat degradation caused by site preparation and mine operation, which directly alters the biotic and abiotic conditions and causes threats to rare species and ecosystems (Wickham et al. 2013; Ganzhorn et al. 2007). Physical and chemical wastes such as dust, aerosols, beneficiation reagents, acid mine drainage cause negative impact to biodiversity over grade distances from the mine site and leave only tolerant species behind (Li et al. 2010). Large quantities of heavy metals released in the environment from mining operations and deposited in soils and waters near the mining area leading to soil and water contamination. These pollutants cause damage to animals, plants and micro-organisms, which play an important role in the ecosystem (Laaouidi et al., 2020). Animals are very sensitive to the noise generated by mining activities and may leave the habitat, migrate to another environment where may be exposed to various predators (Garcia et al. 2019). Mining activity usually leads to vegetation degradation due to reduced soil pH, increased heavy metal concentration and low nutrient levels (Nouri and Haddioui, 2016) forcing animals to migrate due to lack of food. Organisms remaining at mining sites are exposed daily to contaminants resulting in reduced reproduction, altered metabolism and poor physical condition. Increased concentrations of heavy metals also affect the growth of bacteria in the area and negatively affect the nutrient cycle (Singh and Kamal, 2017).

Mining activity may indirectly facilitate additional biodiversity loss by the attraction of human population accompanied by overexploitation (e.g. hunting, fishing) and other land uses such as residential and industrial development (Deikumah et al. 2014).

## **Metallic mine sites in Greece**

Greece is an active geotectonic region with the extensive subduction of the African plate under the Eurasian plate being the main factor in its evolution. The closure of the Tethys Ocean, which takes place since the Cretaceous and continues to the present day, attributes to a large number of magmatic intrusions that migrate from north to south over time as the subduction front moves. Four major provinces of magmatic intrusions are identified that yield mineralization ages ranging from the Oligocene to Pliocene-Pleistocene epochs.

There are two geotectonic phases that create the convenient conditions for magmatic intrusions. The post-orogenic/post-collisional back-arc extension from the Rhodope Massif to the Attic Cycladic zone, as well as the active volcanic arc in the South Aegean. The magmatism in the first zone is mainly calc-alkaline to shoshonitic while in the volcanic arc typical andesitic magmatism appears to predominate.

Hydrothermal deposits are those associated with magmatic intrusions and fluid circulation in the surrounding rocks. They are classified according to the depth of formation, the chemical composition, the temperature, the nature of the surrounding rock, the presence of a fluid phase and the mode of deposition.

Almost all types of hydrothermal deposits occur in Greece and yield deposits of small or large size. The most important deposits, mainly for economic and historical reasons, are associated with metasomatic, epithermal, and porphyry intrusions. Greece has large quantities of metal sulfide ore deposits along the South Aegean volcanic arc and Attic-Cycladic ore belt (where the famous Lavrio mine belongs) as well as in the Rhodopic belt, extended into Northern Greece (where Kassandra mines belong). Sulfide minerals were formed in anoxic environments at depth. During the extraction and the exploitation of the deposit, sulfide minerals are exposed to oxidizing conditions where they are not stable and form secondary mineral phases according to mainly to the time of exposure and the local geochemical environment.

Mining activity in the Kassandra and Lavrio mines dates to ancient times. Gold was mined from Kassandra while silver and lead were from Lavrio. Due to this long-term mining activity, the soils of the areas have been contaminated with significant concentrations of toxic metals, especially lead, nickel, and arsenic, to which we will refer below.

Both areas of mineralization development are not unidimensional. The complexity of the deposit genesis is evident from the abundance of mineralization, its development, and the stages of hydrothermal alteration they exhibit.

The selected sites represent three of the most important mining zones in Greece from antiquity to the present day. Mining activity has been almost uninterrupted for about 2500 years. The result of this continued exploitation is the systematic recording of data concerning the development of ore, the content of the valuable elements but also the deposition of overburdened material (or spoil or waste material) over the centuries according to the environmental standards. The meaning of overburden, as can be readily perceived, changes over centuries, as metallurgy develops. In most cases, the exploitation simply focuses on the most profitable metals of the particular ore. Similarly, environmental rules do not remain the same from ancient times to the



present day. It follows that the tailings of each mining era yield enrichment in strongly varying elements and concentrations.



Figure 1. . Metallic mineral mining of Greece (Tsirambides and Filippidis, 2012).

### ***Lavrio mining area***

The mining area of Lavrio is located 50 km SE of Athens in the prefecture of Attica. It is the western end of the mining province of the Attic-Cycladic Zone and is directly related to the ore deposit of the Cyclades Island complex. The main mineral mined for millennia is silver, associated mainly with metasomatism processes, while Pb, Bi, Cu, As, Sb are also present in the mineralized deposits as a result of metasomatism or epithermal processes. The deposits of Lavrio show great diversity making it difficult to classify them strictly into a hydrothermal type. Several models have also been proposed for the basic mineralized volume of the deposit, which undeniably belongs to the metasomatism type and mainly to the metasomatism Skarn-type deposits.

Findings indicate that the mine has been in operation since 2000 BC, while from the 7th century BC mining was also done underground. Mining is uninterrupted until about the 1st century BC with an estimated by Konofagos (1980) volume of mined material of 1.5 million metric tons. The mined material was rich in Pb (~20%) and Ag (~400 gr/t). The total quantity of each material is estimated at 1.4 million metric tons and 3.5 thousand metric tons, respectively. Modern mining activity from the late 19<sup>th</sup> century to the early 20<sup>th</sup> century was responsible for the extraction of 10 million metric tons of Pb ~7% and Ag ~140 gr/t, also estimated by Konofagos (1980). Modern mining activity also exploits part of the tailings of the ancient activity. The new techniques of the time made it possible to process 1.5 million metric tons of material with contents of 10% Pb and 50g/t Ag.

