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Assessment of contamination potential and environmental risk characterization- the case study of the resources affected by former Sb mine of Montalto

Dissertation for the of Master degree in Mining and Geo-Environmental Engineering

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Resumo

A presente dissertação está incluída num projeto multidisciplinar que visa identificar o estado de contaminação do solo e da água, na área onde operou uma mina de antimónio de Montalto que cessou atividade em 1970. Com a evolução do conhecimento e consciência ambiental atual, o trabalho para restaurar a saúde do solo e da água em antigas áreas mineiras é da maior importância.

Existem mais de duzentos minerais com antimónio. Cada jazigo em que o antimónio poderá ser encontrado terá características especificas quanto à geologia e a sua formação (Rodrigues, 2009). O antimónio é considerado um poluente prioritário pela União Europeia e pela agência de Proteção Ambiental dos Estados Unidos da América. A exposição ao antimónio pode ocorrer por inalação, ingestão e contacto dérmico (Tao et al., 2021).

O caso de estudo desta dissertação, como referido, é a antiga mina de antimónio de Montalto, localizada no distrito do Porto, concelho de Gondomar, na zona do Covelo. No total foram recolhidas onze amostras de solo, sobre as quais foram efetuadas várias análises: análise granulométrica, análise química elementar por fluorescência de raio-X (FRX), determinação do pH do solo, determinação da quantidade de carbono orgânico e do potencial de dissolução de metais pesados a partir de ensaios de lixiviação dinâmica natural. Os resultados obtidos no FRX foram comparados com os valores de referência de solos contaminados definidos pela Agência Portuguesa do Ambiente. A lixiviação dinâmica foi realizada durante 24 h. O pH, Eh, e a condutividade foram medidos após 1 h, 3 h, 12 h e 24h. Finalmente foi realizada uma filtração da qual resultou uma parte liquida que posteriormente foi analisada por absorção atómica e uma parte sólida que foi analisada no FRX.

No dia 18 de abril, foram recolhidas dez amostras de água, pela equipa de investigação do projeto SHS. Foram feitas as medições primeiro no campo, e posteriormente no laboratório, aos seguintes parâmetros pH, a condutividade e o oxigénio dissolvido. Foram analisados quatro elementos, Fe, Pb, Cu e Sb, por absorção atómica, em todas as amostras. No dias 26 de maio, foram recolhidas treze amostras de água por um laboratório externo acreditado, ALS LIFE SCIENCES PORTUGAL S.A.. O laboratório analisou diversos parâmetros incluindo as concentrações em Hg, Ca, Mn, Cu, Zn, Pb, Cd, Ni, Al, As, Sb, Se, Na, K, Mg e Fe. No total foram recolhidas vinte e três amostras de água.

Foi realizada uma avaliação do risco tendo em conta os elementos cujas concentrações na água (superficial e/ou subterrânea) excedem os valores recomendados para água potável. Foram selecionados quatro metais/metaloides (Sb, As, Mn e Zn). A amostra W_1 é a que apresenta concentrações mais elevadas nesses elementos e é uma das amostras com maior probabilidade de contacto com humanos, por ingestão ou contacto dérmico. Com os dados da amostra W_1 foi calculada a dose em caso de ingestão, o índice de perigosidade, a dose em caso de contacto dérmico e o risco cancerígeno no caso do arsénio. A avaliação do risco é obtida através da relação entre a dose de exposição e a dose de referência.

Concluindo, as amostras de solo S1 e S2, recolhidas na propriedade onde a mina era localizada, suscitam a maior preocupação, especialmente devido à concentração de arsénio e antimónio que é superior ao valor de referência definido pela Agência Portuguesa do Ambiente. Com base nas análises realizadas à água, é possível concluir que nenhuma das águas amostradas são aptas para consumo humano. Quatro das amostras (W_1, W_3, W_6, e W_11) não podem sequer ser utilizadas para irrigação. De todas as amostras de água, a amostra W_1 apresenta o maior risco para o ser humano devido à concentração em arsénio e antimónio. O estudo efetuado revela a necessidade de serem tomadas medidas de forma a evitar que esta água esteja em contacto com outras linhas de água ou mesmo com o rio Sousa.

Palavras-chave: antimónio; contaminantes; avaliação de risco; correlação de Spearman; PCA.

Abstract

The present work is included in a multidisciplinary project that aims to identify the environmental effects of the former Sb mine, closed in 1970, by assessing soil and water contamination in that area. With today's knowledge and environmental awareness, work to restore soil and water health in former mining areas is of utmost importance.

There are more than two hundred minerals with antimony. Each deposit has specific characteristics, depending on the geology and formation (Rodrigues, 2009).
Antimony is a critical material and is considered a priority pollutant by the EU and the US Environmental Protection. Exposure to antimony may occur through air inhalation, drinking water, and food intake (Tao et al., 2021).

The case study is the former Sb mine of Montalto, located in Porto district, municipality of Gondomar, in the Covelo area. In total eleven soil samples were collected, and several tests were performed: granulometric analysis, X-ray fluorescence analysis, soil pH, amount of organic carbon, and potential for dissolving heavy metals from dynamic leaching tests. The samples were analyzed by X-ray fluorescence (XRF), and the values obtained were compared to the reference values of contaminated soil defined by APA (Portuguese Environmental Agency). The dynamic leaching was performed for 24 h and the pH, Eh, and conductivity were measured after 1 h, 3 h, 12 h, and 24h. Lastly, a filtration was done to obtain a liquid part that was further analyzed using atomic absorption and a solid part that was analyzed in the XRF.

On the 18 of April, ten water samples were collected, by the SHS project research team. These samples were measured in the field and in the laboratory for pH, conductivity, and dissolved oxygen. The samples were analyzed for four elements, Fe, Pb, Cu, and Sb, using atomic absorption. On the 26th of May, thirteen samples were collected by an accredited external laboratory, ALS LIFE SCIENCES PORTUGAL, S.A.. The laboratory analyzed several different parameters for each sample, including concentrations in Hg, Ca, Mn, Cu, Zn, Pb, Cd, Ni, Al, As, Sb, Se, Na, K, Mg, and Fe. In total twenty-three water samples were collected.

It was performed an analysis of the risk of exposure to the elements whose concentrations in water (surface and/or groundwater) exceed the recommended values for drinking water which were four metals/metalloids (As, Sb, Mn, and Zn). Sample W_1 has the highest concentrations in these elements and is likely to be in contact with humans by ingestion or dermal contact. The concentration used in the calculations is from this sample. It was calculated the dose in case of water ingestion, the hazard ratio, the effective dose in case of dermal contact, and the

carcinogenic risk for arsenic. The risk characterization process is obtained by dividing the exposure dose to the reference dose.

In conclusion, the soil samples S1 and S2, collected from the property where the mine was located, raise the most concern especially due to the concentration of arsenic and antimony which are above the reference value implemented by the Portuguese Environmental Agency (APA). Based on the water analysis performed, none of the water samples are viable for human consumption. Four of the samples (W_1, W_3, W_6, W_11) can't be used for irrigation. From all the water samples, W_1 shows the highest risk to humans due to the concentration in arsenic and antimony. Measures should be taken so that this water is not in contact with other water lines or the Sousa River that flows close to the point where the sample was collected.

Keywords: antimony; contaminant; risk assessment; Spearman correlation; PCA.

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Acronyms, and symbols

AA- Atomic Absorption

AD- Absorbed Dose

APA- Portuguese Environmental Agency

BOD-Biochemical Oxygen Demand

COD- Chemical Oxygen Demand

EC- Electrical Conductivity

EED- Estimated Exposure Dose

EIA- Environmental Impact Assessment

EIS- Environmental Impact Study

EPA-Environmental Protection Agency

EU- European Union

HR- Hazard Ratio

LNEG- National Energy and Geology Laboratory

MRV- Maximum Recommended Value

MAV- Maximum Acceptable Value

ORP- Oxidation Reduction Potential

PCA- Principal Component Analysis

RfD- Reference Dose

TOC- Total Organic Carbon

XRF- X-Ray Fluorescence

ZC- Shear Zone

ZCD- Douro Shear Zone

Chapter 1- Introduction

1.1. Open remarks

Mining is an ancient industry. The unique properties of ores obtained in this activity have enabled most modern life technologies to be developed. This industry contributed to infrastructure development, and the growth of various industrial activities and mining will continue to be necessary, so it must incorporate sustainable practices.

With today's knowledge and environmental awareness, work to restore soil and water health in former mining areas is of utmost importance. This activity contributes to the entire society at large, as it is not only about righting the wrongs of the past but ensuring a better environmental future. Usually, the effects of environmental rehabilitation of abandoned mines are not felt immediately but in the medium to long term

Montalto mine has not undergone any environmental rehabilitation since its closure in 1970 (Sousa, 2017). Due to the proximity of the population to the site where the mine was located, and the fact there is agricultural activity in and around that area, it was necessary to conduct this study.

1.2. Goals

This thesis was developed in the scope of part of a project entitled: "Soil health surrounding former mining areas: characterization, risk analysis, and intervention," with the reference NORTE-01-0145-FEDER-000056. The primary motivation for developing this work was to improve the environmental health of a former mining area by assessing the contamination of that area's water and soil resources.

In this dissertation, there is a practical component, which starts with sampling (sample collection, preparation, and storage), followed by laboratory work (physical-chemical characterization), and quantitative assessment of the state of the surface water, groundwater, and soil in the vicinity of the former Sb Montalto mine.

Chapter 2 – State of art

2.1. Environmental requirements

All activities during the operation of a mine are carefully considered. Environmental protection must be ensured at all stages of a mining operation, from before the opening of the mine to its closure, and after that, monitoring and site assessment visits must be conducted (Rodrigues, 2009).

Specific environmental regulations have been created for the mining industry to meet the requirements of mining and environmental legislation, for example (Fiúza, 2015):

- Environmental Impact Study (EIS),
- Socio-economic Impact Study,
- Environmental Management Plan,
- Environmental Monitoring Program,
- Environmental Audits,
- Rehabilitation Program,
- Compensation Measures,
- Control of Harmful Substances.

Environmental Impact Assessment (EIA) and Environmental Impact Study (EIS) were developed from the need to identify, predict, and assess the work done during the mining activity. EIA is a process of identifying, predicting, evaluating and mitigating the biophysical, social and other relevant effects of proposed developments before crucial decisions are made, and commitments are entered into (Fiúza, 2015). The EIS is a document resulting from the environmental impact assessment that describes the work performed and the conclusions reached (Fiúza, 2015).

2.1.1. Environmental risk assessment

In Europe, environmental risk analysis is understood as a scientific process that identifies, characterizes, and quantifies the potential adverse effects on human health or ecosystems resulting from exposure to single or mixed chemical compounds or chemically hazardous processes or situations (Fiúza & Vila, 2020). The US, EPA defines Environmental Risk Assessment as a process that evaluates the likelihood with which adverse ecological effects may occur because of exposure to one or more contaminants (Fiúza & Vila, 2020).

Environmental risk assessment is a systemic process that can be divided into (Fiúza & Vila, 2020):

1. Hazard identification- study of the contaminant concentrations at the source and screening of contaminants of concern,
2. Risk assessment- qualitative and quantitative assessment,
3. Risk management- eliminate or minimize the adverse consequences identified in the risk assessment by defining action strategies,
4. Risk communication- information exchanged with the affected individuals.

2.2. Hazards and effects of contaminants

There are hazards when there is a potential to cause harm or adverse effects. However, the exposure dictates the damage that can be generated (Fiúza & Vila, 2020). The risk of an impact on public health and the environment results from the existence of a hazard and exposure to the hazard. A risk does not exist if the exposure to a contaminant or to a particular hazard is non-existent (Fiúza & Vila, 2020).

EPA defines a contaminant as any physical, chemical, biological or radiological substance or matter that has an adverse effect on air, water or soil (Fiúza & Vila, 2020). Contaminant and pollutant are both used to describe chemicals found at levels considered higher than what would normally be expected (Fiúza & Vila, 2020). So, to determine a chemical pollutant two criteria are needed: its location and the amount present (Dunnivant & Anders, 2006).

Environmental contaminants can be originated from a natural process or human activities. Natural contaminants include emissions of particles and gases into the atmosphere from active volcanoes, forest fires, the presence of metals and metalloids in some rock occurrences or radioactive products resulting from the decay of uranium minerals (Fiúza & Vila, 2020).

According to their toxic effects, contaminants can be divided into carcinogens and non-carcinogens, teratogens and mutagens (Dunnivant & Anders, 2006).

Table 2.1. presents three examples of different compounds and their carcinogenic and toxic effects.

Table 2. 1. Carcinogenic and toxic effects of some contaminants. Source:(Fiúza & Vila, 2020).