The Attic-Cycladic zone is a tectonic window with high-pressure rocks. It is called a tectonic window because the detachment faults (normal short-angle-dip faults) of Miocene epoch reveal high metamorphic formations such as the Blue Shales. During the operation of these faults, magmatic intrusion of granodiorite composition occurs and a system of vein intrusions of varying chemical composition, from quartz-syenite and quartz-monzonite to granodiorite, is created.

In the mining area of Lavrio two of the most basic units of the Attic-Cycladic zone appear. The metamorphic rocks that occur from the lower section of the zone are the Upper Cretaceous Marbles, the Kaisariani Shales and the Lower Jurassic Marbles. While parts of the mineralized province include parts of the HP/L-MT Blue Shale of the Cyclades unit. The magmatic intrusions mentioned above create metamorphic zones with the main metamorphic skarn zone hosting among others one of the main deposits of Plaka and is also associated with vein 80.

The deposits of Lavrion are mainly located in two main levels, that of the Kaisariani Shale and that of the contact of the Blue Shale with the upper Marble Stage of the Attic-Cycladic zone. The mineralogy of the calc-alkaline contact metamorphic zones indicates high water content and medium to high temperatures (440-600 °C). Much of this mineralogy has been replaced by minerals associated with Skarn-type metamorphic zones. Also distinct is retrograde metamorphism with the re-formation of new minerals. Skarn mineralogy mainly consists of Plagioclase, minerals of Hedenbergite-Diopside group, minerals of Hornblende group (iron-manganese minerals), granates, clinopyroxens and scapolites, while retrograde metamorphism mainly occurs in Epidotes, Actinolites, Chlorites, Calcites and Opaques which consists of sulfides and salts of metal sulfides. The ore tends to increase the content of the valuable/exploitable minerals as the distance of the main magma increases.

Most of the ore deposit is interrupted by tectonic surfaces, the main one being the detachment fault that separates the marbles from the Blue Shales of the overlying zone. The initial and basal ore, associated with the main magmatic intrusion, is intruded by secondary vein systems. During the emergence of the formations, very acidic water circulation re-dissolves the minerals creating new deposits of Fe- and Zn-rich minerals in non-sulfide-bound forms.

More than 430 different mineralogical species have been identified in the mines of Lavrion, while several minerals have been identified in the open dumps where they were formed from by-products of metallurgy and mining over time.

### ***Kassandra mining area (Olympiada-Madem Lakkos/Mavres Petres)***

The mining zone of NE Chalkidiki is one of the most important in Greece and certainly one of the richest in precious metals, either counted in the number of elements they contain or in their quantity. The beginning of the mining activity in the region is placed in the 6th century BC. They were one of the main financiers of the Macedonian Empire and apart from minor interruptions or periods of decline, the mines have been in continuous operation until today. The main elements exploited from the mines under consideration are Ar, Pb, Zn and Au at the Olympiada mine.

The Cassandra mines, as they have come to be called, are located 100 km east of Thessaloniki and are a semi-mountainous area on the borders of the mountain ranges

of Kakkavos and Stratoniko. Olympiada, the northern part of the ore zone, is watered by the Strymonikos Gulf, while Straton, the main settlement of the Madem Lakkos-Mavres Petres mines, is watered by the Gulf of Ierissos.

Geologically, the ore zone is located in the margins of Rhodope and Servo-Macedonian Massif. However, all of the exploration sites are located in the Rhodope Massif, which is geologically called the metamorphic core complex. This classification takes into account the current understanding of the inclusion of the Cordillera unit in the Rhodope Massif as the upper part of the Rhodope Massif. The dominant rocks are continental crustal rocks, which have undergone a high degree of amphibolite phase metamorphism during the Tertiary. In many places, partial melting products such as migmatites are also found. Partial melting phenomena are more pronounced in the southern parts of the zone. The cooling of the rocks lasts until the Upper Miocene for the whole zone, but the area under study during the Upper Oligocene has already approached the 300 °C equilibrium. The area will undergo multiple tectonic changes until its final emergence during which retrograde metamorphic processes of greenschist, main phase are histologically and mineralogically imprinted.

Kerdilia Formation petrologically consists of various composition gneisses, amphibolites, and marbles. The prevailing gneisses rock types are quartz-plagioclase-biotite gneisses and granitic augen gneisses (ophthalmic gneisses), while migmatite phases appear mainly in biotite gneisses.

The metalliferous sites examined are tectonically located in the West by the large detachment fault of Kerdilia Formation, with development ~B-N//BBA-NNA, which is also the geological boundary of this Formation with the Serbo-Macedonian Massif and the Vertiskos Unit. The development of the ore is also determined tectonically with regard to the case of Madem Lakkos and Mavres Petres. Both of two sites are developed along the fault of Straton, with WNW-ESE development, which in turn creates a large mylonite zone (zone of high rates of strain). In the northern parts of the fault of Straton, prevail lithologically marbles and carbonaceous shales, while South of this amphibolites. Both lithologies belong to the Kerdilia zone although in the past some models had proposed that included the amphibolites in the zone of Vertiskos.

## Certain pollutants of metallic mining activity

### **Lead**

One of the most toxic heavy metals in the environment is lead (ATSDR, 2007). Its use for various purposes has been known since ancient Rome. It is a very soft and dense metal, resistant to corrosion, with relatively low electrical conductivity compared to other metals. It has a specific gravity of 11.34, atomic number 82, atomic weight of 207.19, and a melting point of 327.50C. It occurred physically in four isotopes with atomic weights 204, 206, 207, and 208. In the environment Pb exists in 0, I, II, IV oxidation state. Pb(II) is the most stable form. Chlorides, chlorates, and nitrates are the most soluble inorganic salts of Pb (WHO 2001). The most stable form in the soil environment is lead sulfide (PbS), which is formed under reducing conditions when large concentrations of sulfide are present (GWRTAC, 1997). Lead interacts with other elements to form minerals.



Figure 2. Galena, ore of lead.

The natural process of lead accumulation in soils, sediments and water bodies is the weathering of parent rocks. Some anthropogenic sources of lead accumulation in the ecosystems are leaded gasoline, pottery, lead-based painting, boat building, and pigments, the printing of books, battery manufacturing and especially mining and smelting of lead ores. Lead concentrations of surface soils range from 10-67 mg/kg with an average concentration of 32 mg/kg (Kabata-Pendias, and Pendias, 2001). In Miguri gold belt, in Kenya, has been reported 510 mg/kg in mine tailings (Ogola et al. 2002). Lead concentration in soils tends to decrease with soil depth (de Abreu et al., 1998). According to Environmental Protection Agency (Schleifstein, 2011) soils where children play which containing > 400 mg/kg are considered harmful to their health. Although in recent years governments have restricted the use of lead in everyday products, there are however large quantities of lead contamination in the environment from past use (Mayo Foundation, 2019). Once surface soil has become contaminated by Pb, it remains a long-term source of Pb exposure. Many developmental issues in children have been linked to lead exposure. A significant relationship has been determined between soil Pb bio-accessibility and blood Pb in children (Ren et al. 2006). Adverse effects on the kidneys, the blood cells, and the central nervous system were observed which were mainly expressed with hyperactivity, hearing problems, reduced IQ scores, and headaches (Schleifstein,

2011). Anemia is the most characteristic symptom of high exposure to Pb, resulting from the destructive effect of Pb on the formation of red blood cells.

Lead is considered a non-essential element for plant growth; however, it can be easily taken up by certain plants (Sharma & Dubey, 2005), and becomes toxic even at low concentrations. In plants Pb induces toxic effects which include physiological, morphological, and biochemical issues. It is referred by many authors that Pb adversely affects plant growth, seed germination, transpiration, chlorophyll production and cell division (Sharma and Dubey 2005; Gupta et al. 2009, 2010; Maestri et al. 2010), depending on the soil Pb concentration, the duration of exposure, and the stage of plant development.

### ***Nickel***

Nickel comprises about 3% of the concentration of earth's crust and exists in many mineral forms. It dissolves readily in dilute oxidizing acids, but it is resistant to corrosion by alkali, water, and air. It occurs physically in five stable isotopes. Another nineteen unstable isotopes have been also known. In the environment Ni exists in five oxidation states (-1, +1, +2, +3, +4). Ni (II) is the prevalent oxidation state. Nickel enters the surface soil from both physical sources and anthropogenic activities.

Physical sources include weathering of parent material, volcanic emissions, and forest fires. Anthropogenic activities include metal mining and smelting, burning of fossil fuels, emissions of vehicles, application of fertilizers and organic manures, and disposal of industrial and commercial waste (Alloway, 2000). The most common use of Ni is in metallurgy as raw material, in food and chemical in the industry as a catalyst, and in the manufacture of electrical batteries as a component (Easton et al. 1992).



Figure 3. Annabergite, a secondary mineral, is derived from the alteration of sulfide and arsenate minerals of nickel and cobalt in the oxidation zone of hydrothermal deposits.

Ni concentrations in polluted soils may reach 26000 mg/kg (Alloway, 2000). Ni is an essential element for plants (Nieminen et al. 2007). Much more concern has been on the toxicity of Ni than on its deficiency. Ni interferes with the metabolism of other essential metals, such as Fe, Mn, Zn, Cu, Ca, which can suppress its carcinogenic effect. The toxic effect of Ni is probable due to the replacement of other metals in enzymes and proteins (Scott-Fordsmand, 1997). In neutral to alkaline and reducing conditions Ni has low mobility. Acidic soils is very mobile and may pose a risk to the quality of the environment. The soil content of Ni ranges from 3 mg/kg to 1000 mg/kg (Bencko,

1983), and exists in several forms, as inorganic minerals, adsorbed on the organic matter of inorganic cation exchange surfaces, water-soluble, or chelated metal complexes in soil solution (WHO, 1991). Agricultural soils contain 3-1000 mg/kg Ni, but near metal refineries Ni concentration may reach 53000 mg/kg. High Ni concentrations can inhibit cell division at room meristems in plants which decreases plant growth and causes morphological and physiological problems (Satish, 2015). The initial symptoms of exposure to Ni are nausea, vomiting, vertigo, irritation, etc. which last for a few hours. Delayed symptoms of exposure are dyspnea, constant cough, tachycardia, cyanosis, weakness etc. (Kusal, et al. 2017).

### ***Arsenic***

Arsenic is the twentieth more abundant element on the earth. It has atomic number 33, and atomic weight 74.92 g/mol. In nature occurs in inorganic and organic forms, in various oxidation states (-3, 0, +3, +5). Commonly found in the environment as arsenite (As+3) and arsenate (As+5), which is the most stable form (Gupta et al. 2011). In the soil environment, arsenite predominates in reductive conditions, while arsenate is the predominant species in oxidative conditions. Except for the prevailing redox potential, the metabolic functions of certain microorganisms may affect relevant As+3 and As+5 concentrations. Arsenate tends to be adsorbed on soil-charged surfaces more intensively than arsenite, making it more mobile in the soil and causing more negative effects (Omerland et al. 2009). In addition to redox potential, the solubility of As in soils as affected by pH, particle size distribution, inorganic substances, competitive anions, and organic matter content (Adriano, 2001).

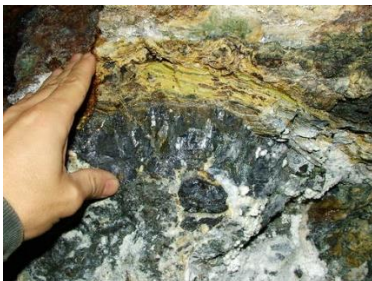


Figure 4. Arsenic from Lavrio.

In plants, arsenate follows phosphate paths in metabolic process, while arsenite interfere with sulfhydryl groups of proteins alters their structure and affects catalytic functions (Zhao et al. 2010). Both forms are harmful for all living organisms including humans. Inhalation, dermal exposure, drinking water and food contaminated with arsenic, are the sources of arsenic intake. Arsenic induces many health hazards to humans like bladder and lung cancers, affection of central nervous system and cardiovascular system, and deterioration of red blood cells (Duker et al. 2005).