Carcinogenic compound	Potential carcinogenic effects	Potential non-carcinogenic effects
Arsenic	Lung cancer	liver damage, neurological damage, and lung fibrosis
Cadmium	Lung cancer in animals	kidney damage, osteoporosis, and anemia
Chromium	Lung cancer	bronchitis, liver, and kidney damage

The potential carcinogenic and non-carcinogenic effects are different for each compound, such as the consequences from the exposure. In Table 2.2 the compounds are associated with the type of cancer that each one can cause. Some of the compounds like arsenic can, by itself cause various types of cancer.

Table 2. 2. Some contaminant induced carcinogenic effects. Adapted from:(Fiúza & Vila, 2020).

Carcinogenic compounds	Associated cancer types
Arsenic	Lungs, skin, hemangiosarcoma
Asbestos	Lungs, mesothelioma
Beryllium and its compounds	Lungs
Cadmium and its compounds	Prostate
Chromium VI	Lungs
Nickel	Nose, lungs

2.2.1. Toxicology

Toxicology is the science that studies the adverse effects caused by the exposure of living organisms to chemical compounds. To produce a toxic effect, the substance has to reach a target organ in sufficiently high concentration and for a certain period of time (Vila, 2014).

Toxicological effects can be (Fiúza & Vila, 2020):

- Immediate or slow acting
- Irreversible or reversible
- Local or systemic effects

The toxicity of metal(lois)s elements in ecosystems is dependent on several factors (Rodrigues, 2009):

- type (organic/inorganic; soluble/insolvable),
- dosage,
- metal exposure time,
- presence of other metals or elements (namely organic matter),
- environmental factors (temperature, pH, salinity, dissolved oxygen, light intensity),
- conditions of the organisms (age, size, life stage, etc.),
- behavioral responses,
- routes of entry of contaminants (ingestion, inhalation, or dermal contact),
- type of metabolic processes to which they are subjected.

The most comprehensive toxicological database today is the Integrated Risk Information System (IRIS), this database is updated monthly and managed by the National Library of Medicine in the USA (Fiúza & Vila, 2020).

2.3. Abandoned mines

Since a very early time, mankind has been using raw materials from the Earth, from copper, iron, gold, to diamonds. The dependence of ores has grown through time. Still, some other fields fail to keep up and help with this growth, such as law making for the mining industry and environmental concern, which led to this industry contributing to a lot of contaminations. Since there were no laws that forced companies to close mines properly when the activity at that site ceased, the mine would be abandoned, so now Portugal has many old mine sites to attend to and to correct the wrongdoing to the environment in those places (Fonseca, 2019).

There are more than 199 abandoned mining areas in Portugal according to EDM. Figure 2. 1 indicates all the licensed mines in Portugal, each color represents a different ore type. This map created by LNEG shows the diversity of ores spread throughout Portugal.

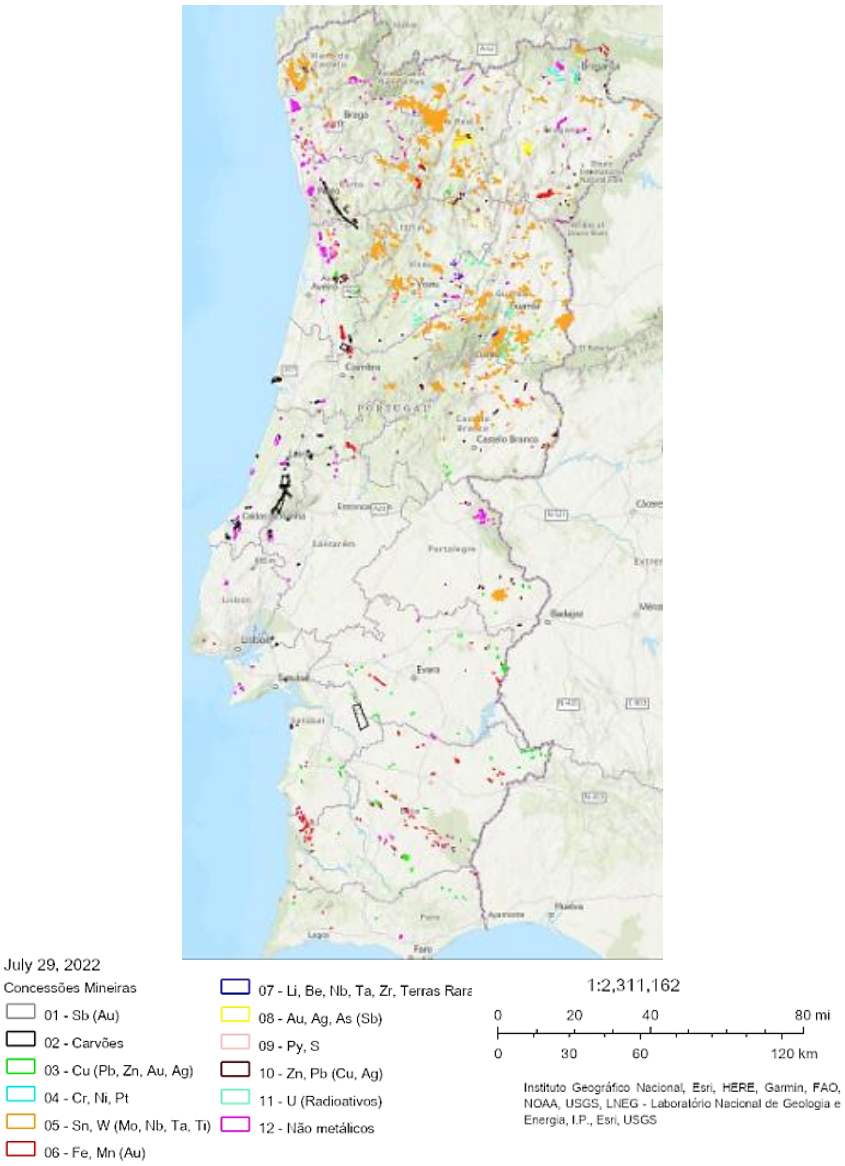


Figure 2. 1. Concession mines in Portugal. Source: Geoportal LNEG.

The mining industry continues to change, and governments keep setting emissions limits and standards for mining and processing operations. At this stage in time, specific legislation has been made in Europe (Fonseca, 2019).

2.3.1. Acid mine drainage

Environmental impact can originate from the mine waste and tailings, due to mineral leaching or to mine acid drainage. Oxidizing conditions are of particular concern in the case of the existence of sulfides, since their oxidation often promotes the occurrence of acid drainage, one

of the most severe environmental impacts related to mining activities (Fonseca, 2019). Acid production depends on numerous factors and is site-specific. Water and oxygen are necessary for the acid generation process. Water serves both as a reactant and transport for the reaction products, and oxygen maintains the oxidation, catalyzed by bacteria at pH below 3.5 (Fiúza, 2015).

In the case of acid drainage, soil and water are particularly affected by the dispersion and mobilization of metals/metalloids (Fonseca, 2019). Contrary to organic contaminants, these are not degradable.

2.3.2. Mining impact on water

The mining impact on water can be from:

- Chemical contamination- reflected by the change in the composition, may affect both surface watercourses and aquifers (Fiúza, 2015).
- Physical contamination- mainly affects surface water, resulting from the entrainment of fine sediments (Fiúza, 2015). The contamination by suspended particles severely affects the fish population.

Some of the parameters that allow a qualitative and quantitative assessment of the extent of the impact, in relation to universally accepted or normatively established, are found in Table 2.3 for both surface water and groundwater.

Table 2. 3. Surface and groundwater impacts and indicators. Adapted from: (Fiúza, 2015).

	Impact	Indicators
Surface Water	Change in quality	pH, dissolved oxygen, BOD, COD, heavy metals, organic compounds, temperature, suspended solids
	Hydrogeological cycle	Evapotranspiration, infiltration, runoff
	Flow alteration	Number of watercourses intercepted
Groundwater	Aquifer depression	Piezometer level variation
	Quality	pH, heavy metals, organic compounds

The measurements of these indicators can be done *in situ* and later in the laboratory, the methodology of some of these procedures will be discussed in chapter 4, only the indicators that best fit the case study timeline and goal will be studied.

2.4. Antimony

Antimony (Sb) is a chemical element of the eleven group of the periodic table (semi-metals). This element is non-ferrous, with no capacity for conducting electricity or heat. Table 2. 4 presents antimony's main physical and chemical characteristics (Batista, 2016).

Table 2. 4. Antimony physical properties. Adapted from: (Batista, 2016).

Antimony Physical Properties	
Atomic number	51
Atomic mass *[g]*	121,760
Density/ Volumic mass *[g/*cm^3*]*	6,691
Hardness [Mohs]	3
State *[300K, 1atm]*	Solid
Fusion Point *[ºC]*	630
Magnetic State	diamagnetic

Based on economic importance and supply risk, the EU's list of Critical Raw Materials (2020) classifies antimony as one of the critical raw materials for the EU, this semi-metal is featured in this list since 2011 (European Commission, 2020).

There are more than two hundred minerals with antimony (Sousa, 2014). Sb can be found in different chemical species, in the Table 2. 5 are presented some examples separated in five different group.

Table 2. 5. Common chemical species of Sb. Adapted from: (Sousa, 2014).

Groups	Phase	Species	Chemical Formula
Group 1	**Solid**	**Minerals**	Stibnite (Sb_2S_3), Valentinite (Sb_2O_3), and Cervantite (Sb_2O_4)
Group 2	**Liquid**	**Water species (Oxidation state +5)**	$Sb(OH)_5$ $Sb(OH)_6^-$ (or SbO_3^-)
Group 3		**Water species (Oxidation state +3)**	$Sb(OH)_3$ (or $HSbO_2$) $Sb(OH)_2^+$ $Sb(OH)_4^-$ $H_2Sb_2S_4$ $H_2Sb_2S_4^-$
Group 4	**Gas**		SbH_3 $Sb(CH_3)_3$

In nature the oxidation states of antimony are Sb (III) and Sb (V). Sb (III) has a bigger stability field (Batista, 2016). Antimony can be shiny, silvery, hard or brittle and in a non-metallic form as a gray powder (Sousa, 2014).

Sb_2S_3 (stibnite) has 71,7 % of Sb and is the mineral that represents the most economic interest (Silva, 2017). Sb_2S_3 can be dissolved and release Sb in oxidizing conditions (Cappuyns et al., 2021).

In the 19^{th} century, the blend between antimony and tin was used in several objects such as candlesticks, tableware, cutlery, among others. Later in the 20^{th} century Sb was applied in the coat of cables, ceramics, glass, plastics and to pigments in the manufacture of paints, among others (Batista, 2016). Nowadays, antimony is mainly used in flame retardants, lead-acid batteries, lead alloys, plastics, glass and ceramics (European Commission, 2020).

2.4.1. Hazards of Sb

Exposure to antimony may occur by air inhalation, drinking water and food intake (Tao et al., 2021). The most common reaction is respiratory irritation, pneumoconiosis, spots on the skin, gastrointestinal symptoms; and antimony trioxide can be carcinogenic to humans (Cappuyns et al., 2021). The toxicity of antimony varies, Sb (III) compounds are usually ten times more toxic than those of Sb (V), and organic antimony species are less toxic than inorganic antimony species (González-Alvarez et al., 2012).

Each deposit has specific characteristics, depending on the geology and formation. Sb can be associated with different ores, such as Au or As (Rodrigues, 2009). The presence of these

elements individually represents a hazard, so this type of diversity must be taken into consideration when calculating the potential of contamination that may be originated (Rodrigues, 2009).

The primary sources of pollution from Sb are metalliferous ore mining and smelting industries (Cappuyns et al., 2021). All the products that contain Sb are also contributing to Sb contamination. Sb can also be released to the environment from non-anthropogenic activities, just by natural processes (Tao et al., 2021).

Chapter 3- Montalto mine

3.1. Geographic and historic setting

Montalto mine is located in the Porto district, municipality of Gondomar, in Covelo area (Sousa, 2017). More precisely, on the right margin of Sousa river (Silva, 2017). The underground mine was opened in 1864 by António Martins Henriques with an area of 117 hectares (Silva, 2017).

Between 1879 and 1889 it produced 2833 tons of antimony and 136 tons of quartz (Sousa, 2017). In 1881 this mine was the most productive of the region (Couto, 2014), and in 1890 the company was sold to the German company Goldbergban am Duero (Silva, 2017). The mine became known in national and international markets for the quality of the ore, and it got awards in several exhibitions (Silva, 2017). In 1970 all activities were ceased (Sousa, 2017).

Figure 3. 1 has a representation of all the different types of land that exist today. The red rectangle indicates the mine location, which is clearly in agricultural land.