## Lavrio mining activity and its impact

The mining area of Lavrio is located in East Attica, approximately 60 Km from the city of Athens (Fig. 6). It is famous for the mixed sulfide Ag-Zn-Pb-bearing deposits (galena, sphalerite and pyrite) (Skarpelis and Argyraki 2009). According to Marinou and Petrascheck (1956), the Phoenicians were the first to discover the ores of Lavrio, and as Xenophon had said, no one has the courage to say when the exploitation of the Lavrio mines began (Chronopoulos 1980).

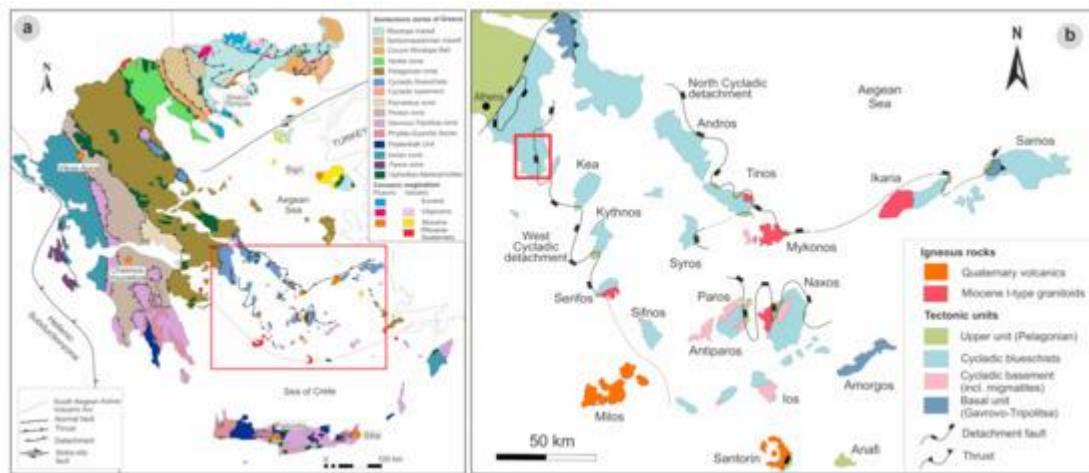


Figure 5. Geological map of Greece (by Voudouris et al. 2021).

The deposit of Lavrio is known for the silver and lead mining. In 483 BC 20 000 kg per year of the precious metals were mining (Konofagos, 1980). In 1860 the minister of finance of the newly established Greek state examined the prospect of the reprocessing of tailings for the extraction of lead and silver. The exploitation right was granted to the Italian company Serpieri-Roux de Fraissine, which reprocessing the tailings and made huge profits from the extraction of lead and silver. In the mid-1870s two mining companies, one Greek and one French, were active in Lavrio. The French company took advantage of the tailings left by the ancients because they were unaware of the use of zinc and produced 1.094.465 tonnes of zinc during 1876-1917. Many innovative metallurgical technologies such as flotation are used; thus, flame furnaces are no longer preferred. In 1981 all mining activity in Lavrio ceased and the industrial complex was given to the National Technical University of Athens for the creation of an area dedicated to the development of environmentally friendly technologies.

Both ancient and most recent mining activity has left behind piles of waste (Fig. 7). These waste piles are divided into three categories (Dimitriadis, Al., 1999), sulfur, carbonates and slags. The sulfide is a flotation waste rich in pyrite, carbonates are enrichment wastes rich in carbonate minerals and finally slags are the residues of the smelting of the ore. The risks arising from such waste is by the acid mine drainage, the transfer of pollution to adjacent land through rainwater, the direct contact of humans with the waste, the inhalation or ingestion of suspended particles, and the consumption of food from crops growth in the area.





Figure 6. Lavrion mine tailings.

In Lavrion there are more than 2,000 ancient mining wells as well as galleries (Fig 8) . These mining constructions contribute to the soil erosion and allow hazardous substances to come into contact with the water table with all the negative consequences that this may entail.



Figure 7. Mining well in Lavrio.

Mining activity requires large amounts of energy to smelt the ore. In many cases this energy came from burning coal or wood, as in the case of Lavrio. The smelting of one tonne of silver-lead ore requires 10,000 tonnes of wood (Hopkins, K., et al, 1988). It has been calculated (Konofagos, K., 1980) that in Ancient Lavrio, for the metallurgy of silver and lead approximately 1.200.000 tonnes of coal and approximately 100.000 tonnes of wood consumed. The strong effects on the ecological balance, due to mining activity did not allow for the rapid regeneration of vegetation and the the regeneration of the forests in the area. Logging has a strong impact on the environment. The most important of these are: Disturbance of the water cycle, climatic changes, and soil erosion.

By-products from exploitation and processing of As-bearing ores may contaminate the ecosystem when arsenic mobilized from tailings by meteoric water and reacts with the mineral phases of the surrounding area. Usually in these cases pollution levels have exceeded the permissible limits. Stamatis et al. (2001) has recorded the impacts of mining activity in the quality of the groundwater of Lavrio area. The research revealed

that there are large concentrations of heavy metals (Pb, Ni, Cd, Zn) at groundwater samples.

Epidemiological studies have shown that the population, and in particular children, have Pb in their blood and As in urine, in concentrations exceeding the maximum acceptable limits (Maravelias et al, 1989; Eikmann et al, 1991; Makropoulos et al, 1991), which may cause cognitive problems.

Sampling of wells in the area of Lavrio (Dimitriadis, Al., 1999), showed that Pb, Cd, and Zn concentrations in the water exceed the maximum acceptable limits. This fact suggests the penetration of the elements into the underground aquifer. Fortunately, from 1984 onwards, the underground resources of Lavrio are not used for the city's water supply. They are, however, used for irrigation purposes.