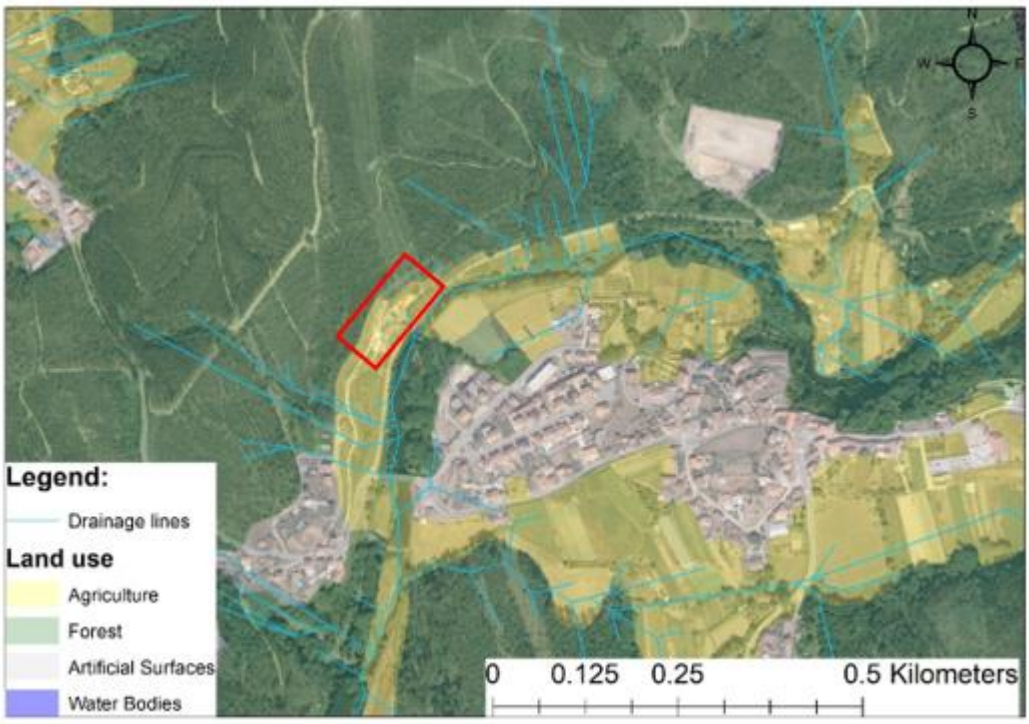


Figure 3. 1. Categories of the fields around the former mining area.

Most land in the Covelo area is agricultural or forest land, agricultural activities are prevalent in the area.

Since the mine's closure, 52 years have passed. According to the latest censuses of 2011 and 2021, the population in the region decreased. Figure 3. 2 has two graphs. On the left graph, it is possible to observe a decrease in several age groups, except for 65-plus which has increased. The right graph shows that a decrease occurred in both genders (INE, 2021).

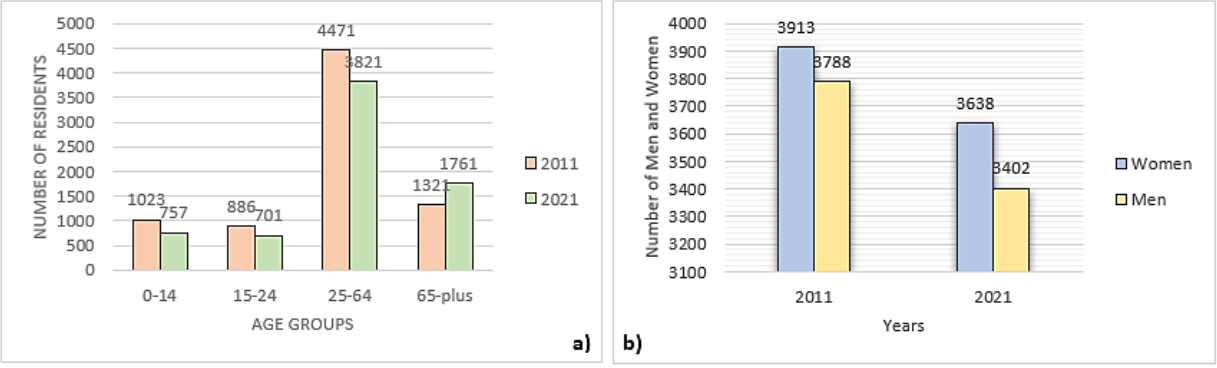
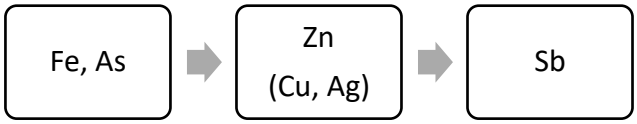


Figure 3. 2. R*esident population of Foz do Sousa and Covelo a) resident population by age group. b) resident population by gender. Adapted from:* (INE, 2021).

3.2. Local geology

Montalto deposit is located on the western flank of Valongo anticline (Silva, 2017). Formation age in this area occurs from Precambrian/Cambrian to the Carboniferous (Couto, 1993a). The deposit paragenesis is Sb-Au with the mineralogical succession of (Couto, 1993a):



In Montalto unit, there are three main lithological associations. The lower lithological association is formed by gray schist, acid volcanic rocks, greywacke and violet schist. The intermediate lithological association is formed by grey laminated sandstone, grayish schist and schist with kaolinite. The superior lithological association is formed by conglomerates with essentially quartz, sandstone with quartz, siltstone with quartz and diabase.

Figure 3. 3 has the stratigraphic column of Montalto where the three-unit referred to previously, are represented.

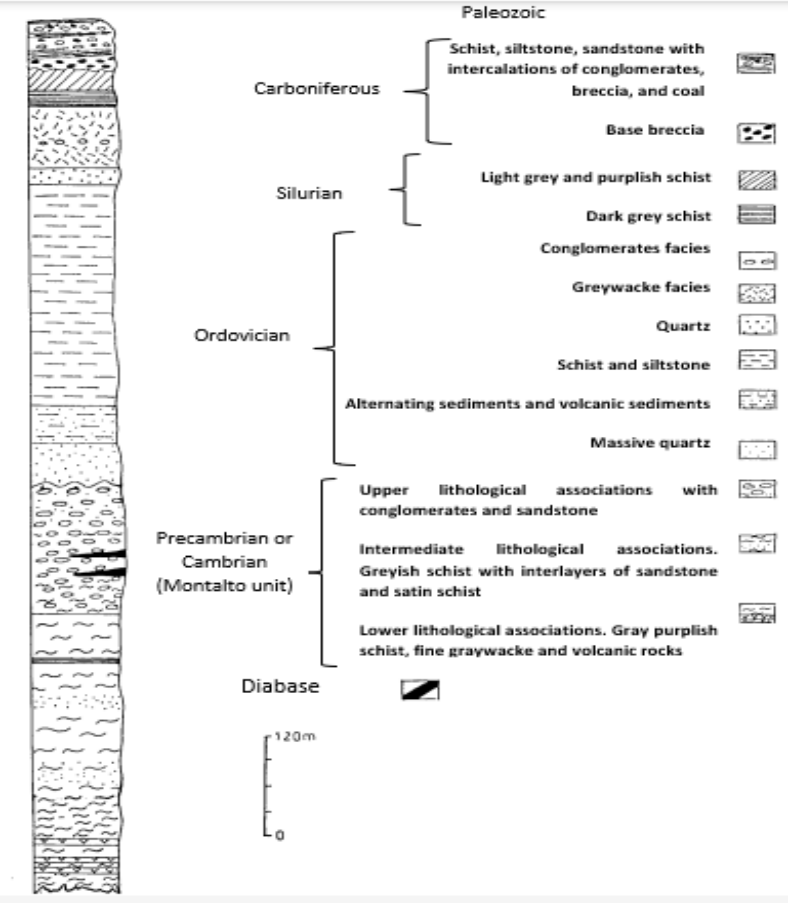


Figure 3. 3. Stratigraphic column of Montalto. Source: (Couto, 1993a).

3.2.1. Structure and Metamorphism

Montalto is within a complex schist greywacke area that has two major shear zones, Douro Shear Zone (ZCD) and Shear Zone (ZC) Sta Justa. Montalto is also affected by an NNE-SSW fault system. The orientation of the primary cleavage in the Montalto unit varies in a hand fan shape, increasing to the west of the mine (Couto, 1993a).

The anticline is a mega structure consisting of geological formations (strata) of different ages, tectonized and metamorphic (Gonçalves, 2013).

The metamorphism in the Montalto unit seems higher than in the southern area, where sedimentary structure is more preserved and the primary cleavage is less present (Terramonte unit) (Couto, 1993a).

3.3. Hydrographic system

This area is in the hydrographic basin of the Douro River, which is developed over an extensive area. This basin has a hydrological domain consisting of nineteen secondary basins. One of these secondary basins is the Sousa River (Gonçalves, 2013).

Figure 3. 4 allows for the visualization of the water lines found in the study site, where the Sousa River that flows into the Douro River passes right in front of the site where the mine was located, indicated by the red circle. The other watercourses that flow into the Sousa River pass through places of great interest for the study in terms of the potential contamination.

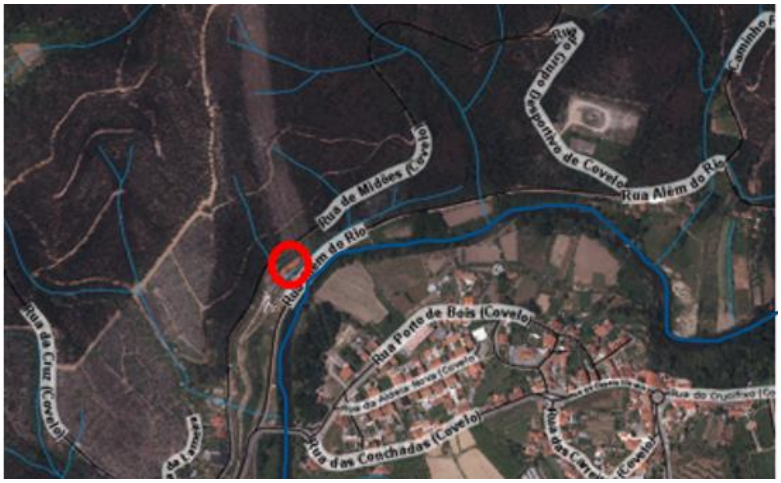


Figure 3. 4. Hydrographic system of the site under study. Source: (Gondomar, n.d.).

The groundwater productivity is mainly affected by fractures and tectonic aspects (faults, veins, and shear). The hydrogeological unit is fissured, leading to sub confined (aquitard) and confined (aquifer) formations. According to the Portuguese hydrogeological map, the Valongo anticline, in terms of aquifer capability, is classified as scarce (<1 L/s per km^2), only areas with quartzite from the lower Ordovician have a higher aptitude (1 a 3 L/s per km^2) (Gonçalves, 2013).

3.3.1. Hydrogeochemical importance

Hydrogeochemical studies the pH, temperature, electrical conductivity and chemical composition of groundwater with the aim to explain the natural or anthropic origin of different mineralization, their path, storage conditions, and the distribution of water points. These must

relate with the geology and population areas to identify possible sources of natural or anthropic contamination (former mining). Hydrogeochemical studies make it possible to create a link between underground hydraulics, the geochemistry of the region and abandoned mining operations (Gonçalves, 2013).

In the vast mining domain of the Dúrico Beirão Mining District, there are metallic mineralogical associations and a history of coal and slate mining. However, even when there were no mining operations, groundwater was already subject to the influence of the geology and geochemical background of the region. (Gonçalves, 2013).

3.4. Local climatology

The northern coast of Portugal, where the Valongo anticline is located, fits into an oceanic climatic context, more specifically in the Atlantic Bioclimatic domain. This area suffers a tremendous maritime influence. The climate in this area is generally mild, with high atmospheric humidity that oscillates throughout the year (Gonçalves, 2013).

The northern region of Portugal is rainy, especially in the mountainous areas, and the atmospheric humidity varies near the ocean, therefore there is an increase in atmospheric humidity (Gonçalves, 2013).

The x-axis in Figure 3. 5 identifies the years analyzed. The y-axis contains the average temperature in ºC.

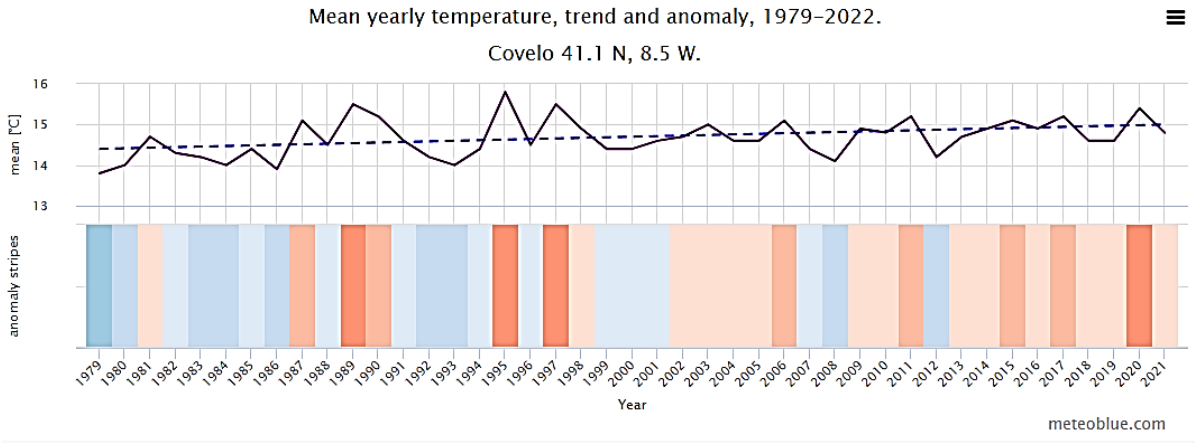


Figure 3. 5. Graphic of the mean yearly temperature, trend, and anomaly, 1979-2021, for the study area (Covelo). Source: (Meteoblue, n.d.).