According to Xenidis et al. (1997) a TCLP test (Toxicity characterization leaching procedure) proposed by EPA (Environmental Protection Agency) that conducted in sulfuric and oxidic tailings in Lavrio shows that they are active sources of pollution. The pH value of acidic waters collected in ponds after rainfall was extremely low reaching the value of 1.9, while the Pb and As concentrations determined was 0.5-0.7 and 43-800 mg/L, respectively. The permeability of the tailings was high and therefore the water infiltrates easily into, reacts with the tailings, produce acid mine drainage and dissolution of the elements. The bioavailable soil fraction of heavy metals was extremely high. Lead content in olives and grapes growth on tailings determined in 5.6 and 8.7 mg/kg, respectively, when the EU recommended limits are 0.1 mg/kg for both, indicating that the plants uptake Pb.

In Table 3 are presented the total concentrations of As, Pb, and Ni, according to results obtained by Kalyvas and his co-workers (2018), who studied the topsoil pollution of mining activity in Lavrio. As we can see the median total concentrations of As, Pb, and Ni, in Lavrio topsoils were significantly higher than the corresponding background levels, leading to the conclusion that there is an effect of human activity. The median total concentration of Pb was 9 times higher, median Ni concentration was 4 times higher, while median As concentration was 17 times higher than the critical Netherlands Regulations (Netherlands MHPPE, 2000). Lead was found as grains of size < 10 µm within the Al-Si soil components and constitutes more than 80% of the grain (Kypridou and Argyraki, 2020).

Table 1. Total concentrations of Pb, Ni, and As in topsoils of Lavrio, geochemical background levels and Dutch intervention values (mg/kg).

Elements	Geochemical background <sup>a</sup>			Total concentrations			Dutch intervention values <sup>b</sup>
	mean	median	range	mean	median	range	
Pb	76.85	22.00	<1.0-1850	8668	4625	1219-40313	530
Ni	168.30	54.50	<1.0-1600	229	152	43-1066	210
As	62.80	15.60	<0.5-1032	1415	921	204-5001	55

<sup>a</sup>Demetriades, 2010

<sup>b</sup>Netherlands MHPPE, 2000

The fractionation of the elements into soil fractions is of grade interest (Fig. 9). The partitioning of these elements shows that Pb was associated mainly with the reducible fraction (>65%) and only 4.7% associated with the exchangeable fraction. A significant amount of total Pb concentration was found in the oxidizable fraction. This is justified by relative high soil pH values which may favors the formation of stable Pb-organic complexes (Martinez and Motto, 2000). Given the high total Pb concentration in the studied topsoils, the 4.7% of the total concentration that fractionated in the exchangeable/acid fraction is a considerable amount of Pb that is more readily of potentially available to plants and soil biota and is capable of causing toxicity problems. The problem may be much more serious as the researchers say the selected fractionation method has flaws that lead to underestimation of this fraction.

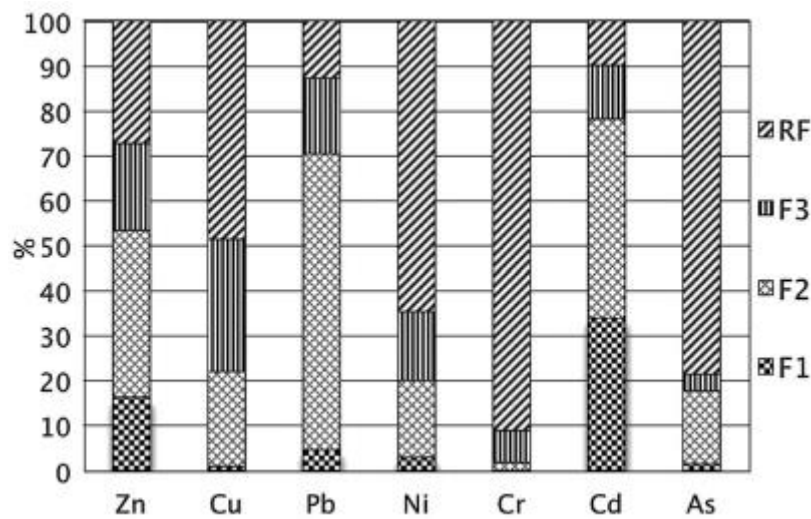


Figure 8. Relative percentages of mean Zn, Cu, Pb, Ni, Cr, Cd, and As concentrations in the chemical fractions of the studied soils. F1-exchangeable/acid soluble, F2-reducible, F3-oxidizable, and RF-residual. (Kalyvas et al. 2018).

Ni was associated with the residual fraction (> 60% of the total amount) and the lowest amount was found in the exchangeable/acid soluble fraction (3.1% for Ni). Nickel tends to replace Fe and Al atoms in the lattice of clay minerals during isomorphic substitution and is therefore mainly found in the residual phase (Favas et al. 2011). Arsenic is mainly associated with the residual fraction (>78% of the total concentration) indicating his preference to retained in the lattice of the primary minerals. The most readily or potentially available fraction (the exchangeable/acid soluble) was found to be 1.6% of the total As concentration. Particular attention should also be given to the reducible fraction (associated with Fe-Mn oxides) which may become available when reducing conditions prevail leading to the dissolution of the oxides. Such reducing conditions can be created by increased irrigation levels or heavy rainfall and pose a threat to the ecosystem. A recent study conducted by Antoniadis et al. (2022) on soil samples taken from parks and schools in Lavrio area showed that the levels of many heavy metals were very high. In particular, the pseudo-total concentration of As ranged from 7.3 – 10,880 mg/kg, while Pb concentration

ranged from 36.7 – 31,300 mg/kg. The health risk indices identified exceeded the threshold limits indicating that Lavrio requires immediately a remediation plan.