If anomalous temperatures are detected, they are identified by a color system. The slope of the line, of the average temperature, is not very steep although it tends to increase over the years. Thus, the difference in the temperature between 1970 and 1979 would not be significant. In 1970 it would be somewhat lower.

The precipitation graph in Figure 3.6. is identical to the temperature graph but identifies the rainfall occurred from 1979 to 2021.

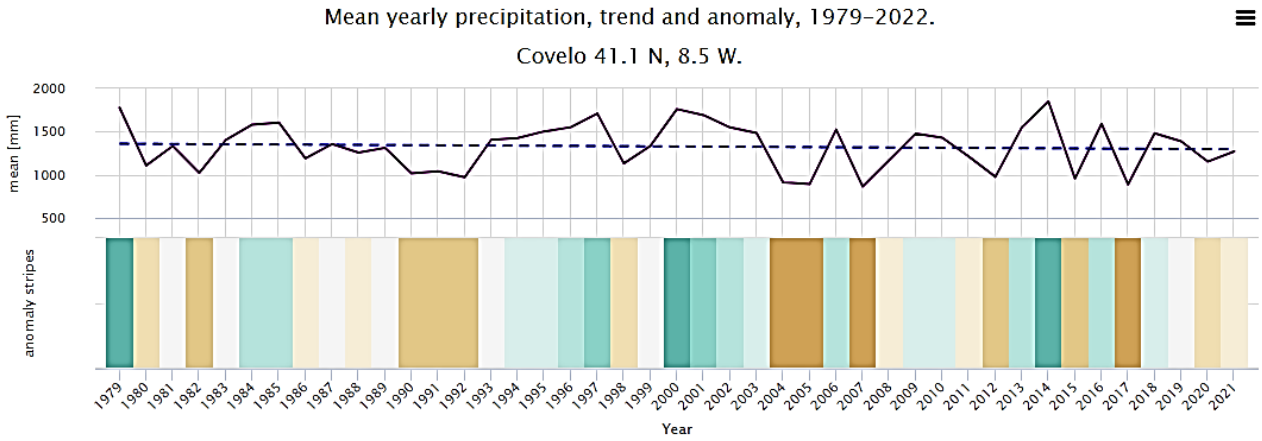


Figure 3. 6. Graphic of the mean yearly precipitation, trend, and anomaly, 1979-2021. Source: (Meteoblue, n.d.).

The x-axis of the graph in the Figure 3. 6 has the years analyzed, and the y-axis the average precipitation, and if anomalies were detected they are identified by a color system. The slope of the line, of average precipitation, visually does not seem to show changes as the amount of rain has not had a significant change over the years, and in fact decreases more in recent years. Thus, the difference in precipitation between 1970 and 1979 would not be substantial. In 1970, it might have been slightly higher.

3.5. Mining exploitation

In 1863 mining began, with only antimony being mined until 1881, then gold also began to be mined. The exploition was done in vertical shafts that could reach between 37 and 160 meters in depth and a horizontal radius of up to 700 meters (Sousa, 2017). Three galleries, Sto. Agostinho, S. João, and Sto. António and a master well have been identified (Couto, 1993a).

The longitudinal profile in Figure 3.7 of the underground mine shows the three galleries, the master well and the advances made on each floor.

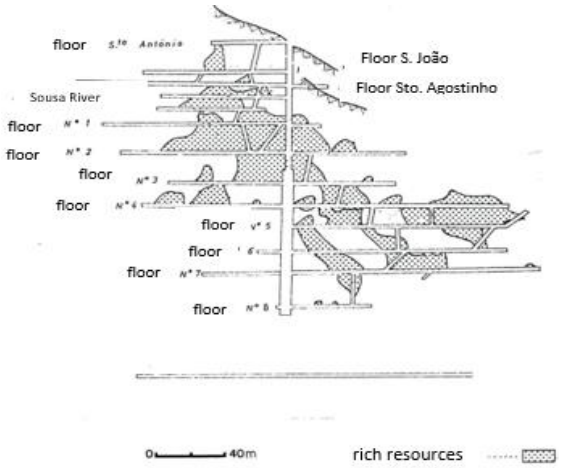


Figure 3. 7. Longitudinal profile of the underground work at Montalto mine. Adapted from: (Couto, 1993a).

The ore extracted was selected from within the excavation and transported by a mine car on iron rails to the main shaft, from where buckets were loaded and lifted to the outside by a hydraulic wheel (Sousa, 2017). According to the industrial survey of 1890 this mine had a hydraulic wheel with 30 steam horsepower, a turbine with 27 steam horsepower, two fixed steam engines with a strength of 32 horsepower and a mobile one with 14 horsepower (Silva, 2017). The mine harnessed the motive force of the Sousa River water (Silva, 2017).

In the first gallery occurs the first grayish colored quartz, poorly mineralized and filled by white quartz mineralized with stibine (Couto, 1993a). In other parts, the quartz shows oxidations, probably from sulfides. From floor five onwards, small gold flakes and gold threads appeared, accompanied by crystals of sphalerite, pyrite, iron and nacrite (kaolinite group). On the sixth floor, there were gold nuggets that reached 12 g (Couto, 1993a).

Between 1864 and 1888, the exploitation reached a depth of 190 m and an extension of 225 m, which corresponds to a production of approximately 6763 tons of stibine (Couto, 1993a). The most productive mineralization was observed at more than 100 m depth (Couto, 1993a).

3.5.1. Ore processing

In Montalto, there were occurrences of antimony, gold, stibine, pyrite, arsenopyrite, limonite, sphalerite, chalcopyrite, bornite, covellite, rutile and argentiferous gold. This mine had a great length and mineralization contents (Couto, 1993a). The Sb content would be 0.2 % or higher, Ni, Co, and Cu less than 0.2 %, and the gold content would range from 5 g/t in the schist, increasing to 60 to 180 g/t in the stibine samples, reaching the maximum content in the white quartz with gold nuggets containing 90 to 500 g/t. Until 1889 production was approximately 13 kg of gold. Gold could be associated with silver, stibine or both. The silver contents vary between 20 to 460 g/t, with a total production of 7 kg (Couto, 1993a).

The material removed from the mine, after reaching the surface, was sent to the mechanical separation zone where trommels of different aperture sizes sorted the material according to its diameter. The hydraulic sieves, of different sizes, sorted the material according to the density levels and finally the ore was subjected to a washing process (Sousa, 2017). In total there were 2 crushers, 6 trommels, 1 continuous elevator, 6 sieves and a centrifugal pump (Silva, 2017).

The final product would be the concentrate, antimony, that then was stored in wooden barrels which were taken by oxcarts to the Lixa beach, where it was shipped by boat along Douro River to the city of Porto, where it then could be exported to other countries such as England (Sousa, 2017).

Chapter 4- Materials and methods

4.1. Initial survey

The first step to perform the environmental risk analysis, as mentioned, is hazard identification. Is assessed whether a potentially contaminated site poses a danger to human health or the environment (Fiúza & Vila, 2020). First, was necessary to sample and study the area.

The first map studied was the geological map in Figure 4. 1. From this map, it was possible to know where the galleries were located, where the exploitation was done, and where the tailings were placed. These places are significant since they are most likely, to have higher contamination values.

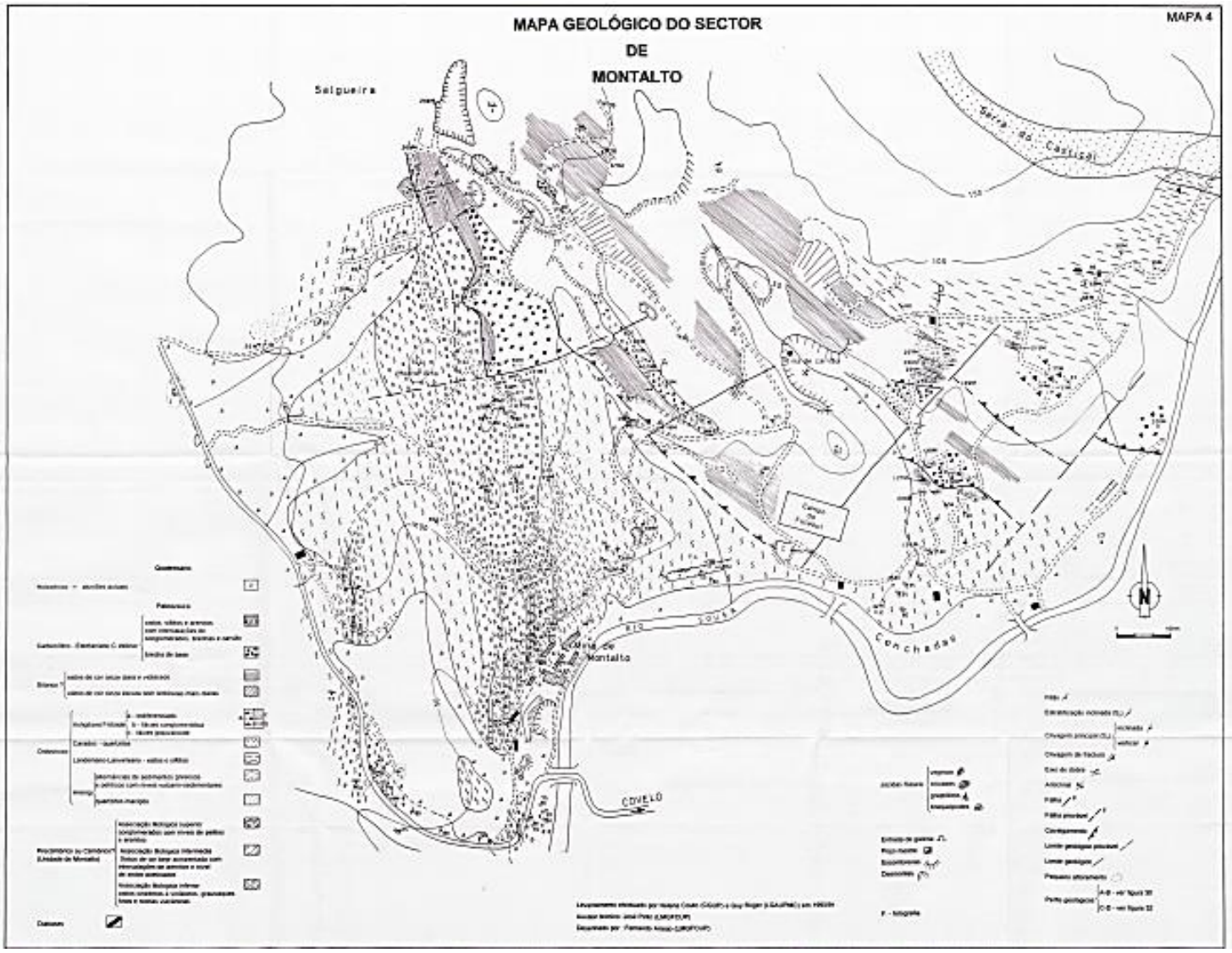


Figure 4. 1.Geological map of Montalto. Source: (Couto, 1993b).

The initial goal was to verify:

- Existence of toxic contaminants,
- Concentrations of contaminants,
- Contaminated places where there is human exposure,
- Contamination in sensitive environments.

4.1.1. Selection of the sampling locations

The sampling location was chosen using judgment sampling, so chosen based on knowledge held, after the study of maps, the area in self, and the history behind that area (Pennock et al., 2008). Due to the site's proximity to the Sousa River, it is necessary to collect water samples from the river. The river flow is mainly considered turbulent since a chemical mix is always produced over a considerable distance (Fiúza & Vila, 2020).

Eleven soil samples (S1, S2, S3, S4, S5, S6, S7, S8, S9, S10, S11), and ten water samples (W1, W2, W3, W4, W5, W6, W7, W8, W9, W10) were collected, at the locations indicated in Figure 4. 2.