The high Pb concentrations identified in the soil of Lavreotiki (Dimitriadis et al., 1994) have significantly affected the diversity of the endemic flora (Chronopoulos and Chronopoulou-Sereli, 1986, Chronopoulou-Sereli and Chronopoulos, 1991). A decrease in the number of native species in the area and the creation of ecotypes of plant species that accumulate high concentrations of metals, i.e. plant species that accumulate high concentrations of heavy metals in their roots and shoots. It has been also found that high Pb concentrations are responsible for the change of color in flowers of the plant species *Matthiola fruticulosa* as well as for the serious morphological modifications in flowers of plant species *Silene colorata* and *Papaver rhoeas*. Other tolerant plant species showed a satisfactory growth in this heavily polluted environment.

It was found (Kannavou, 2009) that 93% of the soil and 99% of the plant species of the Lavrio peninsula are highly Pb-loaded due to the high concentrations of available Pb in the soils, even though soil conditions are not favourable for Pb uptake (96% of the soils are alkaline and 73.6% calcareous). Increasing its concentration in the soil reduces the rate of coverage to 87% of plant species. In the plant species *ballota acetabulosa*, *Piptathenm miliaceum* and *Thymus capitata* no significant difference in cover was found between pollution levels, which affects the vegetation composition in areas with elevated Pb concentrations, as when the Pb concentration in the soil increases, there is no significant decrease in the cover of the above plants, as is the case in the other plant species studied. In soils with soil available Pb concentration higher than 800 mg/kg, i.e. highly toxic levels, which are a deterrent for the growth of most plant species, *Glaucium flavum*, *Silene colorata* and *Matthiola fruticulosa* species prevailed with high percentage of infestation and good vitality. This means that at very high Pb concentrations in soil, not only the total cover but also the vegetation composition is affected. The plant species *Ballota acetabulosa*, *Piptathenm miliaceum*, *Thymus capitata*, *Glaucium flavum*, *Silene colorata* and *Matthiola jruticulosa* can be used in soil remediation through phytoremediation, as they have suitable mechanisms to dominate other plant species under conditions of extremely elevated soil pollution with heavy metals. The study of such plant populations and their appropriate management can contribute to the restoration of heavy metal contaminated areas in arid environments.



## Kassandra mining activity and its impact

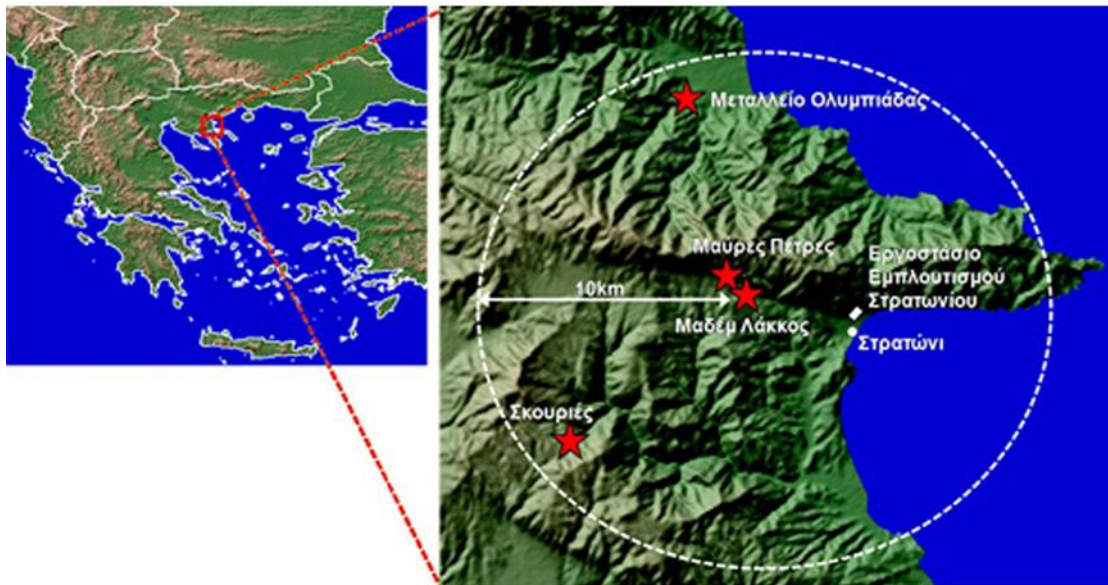


Figure 9. Kassandra gold mine sites.

The exploitation of Kassandra mixed-sulfide deposits dates back to 600 BC. 350 000 tonnes were exploited during the era of Phillip II and Alexander the Great (Arvanitidis et al., 1994). According to Papakonstantinou et al. (1996), 18 million tonnes of pyrite and 10 million tonnes of sulfide ore were extracted from Kassandra mines between 1970 and 1990, referring to the mines at Olympias, Mavres Petres, and Madem Lakkos. Associated mining activities that took place included a metal processing factory and a loading harbor in the coast of Stratonii town. All the waste from recent mining activity such as mine tailings, slags, and pyrite stockpiles, were deposited in the surrounding area, mainly along the streams (Papakonstantinou et al. 1996). Measures to prevent acid mine drainage had not been taken until 1986. Since then, the stockpiles had been covered with a PVC shield, and some cement canals were constructed to control the acid mine drainage (Adam and Gazea, 1994).

Gold mine tailings include the ground in fine particles deposit that is left after the retrieval of the precious minerals and the water used for the processing. The physicochemical characteristics of the tailing's particles are determined by the geochemistry of the ore, the particle size of the ground material, and the chemical process selected for the extraction of the ore. In general, gold mine tailings are characterized by poor aggregation and cohesion ability, but high hydraulic conductivity and salinity. Also, they have low content of nutrients and organic matter (Vega et al. 2006). The groundwater in the vicinity is characterized by high acidity and metal concentration because of the sulfides content (Vega et al. 2004). In gold mine tailings in Iran was reported a pH value 7.35 (Rafiei et al. 2010), while in South Africa was reported a pH value 3.25-6.28 (Mitileni et al. 2011). Da Silva and his co-workers (2004) pointed out the elevated concentrations of many toxic metals such as mercury, lead, arsenic, nickel, and cadmium in gold mine tailings. Knowing that in such tailings the large fraction of heavy metals concentration exists as silicates (residual fraction)

(Hayes et al. 2009), that is immobile and consequently not available to inhabitant bacteria, new bacterial species more resistant to the present conditions are growth and alters the bacterial diversity. All these characteristics of the mine tailings differentiated them from the soils of the surrounding area.