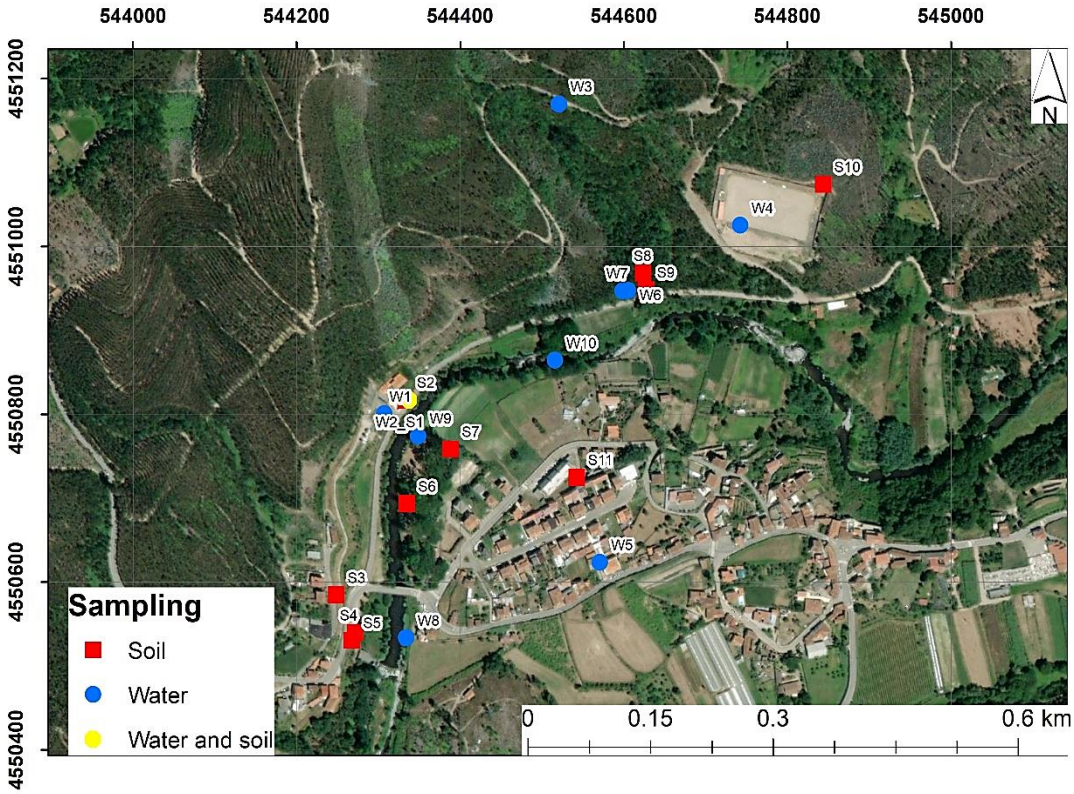


Figure 4. 2. Water and soil sampling locations.

The results obtained from the physical-chemical analysis of the water samples provided information that was used to select the locations for the second water sampling.

4.2. Soil samples

The eleven samples collect are from superficial soil (5-15 cm depth). They were placed in separate bags (Figure 4. 3 A), properly identified (reference name, date), and then taken to the laboratory where the soil samples were studied. Each sample was studied for its granulometry (Figure 4. 3 C and E), and chemical composition (Figure 4. 3 B and D).

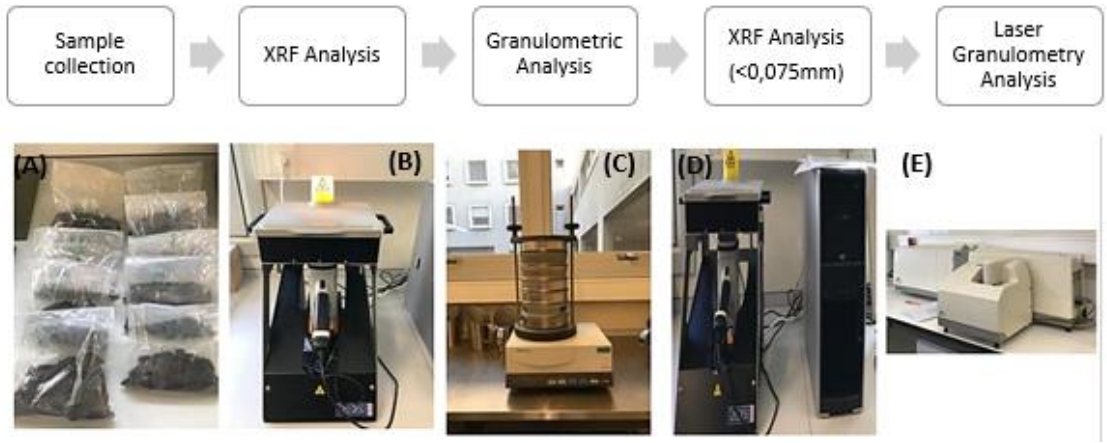


Figure 4. 3. Sequence of laboratory work starting with (A) the collection of samples, then (B) elemental chemical analysis by x-ray fluorescence, (C) particle size analysis, (E) granulometry analysis by laser diffraction- wet process, and (D) elemental chemical analysis by x-ray fluorescence.

Firstly, it is possible to do a visual analysis (Figure 4. 4): there is an array of colors, which is an initial indicator of the diversity of the sample.



Figure 4. 4. Eleven different soil samples.

After the samples were collected, they were weighted and dried. The water content was calculated by subtracting the dry sample weight to the sample weight and divide by the sample weight.

4.2.1. Chemical analysis

The chemical analysis was performed by the XRF equipment Oxford Instruments, model XMDS2726 (Figure 4. 3 B and D), using the mining mode.

Each sample was examined three times to ensure accuracy. Each time, the sample bag was stirred and placed again in the equipment. The analysis report has the three readings and the average and standard deviation obtained for each element in the eleven samples.

4.2.1.2 Statistical analysis

Spearman is a non-parametric method that measures the monotonic association between two variables (Laerd statistics, n.d.). This method doesn't require a normal distribution or that the absence of outliers is ensured (Laerd statistics, n.d.). The main reason for choosing the Spearman rank correlation was that it is suitable for variables that don't have a linear behavior.

The Spearman correlation was used on the data collected from the element chemical analysis. To calculate the Spearman correlation was used the software XLSTAT, which is a data analyzer and statistical solution for Microsoft Excel with several features available. With this tool, it was possible to obtain two matrices, one for the Spearman correlation and the other for p-values.

The p-value, which is a probability that measures the evidence against the null hypothesis (H0).

H0 = There is no association between the elements.

A smaller p-value provide stronger evidence against the null hypothesis. So, the p-value is used to determine whether the correlation coefficient is statistically significant (Minitab, 2021).

Being the significance level 0.05, and a level of confidence of 95% (Minitab, 2021):

- p-value ≤ 0.05: the correlation is statistically significant.

In this case the H0 must be rejected. It is also possible to conclude that the correlation is statistically significant.

- p-value ≥ 0.05: the correlation is not statistically significant.

H0 can be accepted, there are not enough evidence to conclude about the correlation is statistically significant.

This statistical analysis allows studying the relation between all the elements detected, and to understand if their appearance has some correlation.

4.2.2. Particle size analysis

Particle size analysis determines the size of the particles in a sample (Leite, 1987). The sieves were selected based on the Tyler series (Leite, 1987), from the 0.075 mm sieve using a multiplication factor ($\times \sqrt{2}$), the mesh size of the following sieves was determined.

Since there were a lot of sieves to do a single series, they were separated into two series, Figure 4. 5, the material under 0.600 mm was used in the second series.

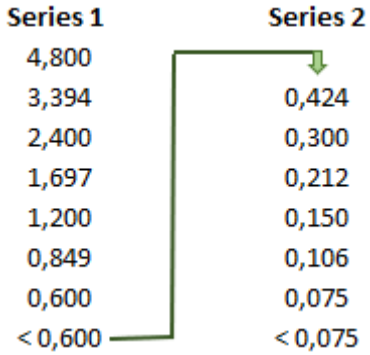


Figure 4. 5. Two series used in the granulometric analysis

The sieving process occurred for fifteen minutes with an amplitude of one mm/"g" using the equipment showed in Figure 4.6.



Figure 4. 6. Sieving equipment, Retsch AS 200 with one of the series.

The sieving analysis was carried out for particles larger than 0.075 mm. For particles smaller than 0.075 mm, the analysis was performed for the eleven samples, with the granulometer laser Malvern, MS2000 HydroG (Figure 4.7).

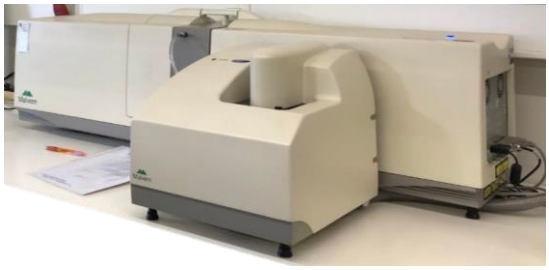


Figure 4. 7. Granulometer Malvern, MS2000 HydroG.

In each analysis, a minimal amount of sample was added to the water until it showed on the monitor that no more needed to be added. A report was automatically produced for each sample, by the program, with a table and a graph with the particle size (µm) classes and the volume (%) of particles within each that size class.

4.2.3. Soil pH determination

The pH in the water indicates the active acidity (Dinis, 2018). In this procedure, distilled water is added to dissolve the salts present in the samples. The measured pH value is usually 0.2 to 0.5 units higher than natural water. One way to overcome this problem is to use a solution of $CaCl_2$ with 0.01 M (Dinis, 2018).

In this experiment, 20 g of soil were used and added with 20 mL of distilled water (Figure 4. 8), stirred for 20 minutes (Figure 4. 9 a) and rested for 30 minutes. Subsequently, the pH of the clarified liquid fraction was measured (Figure 4. 9 b). In another beaker, 10 g of the same soil (Figure 4. 8), were added to 20 mL of $CaCl_2$, stirred for 20 minutes and then after resting for 30 minutes the pH of the clarified zone was measured. The same procedure was repeated for all samples.

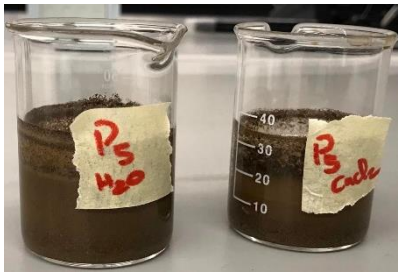


Figure 4. 8. Beaker on the left has soil with distilled water and beaker on the right has soil with $CaCl_2$.

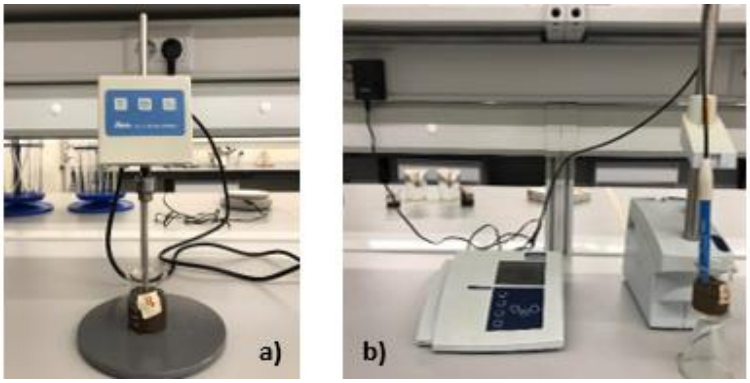


Figure 4. 9. a) Nahita mechanical rod stirrer 686/1. b) Measurement of pH, with WTW, inoLab pH Level 1, in the clarified fraction

4.2.4. Soil organic carbon and organic matter

Different forms of carbon can be in the soil. The soil stores more carbon than the atmosphere and plants combined (Queensland Government, 2022). Organic carbon includes soil organisms and microbes, decaying plant matter, proteins, carbohydrates, resins, and organic acids (Queensland Government, 2022).

Organic matter and organic carbon are important indicators of soil health. The organic matter supplies especially nitrogen, phosphorous, and sulfur. Additionally improves soil structure as well as the soil's ability to hold water and resist acidification (Queensland Government, 2022).

To determine the percentage of organic carbon in the soil was applied the Walkley-Black direct method. In this direct method, all inorganic carbon is initially removed by acidification of the sample, and subsequently, the organic carbon is decomposed into CO_2. Organic carbon is oxidized by dry or wet combustion or chemical oxidation (Vila, 2021). The Walkley-Black method does chemical oxidation by using potassium dichromate with a concentration of 0.167 mol/L,

which is a powerful oxidizing agent (Eq.1). The excess dichromate ensures complete oxidation of the organic material (Vila, 2021).

$$3C + 2Cr_2O_7^{2-} + 16H^+ \rightarrow 4Cr^{3+} + 8H_2O + 3CO_2 \qquad Eq.\ 1$$

After the reaction has occurred, the excess dichromate is titrated with a 0.5 mol/L solution of ferrous sulfate (Eq. 2) to quantify the amount of dichromate used with the carbon (Vila, 2021).

$$Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \rightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O \qquad Eq.\ 2$$

The sample size varied between 0.2 to 1 g of milled soil (Figure 4. 10 a) since the amount of organic carbon in each sample is different. It was added, to the soil, 5 mL of potassium dichromate, 10 mL of sulfuric acid, 15 mL of distilled water, and three drops of Ferroin (Figure 4. 10 b). The titration (Figure 4. 10 c) was done with ferrous ammonium sulfate solution.