Surface water that filtrated through gold tailings leads to large toxic metals and sulfate concentration leachates that pollute the lakes and rivers of the area (Edwards et al. 2000). This creates acid mine drainage that has very negative effect on water bodies of the ecosystem. Acid mine drainage is a major problem where there are tailings of sulfide deposits. An additional problem is the dewatering of the aquifer as a consequence of the influx of surface water into underground mine galleries (Banister et al. 2002).

Chemicals that used in the processing is another major concern in gold mining activities. When the cyanidation extraction method was used, hydrogen cyanide emitted to the atmosphere, vast amount of energy was consumed and huge amounts of tailings rich in toxic metals was produced (Bambas-Nolen et al. 2013).

The soils in Kassandra mines which are related to metamorphic rocks are lack clay minerals and therefore have a low cation exchange capacity, which was determined on average to be 17 meq/100 g. There are no carbonate phases and therefore a mean pH value of 5.8 (mildly acidic) was recorded. The average value of organic matter content was 4.46. Lead was found to be associated with phosphorous and Fe-Mn phases which contains > 23 wt% Pb (Kypridou and Argyraki, 2020).

In Table 1 are presented the threshold limits given by UK and Netherlands regulations for metals that are characteristic of a sulfide ore (Alloway, 1995). The upper limit concentration of Pb has been set at 600 mg/kg by the Netherland regulations and 1500 mg/kg for open spaces according to UK legislation, 500 mg/kg and 35-70 mg/kg for Ni, and 50 mg/kg and 40 mg/kg for As, respectively.

Table 2. Critical concentrations (in mg/kg) of potentially toxic elements in polluted soils (Alloway 1995).

Element	Netherlands			UK (DOE-ICRCL)			
	A	B	C	Small garden	Large garden	Amenity grass	Open space
Pb	50	150	600	550	550	1500	1500
Ni	50	100	500	35	35	35-70	35-70
As	20	30	50	20	10	40	40

A: background value

B: indicates need for further investigation

C: clean up required

DOE-ICRCL: Department of the Environment, Interdepartmental Committee on the Redevelopment of Contaminated Land

Kelepertzis and his co-workers (2006) recorded the concentration of some toxic heavy metals in the wider area of Kassandra mines and found high metal concentrations in soils. Specifically, the mean concentration of Pb was 895 mg/kg, much more than 600 mg/kg that set by the Netherlands regulations and very close to the limit set by UK regulations for open spaces. The mean concentration of Ni was 161 mg/kg and exceeds

the critical limit of UK regulations. For As, the mean concentration has been determined to be 363 mg/kg, which is about eight to nine times above the limits. The authors make an effort to compare the mean concentrations of Pb and As with the trigger concentrations established for mine spoil-contaminated soils, which were determined at 1000 mg/kg for Pb, and 500 mg/kg for As, respectively (ICRCL, 1990) (Table 2). These concentrations are acceptable in the case of spoil contaminated soils as well as the elements in spoils are in more stable forms than in typical soils and therefore are less available to plants and animals. By comparing the mean concentrations of Pb and As, only mean concentration of Pb approaches the critical limit of 1000 mg/kg for grazing live-stock.

Table 3. Triggering concentrations of toxic elements (in mg/kg) in mine spoil-contaminated soils (ICRCL 1990)..

Element	Threshold trigger concentration	Maximum concentrations (action trigger)	
		For grazing live-stock	For crop growth (risk of phytotoxicity)
Pb	300	1000	-
As	50	500	1000

According to the research conducting by Argyraki et al. (2007) in soil samples from garden soil in a Kassandra village, mean Pb concentration was recorded to be 1090 mg/kg, higher than 878 mg/kg that was the mean Pb concentration determined by Kelepertzis et al. (2006) in the soils of the wider area. This concentration is slightly higher than 1000 mg/kg, the maximum concentration in industrial areas (Levinson, 1980), and much higher than the upper limit in small garden soils 550 mg/kg as proposed by ICRCL, (1990). The high correlation identified between different heavy metals such as Cu, Cr, Zn, Cd, indicates the common source of origin, which is the presence of metallic minerals and the release of these elements into soils by weathering. Pb was associated mainly with the residual fraction of the soil (53% of the total concentration), as well as with the redusable phase of Fe-Mn oxides (40% of the total concentration). Also, a significant correlation was found between Pb and Fe of the residual fraction, suggesting the coexisting of the two elements in soils may be in grains of metallurgical slag. It seems that the physico-chemical conditions of the studied soils, favors the formation of stable solid phases of Pb, either in the residual or the redusable fraction, limiting its mobility and bioavailability. The Fe-Mn oxides of the redusable fraction are abundant in the surface soil environment and they can act as Pb scavengers.

In the soil leachates lower metal concentrations were recorded than in the bulk soil. The soil leachates were yellow-brown in color indicating a high content of Al-Fe colloids (21.5 mg/kg Al, 15.2 mg/kg Fe), and has significant phosphorus and sulfur content (>240 mg/L Sulfur in porewater). 65-77% of the total Pb concentration is mobilized as  $Pb^{2+}$  and in conjunction with high sulfur concentration the formation of  $PbSO_{4(aq)}$  is favored. Taking into account the  $\log K_{sp}$  of lead phosphates ( $-23.8 < \log K_{sp} < -84.4$ ) it shows high stability and as a result lower water-leachable Pb concentrations.



The release of Pb into the soil solution is favored by the high sulfate concentration in the soil leachates (6 mg/kg) as primary sulfide such as galena and sphalerite are oxidized and release Pb. Generally, dissolved heavy metals are mainly present as free cations and sorbed by Fe-oxyhydroxides formed ternary complexes as Fe-hydroxide/metal/SO<sub>4</sub> (Swedlund et al. 2003, 2009).