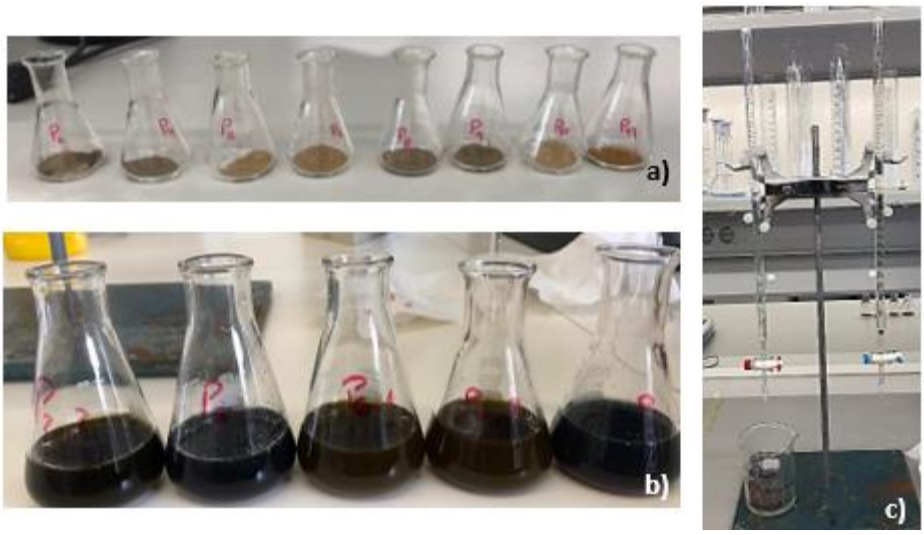


Figure 4. 10. a) Soil used in each sample. b) After adding all the solutions. c) Titration equipment.

The percentage of organic carbon and of organic matter in the soil was calculated with the following two equations.

$$\text{Organic carbon [\%]} = \frac{(\text{meq } K_2Cr_2O_7 - \text{meq } Fe(NH_4)_2(SO_4)_2) \times \left(0.003 \frac{\text{meq}}{\text{g}} \text{-C}\right) \times (100) \times f}{\text{g} \times \text{soil}} \qquad Eq.\ 3$$

$$f = 1.33 \qquad \text{Organic matter [\%]} = 1.7 \times \text{organic carbon [\%]} \qquad Eq.\ 4$$

4.2.5. Natural dynamic leaching tests

Natural leaching is used to determine the behavior of a substance during the physical and chemical phenomena that occur during percolation (Nunes, 2015). Thus, this experiment seeks to reproduce in the laboratory the dilution phenomena that happens by the passage of water through the soil (Nunes, 2015). Natural dynamic leaching represents the natural long-term leaching phenomenon.

When the dynamic leaching occurs there's a simultaneous displacement of the solid and liquid phases when in the agitated reactors (Fiúza, n.d.). The agitation must be intense enough to prevent creating static areas or weak pulp movement (Fiúza, n.d.).

Natural leaching depends on temperature, the type of solution used to do the leaching, the relation between the amount of soil and leaching solution, the specific surface of the soil particles, and the agitation velocity used (Nunes, 2015). For this leaching process, it was used 50 g of soil, and 500 ml of distilled water. The stirring was performed by a magnetic agitator (Figure 4. 11 a) for 24 h at 200 rpm speed. After 1 h, 3 h, 12 h, and 24 h the pH, Eh, and conductivity were measured. Lastly, a filtration was performed (Figure 4. 11 b). The liquid part obtained (Figure 4. 11 c) was further analyzed using atomic absorption and the solid part was analyzed by X-ray fluorescence(XRF).

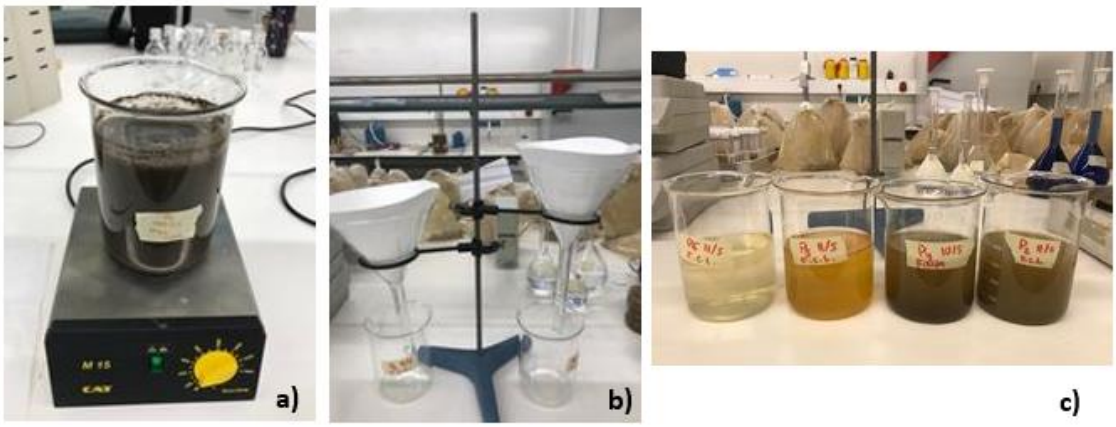


Figure 4. 11. Leaching process, a) stirring with magnetic agitator, b) filtering process, c) filtered solution.

The report that XRF equipment creates has the content (Eq.5) of each element found in the sample.

$$Content\ [\frac{mg}{kg}] = \frac{Mass\ of\ element}{Mass\ of\ soil} \qquad Eq.\ 5$$

The quantity of soil analyzed after the leaching process is approximately the same as before the leaching. The analysis of content for each element is representative of the whole sample, however, is important to highlight that the average is a statistical parameter that is very influenced by extreme values.

4.3. Water samples

The exposure to water and its components can occur through ingestion, dermal absorption during showers or swimming, food consumption (irrigated with surface water), and fish consumption (Fiúza & Vila, 2020).

The water samples were collected in two stages. Firstly, on the 18 of April ten water samples were collected from the locations indicated in the Figure 4. 2, by the SHS project research team. The samples were stored in plastic bottles (Figure 4. 12 A), when in the laboratory they were kept in the fridge. The samples from the river were collected with a bucket (Figure 4. 12 B), due to the distance from the margin river to the water.



Figure 4. 12. Water sampling. A) Plastic bottles to store the water samples. B) Bucket to collect samples from de river.

On the 26th of May thirteen samples were collected by an accredited external laboratory, ALS LIFE SCIENCES PORTUGAL, S.A.. Fifteen sampling points were chosen, adding five new points to the first sampling plan. However, physical barriers that arose in the meantime, only allowed the laboratory to collect thirteen samples. So, three new sampling points were added to the

previous sampling campaign, W_11 which was collected in a lagoon, W_14 and W_13 that were collected in the Sousa River (Figure 4. 13).

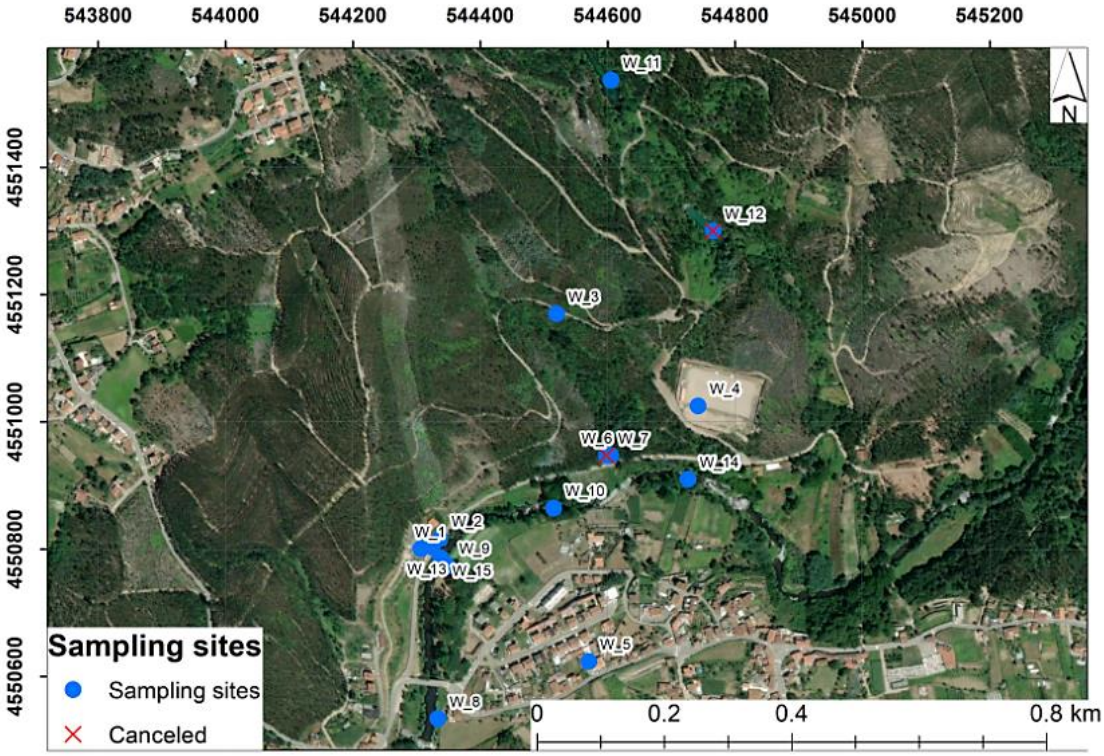


Figure 4. 13. Map of the second sampling locations.

There are six groundwater samples: W_1; W_2; W_3; W_4; W_5; W_13. The remaining samples are superficial: W_6; W_8; W_9; W_10; W_11; W_14; W_15.

4.3.1. Physical-chemical parameters

On the 18 of April to measure the dissolved oxygen, pH, and conductivity, in the field and in the laboratory, it was only necessary to introduce the sensors into the sample, after a moment the value stabilized, and it was registered.

In the field the measurements were made with portable devices (Figure 4. 14 a)):

- Dissolved oxygen (Figure 4. 14 b)): Hanna instruments, HI9146.
- pH (Figure 4. 14 c)): WTW 3210 SET 2.
- Conductivity (Figure 4. 14 d)): WTW 3110 SET 1.



Figure 4. 14. a) Portable measure devices. b) Dissolved oxygen equipment. c) pH equipment. d) Conductivity equipment.

In the laboratory the measurements were made with:

- Dissolved oxygen (Figure 4. 15 a)): WTW, inoLab Oxi Level
- pH (Figure 4. 15 b)): WTW, inoLab pH Level 1.
- Conductivity (Figure 4. 15 c)): WTW, inoLab Cond Level 1.

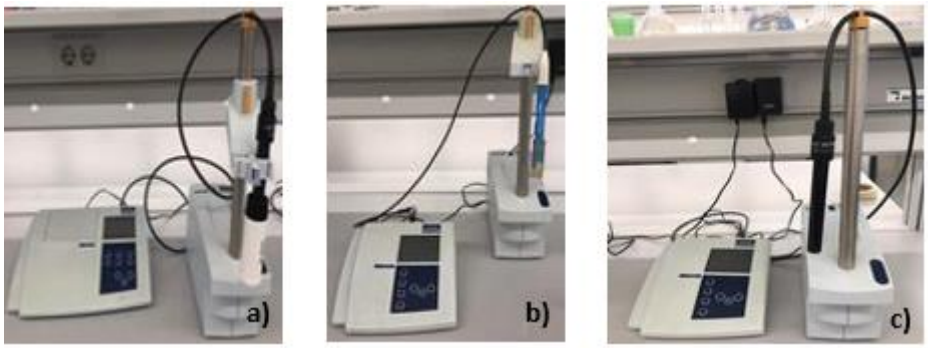


Figure 4. 15. Laboratory equipment. a) Dissolved oxygen equipment. b) pH equipment. c) Conductivity equipment.

The ALS LIFE SCIENCES PORTUGAL, S.A.. laboratory sample process followed the ISO 5667-5:2006.

4.3.2. Chemical analysis of main inorganic ions

Four elements were chosen to be analyzed with the Analytik jena, ZEENIT 700 P (Figure 4. 16), Fe, Pb, Cu, and Sb. All were found in the elemental chemical analysis described in 4.2.1.



Figure 4. 16. Analytik jena, ZEENIT 700 P equipment.

To be able to analyze the four elements the first step was to establish calibration curves for each element. Different concentrations were selected and using standard solutions, six solutions were prepared for each. After the program read all the solutions and created the curve is ready to start analyzing the water samples. First the eleven water samples were analyzed, then the liquid part resulted from the leaching process (referred in 4.2.5.1). The program creates separate reports for each element with the concentration [mg/L] found in each sample.

The ALS LIFE SCIENCES PORTUGAL, S.A.. laboratory analyzed sixteen elements: Hg, Ca, Mn, Cu, Zn, Pb, Cd, Ni, Al, As, Sb, Se, Na, K, Mg, and Fe.

4.3.3. Water statistical analysis

A principal component analysis (PCA) was performed, using XLSTAT, on the results obtained in the second sampling made by the ALS laboratory, with the intent of reveling the correlation between variables, and samples.

PCA is a statistical methodology for multivariate exploratory data analysis, when no pattern of causality is known *a priori*, allowing to correlate the observable variables with non-observable hidden variables, which are responsible for the global behavior and compressing and retaining the essential information (Fiúza et al., 2019).

4.3.4. Risk characterization

It was performed an analysis of the risk of exposure to the elements whose concentrations in water (surface and/or groundwater) exceed the recommended values for drinking water which

were four metals/metalloids (As, Sb, Mn, and Zn). Of these, only arsenic is classified as a carcinogen. All four have toxic effects. The sample W_1 has high concentrations in these elements and is located on the property where a family is currently living. This water is likely to be in contact with humans by ingestion or dermal contact. The concentration used in the calculations is from this sample.

First was calculated the dose in case of water ingestion using the formula proposed by the Agency for Toxic Substances and Disease Registry (Eq. 6), to estimate the exposure dose resulting from contact with a contaminated medium:

$$D = \frac{(C \times IR \times EF)}{BW} \qquad \textit{Eq. 6}$$

where D is the exposure dose (mg kg^{-1} day^{-1}), C is the average concentration of the contaminant in water (mg L^{-1}), IR the ingested quantity (L/day), EF the exposure factor (no dimension) and BW is the average human body weight (kg). The exposure factor (EF) will equal to 1 - representing a daily exposure to the contaminant.

The risk characterization process is obtained by comparing the RfD (reference dose) and the estimated (calculated or measured) exposure dose (EED). The EED should include all sources and routes of exposure involved. If the EED is less than the RfD, the need for regulatory concern is likely to be small (EPA, 2022).

The Hazard Ratio (HR) can be calculated (Eq. 7) by dividing the dose (D) by the reference dose (RfD). If HR is greater than 1 the situation should not be tolerated (Fiúza & Vila, 2020).

$$HR = \frac{D}{RfD} \qquad \textit{Eq. 7}$$

In this case of dermal contact, the effective dose was estimated using Eq. 8 (Fiúza & Vila, 2020):

$$DDC = \frac{C \times SA \times CP \times DE}{BW \times EP} \qquad \textit{Eq. 8}$$

DDC is the dose of dermal contact (mg/kg. d), SA the average superficial are of human body (cm^2), CP is the coefficient of permeability (cm/day), DE is the duration of exposure (day), BW is the body weight (kg), finally EP are the exposure period (days) (Fiúza et al., 2021)

The carcinogenic risk must be calculated for the As (Eq. 9). Using the Cancer Power Factor (CPF), which represents the slope of the dose-response curve at very low concentrations $(kg.day/mg)^{-1}$ for ingestion. This index is also called slope fact (slope facto or SF) in American literature.

$$Risk\ Intake\ =\ CPF\ \times\ D \qquad \textit{Eq. 9}$$

Chapter 5- Results and discussion

5.1. Soil samples

This chapter presents the discussion of the results obtained in the experimental component of this dissertation.

Table 5. 1. Soil samples weight and water content

Soil samples- Montalto							
Samples	**Date**	**Sample + Tray [g]**	**Tray [g]**	**Sample [g]**	**Dry sample+ Tray [g]**	**Dry sample [g]**	**Water content [%]**
S1	01/02/2022	545	280	265	481	201	24
S2	01/02/2022	438	278	160	395	117	27
S3	01/02/2022	510	278	232	484	206	11
S4	01/02/2022	918	278	640	896	618	3
S5	01/02/2022	668	275	393	606	331	16
S6	01/02/2022	784	279	505	690	411	19
S7	01/02/2022	647	280	367	553	273	26
S8	01/02/2022	652	278	374	632	354	5
S9	01/02/2022	640	276	364	547	271	26
S10	18/04/2022	593	276	316	566	290	8
S11	18/04/2022	807	276	531	724	448	15

As shown in Table 5. 1. the samples S2, S7, and S9 have the highest water content. They were collected from different places, as shown on the map (Figure 4.2). The water content in the soil between these samples, may indicate that there is some correlation between them. Could be the soil characteristic, or the content in contaminants. More parameters are needed to ascertain this possible correlation, just the water content is not sufficient.

5.1.1. Element chemical analysis

The exact analysis process was repeated: for the sample as collected (A1), the soil with less than 0.075 mm (A2), and the milled soil (A3). The results are present in tables in attachment I. Some elements may not be on the report. However, this doesn't mean that they are not present in the sample. The equipment has detection limits and if the content of that element is higher or lower than the limit it may not be shown in the report.

In all samples there is: Fe, Ti, Zr, Rb, and Sr. In most samples, there is also Mn and Zn. In all samples, the element with the highest content is Fe. The samples S1, S2, S3, S4, S5, and S6, have content of Sb.

Comparing the three analyses:

- A1 *versus* A2- Fe, Ti, Mn, As and K showed the greatest differences, with decreases and increases in content.
- A1 *versus* A3- decreases mostly occurred in A3, which corroborates the argument that the granulometry, more specifically the larger size particles, leads to the extrapolation of the content value. The elements that present these differences were Fe, Ti, and Mn.
- A2 *versus* A3 – Fe, Ti, K, Pb and As present the most differences. Mostly, there were decreases in content.

This comparison was performed to understand the differences between the analyses with the same samples with different particle sizes. Seemingly, the elements in the analyses carried out in A1, A2, and A3, showed that the biggest content differences was in Fe, and Ti.

5.1.1.1. Reference values for contaminated soil

The results obtained from the XRF were compared with the reference values in the technical guide of contaminated soils published by APA, specifically with the values in: "Table B- Reference values for soil at less than 30 m from surface water" (APA, 2019). Of the elements in table B, nine elements (Sb, Zn, As, Pb, Ba, Cu, Co, Ni, and V) were detected in the samples.

A simple classification was created, if the average value obtained by the equipment was higher than the reference value, then it was colored light red otherwise has the color light green.

In Table 5.2, it is visible that the most common contaminant is As, which was detected in six of the eleven samples, followed by Sb found in five samples.

Table 5. 2. Comparison of the sample values obtained with the reference values (A1).

A1	Sb		Zn		As		Pb		Ba		Cu		Co		Ni	
Samples	[mg/kg]	±	[mg/kg]	±	[mg/kg]	±	[mg/kg]	±	[mg/kg]	±	[mg/kg]	±	[mg/kg]	±	[mg/kg]	±
S1	900	0.001	300	0.001	300	0.001	300	0.001	0	0.000	100	0.002	0	0.000	0	0.002
S2	1500	0.001	2200	0.055	500	0.002	500	0.003	0	0.000	100	0.002	0	0.004	100	0.006
S3	400	0.007	200	0.001	100	0.001	0	0.000	0	0.000	0	0.001	100	0.008	0	0.000
S4	5700	0.124	100	0.001	1500	0.007	300	0.019	0	0.000	0	0.001	0	0.000	0	0.001
S5	200	0.002	200	0.002	100	0.002	0	0.007	0	0.000	100	0.001	0	0.000	0	0.000
S6	0	0.000	100	0.001	0	0.000	0	0.000	0	0.000	0	0.000	0	0.000	0	0.000
S7	0	0.000	100	0.002	100	0.001	0	0.000	0	0.000	0	0.000	0	0.000	0	0.000
S8	0	0.003	0	0.000	0	0.001	0	0.000	0	0.000	0	0.001	0	0.002	0	0.001
S9	0	0.000	100	0.001	0	0.000	100	0.001	1100	0.013	0	0.000	100	0.010	0	0.000
S10	0	0.000	0	0.000	0	0.000	0	0.000	0	0.000	0	0.000	0	0.000	0	0.000
S11	0	0.000	100	0.000	0	0.000	0	0.000	0	0.000	100	0.001	0	0.000	0	0.000
Reference values [mg/Kg]	1		290		11		45		210		62		22		37	

The samples with the most contaminants are S1 and S2, located at the Montalto mine site. Some elements can increase the presence of Sb, for example, Al, Fe, and Mn-oxide that naturally retain Sb in the soil (Bolan et al., 2021).

The most common contaminants in the soil with less than 0.075 mm (A2), Table 5.3, are As, Sb and Cu.

Table 5. 3. Comparison of the sample values obtained with the reference values (A2).

A2	Sb		Zn		As		Pb		Ba		Cu		Co		Ni		V	
Samples	[mg/kg]	±	[mg/kg]	±	[mg/kg]	±	[mg/kg]	±	[mg/kg]	±	[mg/kg]	±	[mg/kg]	±	[mg/kg]	±	[mg/kg]	±
S1	900	0.025	400	0.003	400	0.001	400	0.002	400	0.050	200	0.002	0	0.000	100	0.001	0	0.000
S2	1000	0.007	1900	0.011	800	0.008	600	0.002	0	0.000	200	0.002	0	0.003	100	0.002	0	0.000
S3	400	0.006	200	0.001	200	0.001	0	0.000	900	0.067	100	0.000	0	0.004	0	0.000	0	0.000
S4	6800	0.125	100	0.000	2400	0.005	600	0.000	0	0.000	100	0.001	0	0.000	0	0.001	0	0.000
S5	100	0.004	200	0.001	100	0.000	0	0.000	0	0.000	100	0.002	0	0.000	0	0.000	0	0.000
S6	0	0.000	100	0.001	100	0.001	0	0.000	0	0.000	0	0.000	0	0.000	0	0.000	0	0.000
S7	0	0.000	100	0.004	0	0.003	0	0.000	0	0.000	0	0.000	0	0.000	0	0.000	0	0.000
S8	0	0.002	0	0.000	0	0.001	0	0.000	0	0.000	0	0.000	0	0.000	0	0.000	0	0.000
S9	0	0.000	100	0.001	0	0.000	100	0.005	1500	0.024	0	0.000	300	0.002	0	0.000	100	0.010
S10	0	0.000	0	0.000	100	0.001	0	0.000	600	0.078	0	0.000	0	0.000	0	0.000	0	0.000
S11	0	0.000	100	0.000	0	0.000	0	0.000	0	0.000	0	0.001	0	0.000	0	0.000	0	0.000
Reference values [mg/Kg]	1		290		11		45		210		62		22		37		86	

The samples with more contaminants are S1 and S2, the same as in the previous table. Possibly this samples have more contaminants because they were collected directly from the location where the mine was. In this analysis in sample S9, V was detected in content higher than the recommended. However, only in this analysis was this element noticed.

In A2, more contaminants were detected than in the analysis performed initially (A1). The presence of these contaminants in A2 may be due to: the soil composition, which naturally can vary, and different elements can be found in different granulometry; material of different origins and granulometry have been placed over time in this location; the larger size particles did not allow an efficient reading of the sample.

In these two initial analyses, samples S1 and S2 raise the most concern. These two samples were collected from the garden of a house where it takes place some agriculture and animal farming, so the contaminants found, may have a higher possibility of being exposed to humans.

The samples in Table 5.4 were subjected to a milling process.

Table 5. 4. Comparison of the sample values obtained with the reference values (A3).

A3	Sb		Zn		As		Pb		Ba		Cu		Co		Ni	
Samples	[mg/kg]	±	[mg/kg]	±	[mg/kg]	±	[mg/kg]	±	[mg/kg]	±	[mg/kg]	±	[mg/kg]	±	[mg/kg]	±
S1	300	0.007	100	0.002	100	0.000	0	0.000	0	0.000	0	0.000	0	0.000	0	0.000
S2	900	0.090	1200	0.014	400	0.003	400	0.030	0	0.000	100	0.003	0	0.000	0	0.004
S3	200	0.008	100	0.001	100	0.001	0	0.000	0	0.000	0	0 ± 0	0	0.000	0	0.000
S4	4300	0.035	100	0.001	2200	0.014	0	0.000	0	0.000	0	0.001	0	0.000	0	0.000
S5	200	0.004	200	0.001	100	0.001	0	0.000	0	0.000	0	0.002	0	0.000	0	0.000
S6	0	0.000	100	0.001	0	0.002	0	0.000	400	0.053	0	0.000	0	0.000	0	0.000
S7	0	0.000	100	0.001	100	0.000	0	0.000	0	0.000	0	0.000	0	0.000	0	0.000
S8	0	0.000	0	0.000	0	0.002	0	0.000	0	0.000	0	0.000	0	0.000	0	0.000
S9	0	0.000	100	0.001	0	0.000	0	0.000	1200	0.027	0	0.000	0	0.000	0	0.000
S10	0	0.000	0	0.000	0	0.000	0	0.000	0	0.000	0	0.000	0	0.000	0	0.000
S11	0	0.000	100	0.005	0	0.000	0	0.000	0	0.000	0	0.002	0	0.000	0	0.000
Reference values																
[mg/Kg]	1		290		11		45		210		62		22		37	

In this analysis, fewer contaminants were detected, the most common contaminant, is As, present in six of the eleven samples, such as previously. Sb is in five samples. Sample S2 has the most contaminants, and unlike the previous analyses, sample S1 only has two contaminants, Sb and As.