Research conducted by Hadjibiros and his co-workers (2006) to determine the total concentration of some metals in dams of Kassandra mining area and its fractionation in soil fractions, adding up the percentages of the four metal fractions showed that lead has the lowest toxic potential (40.6%) comparatively to cadmium and zinc, but but lead can pose a significant risk to the environment because of its high total concentration (Table 3).

Table 4. Potentially available forms of metals in dams of Kassandra gold mine area. (from Hadjibiros et al. 2006).

Fraction	Heavy Metal		
	Cd	Pb	Zn
Exchangeable (%)	13,5	0,13	0,75
Bound to carbonates (%)	24,5	10	30
Bound to Mn and Fe oxides (%)	22	25	22,5
Bound to organic matter (%)	9,5	5,5	16,5
Residual (%)	30,5	59,37	30,25
Total potentially toxic forms	69.5	40,63	69,75
Total concentration, (mg/kg dm)	108.5	22650	22875
EPA limit (mg/kg dm*)	100	1500	35000

\*dm=dry matter

The risk to the environment increases when dums have a surface greater than 2ha, and run-off flows into water bodies used for irrigation or human consumption. According to this approach, mining dams in Chalkidiki can be considered as high hazard dams in the case of lead, containing total lead concentration much higher than the EPA limits. With the change of conditions (pH and oxygen concentration) the contaminant would be more available and scattered in the surrounding environment.

## Remediation potentials of mine sites

Mining activity is a main source of heavy metals contamination of the whole environment. In gold mining areas heavy metals such as Pb, Ni, and As are essential environmental pollutants (Jadia and Fulekar, 2009). Since the past decade, there has been a significant emphasis on the elimination of heavy metal pollution of the environment as it is irreversible and degrades air, water, and soil quality. This has a remarkable impact on the plants, animals, humans, and microorganisms' health (Kristensen and Taylor, 2016). Their entrance in the organisms is mostly through food, water, or respiration (Jose and Ray 2018). The scientific community has become aware of this issue. Firstly, it is trying to record the levels of pollution in areas adjacent to mines and then propose efficient and inexpensive methods to overcome its negative impacts.

Various physical, chemical and biological techniques have been applied to remediate heavy metal and metalloid contaminated soils (Gasparatos, 2012). Conventional remediation methods such as soil washing, landfilling, and electrochemical separation methods cannot be applied for the decontamination of large areas because of the increased costs and the risk of causing irreversible changes in the physico-chemical properties of the soils. Phytoremediation can be considered as an alternative method of remediation, environmentally friendly and cost-effective (Willscher et al. 2017). Phytoremediation is a method based on the use of plants that can hyper-accumulate metals and metalloids in aboveground biomass, which can then be recovered and removed (Kidd et al. 2009). A plant is considered as a metal hyperaccumulator when exhibits certain characteristics such as good adaptation, easy reproduction, extensive root system, high biomass production, tolerance to toxicities and a high transfer coefficient of the targeted elements from the roots to the aboveground part (Evangelou et al. 2007). However, soil decontamination by phytoremediation is a relatively slow process due to the low bioavailability of metals in soil, as they are mainly present in low solubility chemical forms and therefore little available to plants. In order to enhance phytoremediation, various chelating agents have been applied to the soil to increase the solubility of metals (Sheoran et al. 2011). EDTA as a chelating agent, sodium bisulphite as a reducing agent and mill effluents, which exhibit both complexing and reducing properties in soils, are among those additives used for the redistribution of scrap metals in the components of the soil solid phase in order to increase their mobility/bioavailability. In polluted areas, a risk assessment study is carried out which involves identifying and recording the source of pollution, using statistical analyses and models to quantify the risk.

The success of phytoremediation depends on the selection of the appropriate plant species; hyperaccumulator plants should thrive in the physico-chemical conditions of the soil and the climatic conditions of the area. For this reason, it is advisable to select native plant species. In the case of Kassandra, which is characterized by hot Mediterranean climate (Batlas, 2007), according to the study of Charvalas et al. 2021, the native plant species *Populus tremula*, *Quercus ilex*, *Platanus orientalis*, *Pinus sylvestris*, and *Pteris vittata*, are proposed for phytoremediation. *Pteris vittata* has also been proposed in the case of phytoremediation of Lavrio as it is a versatile, fast-growing plant that accumulates arsenic in its fronds (Kalyvas et al. 2018).

## **Conclusions and perspectives**

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As was evident throughout this literature review, despite the fact that there were multiple common characteristics between the sites analyzed such as mineralogy, heavy metals As, Pb and Ni as major contaminants, long term mining operations, etc., the data summarized revealed important differences of key importance for site management and data gaps. In particular, what was strongly observed was that in the majority of cases where data on total metal concentrations in soils peripheral to the mines were available, the variation in values was very large, while data on sequential extraction patterns were mostly absent. This means that despite many years of engagement of the scientific community with these areas, the detailed knowledge provided is spatially localised, while the increased environmental risk is a general assumption. A key prerequisite for the management of heavy metal contaminated sites, either with the aim of restoring them (chapter) or exploiting them by growing non-edible crops, is a very thorough understanding of the geochemical behaviour, mobility and bioavailability of the elements concerned. Especially in the case of mine soils, a very good monitoring of the total and available concentrations of heavy metals and the determination of their chemical forms is crucial in order to understand whether the pollution is mainly due to the parent material or to anthropogenic activity, which is essential information for any management planning. In addition, an indirect but key conclusion that emerged is that studies in the specific areas that address the microbiome of these agro-ecosystems and the interaction that the microbial community has with heavy metals are essentially absent from the literature. Given the context of the strategies being developed by the European Union for sustainable agriculture, for safety standards concerning agri-food products, for the management of soils as non-renewable natural resources, with all that this implies, and the continuing trend of decreasing areas of cultivated soils globally, the need for further engagement of the research community with soils and areas such as those addressed in this study is evident.

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