5.1.1.2. Statistical analysis

The Spearman correlation coefficient can vary from -1 to 1. The bigger the absolute number of the coefficient, stronger is the relation between the variables, in this case, elements. The Spearman correlation was performed for A1, A2, A3, and between A1 and A2, as shown in Table 5.5.

Table 5. 5. Spearman correlation values.

Analyses	Variables	Spearman correlation
A1	Zn and Ca	0.831
	Sb and As	**0.924**
	Sb and Sn	0.866
	Cr and Ba	**1**
A2	Zn and Ca	0.871
	Cu and Ca	0.832
	Rb and Mn	0.811
	As and Sb	**0.912**
	Cu and Sb	**0.932**
	Cu and Zn	0.858
	Cu and As	0.836
	Cr and Co	**1**
	Nb and Co	**1**
	Nb and Cr	**1**
A3	**Sb and Ca**	**1**
	Sb and As	0.896
	Cu and Pb	**1**

Analyses	Variables	Spearman correlation
A1 vs A2	Ca_A1 and Zn_A2	0831
	Sb_A1 and As_A2	**0.912**
	Sb_A1 and Cu_A2	**0.932**
	Zn_A1 and Ca_A2	0.871
	Zn_A1 and Cu_A2	0.858
	As_A1 and Sb_A2	**0.924**
	As_A1 and Cu_A2	0.857
	Sn_A1 and Cu_A2	0.837
	Sn_A1 and Sb_A2	0.866
	Sn_A1 and As_A2	0.821
	Ba_A1 and Co_A2	**1**
	Ba_A1 and Cr_A2	**1**
	Ba_A1 and Nb_A2	**1**
	Cr_A1 and Co_A2	**1**
	Cr_A1 and Nb_A2	**1**

The variables with the highest correlation, above 0.8, are shown in Table 5.5. in bold. These elements show a stronger likelihood of appearing together. Sb and As are present in all analyses with a very strong correlation. From this statistical study it seems likely that these two elements appear together naturally, which may be due to the geology of the area.

Moving to the p-value, the elements that presented the lowest p-value are presented in Table 5.6. The closer to zero the p-value is, greater the association between the elements and H0 must be rejected.

Table 5. 6. Most significant results obtain from the p-value matrix a) from analysis A1 b) from analysis A2 and c) from the analysis A3

Elements	p-value
Sb and As	<0.0001
Ba and Cr	<0.0001
Sb and Sn	0.001

a)

Elements	p-value
Sb and As	<0.0001
Sb and Cu	<0.0001
Co and Cr	<0.0001
Co and Nb	<0.0001
Cr and Nb	<0.0001

b)

Elements	p-value
Cu and Pb	0
As and Sb	0.0002
Sb and Ca	0.0009

c)

In A1, the elements with a higher association are Sb and As, Sb and Sn, Ba, and Cr. In A2, the elements with a higher association are Sb and As, Sb and Cu, Co and Cr, Co and Nb, Cr and Nb. In A3, the elements with a higher association are Cu and Pb, As and Sb, Sb and Ca.

The elements shown in Table 5.5 are also in Table 5.6, so the p-values corroborates the results obtained in the Spearman correlation matrix.

5.1.2. Particle size

The graph in Figure 5. 1 contains the information obtained in the sieving and from the granulometry analysis by laser diffraction- wet process, thus creating a complete granulometric analysis of each sample.

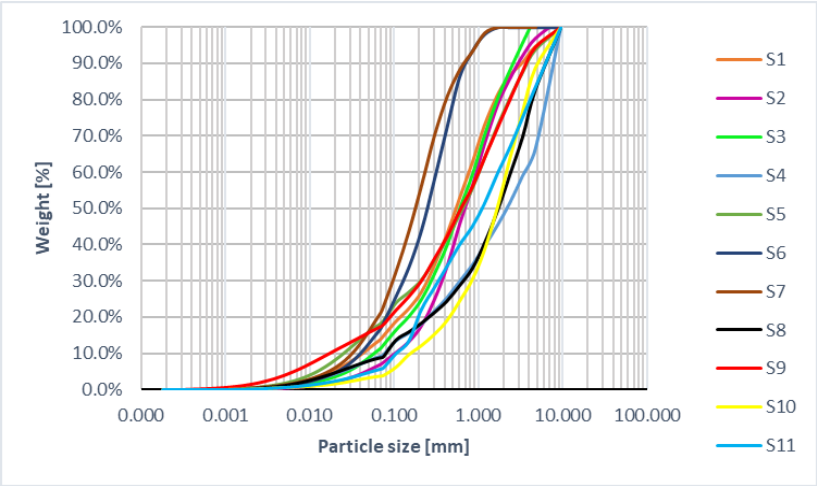


Figure 5. 1. Particle size distribution- Lower Cumulant

The cumulant curve allows the analysis of the particles size (Leite, 1987). Through the curvatures of the various sections, it is possible to obtain information about the uniformity and particles size range extension in the particulate population (Leite, 1987).

The graph of Figure 5. 1, the x-axis is on a logarithmic scale. Using this scale, the results are equally compared in the chart, from the larger size particles to the smaller particles (Leite, 1987). Without the logarithmic scale, the particle size distribution leads to poor definition, especially in the smaller particles (Leite, 1987).

Analyzing the cumulant, the greater the general inclination, the smaller the granulometric extension of the population, and greater uniformity is to be expected (Leite, 1987). The shape of the lower cumulant approximates an S (Leite, 1987).

The curve that shows a greater inclination is S7 (brown). Therefore, there is a smaller particle size range and greater uniformity. The curve S10 (yellow) presents the lowest inclination. Thus, greater granulometric extension and less uniformity.

The granulometry of the samples increases from the cumulative curves on the left to the cumulative curves on the right (Figure 5. 1), that is, the furthers to the left the curve is represented, the finer the granulometry will be.

In Table 5.7. are the average particle sizes, D50 witch is one of the most important parameters for characterizing particle size and is usually used to represent the particle size of a group of particles (Leite, 1987). D50 represents the average diameter or the average value of a particle at 50% in the cumulative distribution (Leite, 1987).

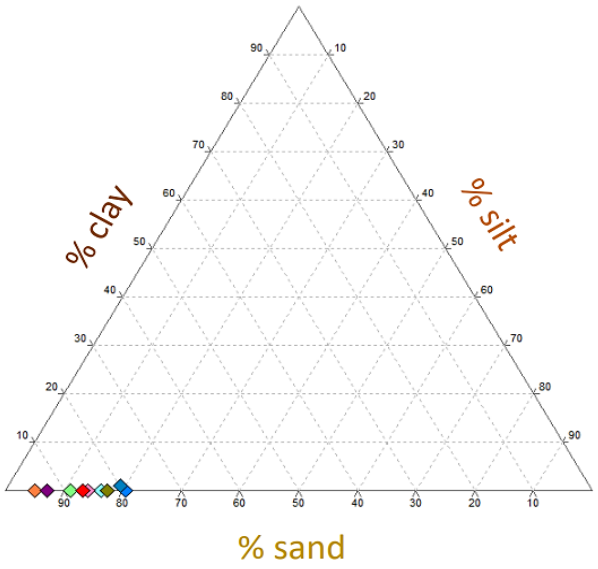
Table 5. 7. Average particle size value (D50).

Sample	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	S11
D50	0.55	0.70	0.59	2.19	0.66	0.25	0.18	1.73	0.62	1.67	1.11

The highest D50 in Table 5.7. is 2.19, which indicates that 50 % of the particles in the sample S4 are larger than 2.19 mm, and 50 % are smaller than 2.19 mm. The lowest D50 is 0.18, so in S7, 50% of the particles are larger than 0.18 mm, and 50 % are smaller.

The higher the D50, the greater the granulometry of the sample. The samples with the highest D50 are S4, S8, S10, S11, and the samples with smaller D50 are S7, S6, S1, and S3. In agreement with the graph in Figure 5. 1, the curves of the samples with higher D50 are all on the right, and all the curves of the samples with smaller D50 are on the left.

Another summary way to classify soil, as to its granulometry, is by using USDA (United States Department of Agriculture). According to this classification the samples under study were classified in the triangular diagram, using Triplot. The triangle in Figure 5. 2 has the soil textural representation. To mark the points represented in the triangle it was necessary to mark the percentage of clay, silt, and sand of each sample. The points are the intersection of these values.



Sample	A: Clay (%)	B: Sand (%)	C: Silt (%)	Symbol
S1	0.2028	81.8355	17.9617	
S2	0.1337	92.6135	7.2527	
S3	0.3204	88.1788	11.5007	
S4	0.6190	82.9634	16.4176	
S5	0.6412	78.4623	20.8965	
S6	0.3576	85.4343	14.2081	
S7	0.4616	81.8020	17.7363	
S8	0.4736	85.6396	13.8869	
S9	1.7673	79.0888	19.1439	
S10	0.3387	94.3385	5.3228	
S11	0.2695	92.0191	7.7114	

Figure 5. 2. Soil textural triangle.

On the triangle, the samples represented further to the right are of smaller particle sizes and classified as loamy sand (S1; S4; S5; S7; S9). The samples classified as sand (S2; S3; S6; S8; S10; S11) have a bigger granulometry. Comparing the curves placement and the soil sample classification they are coherent. Samples S2, S3, S6, S8, S10, and S11 are the cumulative curves further to the right, and on the triangle more to the left.

5.1.3. Soil pH

Some samples were collected in agricultural land (S1, S2, S3, S4, S5), others in forest land (S6, S7, S8, S9, and S10), and from an urbanization area, classified in Figure 3.1. as artificial surfaces (S11). The average pH of each location is different. The soil pH is expected to be lower in the forest, while in agricultural land higher (Reuter et al., 2010). The rock formation/parent material also influences de pH of the soil (Reuter et al., 2010). In this case, Montalto is within complex schist greywacke, so lower/acid pH values were expected.

Table 5.8. presents the pH values obtained when using H_2O and $CaCl_2$. With H_2O the pH was always higher than the pH measured with $CaCl_2$. This occurs since Ca^{2+} displaces H^+ and Al^{3+} ions in the soil, resulting in a pH decrease of about 0.5 units lower than water in equilibrium with the soil (Dinis, 2018). The difference between the pH using H_2O and $CaCl_2$ was greater in S10 and less in S2. The differences between these values may be due to errors when performing the experiment, for example, if not enough time had passed the pH wasn't stabilized the recorded value was not accurate.

Table 5. 8. Results obtained in the soil pH analyses.

	Sample	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	S11
pH	H_2O	5.495	6.021	6.43	5.947	7.181	5.265	5.307	4.388	3.742	4.151	4.948
	$CaCl_2$	5.31	5.961	6.258	5.346	6.972	4.802	4.981	3.799	3.543	3.43	4.494

The pH values range from 3.7 to 7.2. The samples S1, S4, S6, S7, S8, S9, S10, and S11 have an acid pH. The samples S2, S3, and S5 are almost neutral.

The pH measure should be used with caution when characterizing the soil conditions. There are a lot of variables that can influence this parameter (Arnesen et al., 2018). The pH value is not enough to classify the soil contamination state.

To further study the influence of the different elements on the pH a statistical analysis was performed.

5.1.3.1 Statistical analysis of the pH results

The statistical study was made with the results of the pH analysis using water (Table 5.8.) and the content values of the elements obtained with XRF in A1 and A2, since a mix of these soil size particles, was used in this test.

In Table 5.9. the maximum correlation is 0.761, with As. Ca, Sb, Zn, Sn, present values greater than 0.5. Therefore, these elements may have an impact on the pH value, the presence of these elements in the soil might change the pH.

Table 5. 9. Spearman correlation with pH values (A1).

Variables _A1	Fe	K	Ca	Mn	Sb	Ti	Zn	As	Zr	Pb	Rb	Sn	Sr	Ba	Cu	Co	Cr	Ni	Nb	pH
pH	0.200	0.181	0.654	0.367	0.748	-0.264	0.757	0.761	-0.083	0.185	0.103	0.625	-0.135	-0.500	0.418	-0.075	-0.500	0.300	0.000	**1**

In Table 5.10. the maximum correlation value is 0.790 with Ca. Sb, Zn, As, Sn, Cu, present values greater than 0.5. Therefore, these elements may have an impact on the pH.

Table 5. 10. Spearman correlation with pH values (A2).

Variables _A2	Fe	K	Ca	Mn	Sb	Ti	Zn	As	Zr	Pb	Rb	Sn	Sr	Ba	Cu	Co	Cr	Ni	Nb	pH
pH	0.164	0.233	0.790	0.442	0.748	-0.205	0.757	0.639	-0.115	0.185	0.139	0.534	-0.400	-0.284	0.779	-0.500	-0.500	0.298	-0.500	**1**

This statistical analysis indicates that Ca, Sb, Zn, Sn, and Cu might influence the pH value.

5.1.4. Soil organic carbon and organic matter

Figure 5.3. shows the percentage of organic carbon and organic matter obtained in each sample.

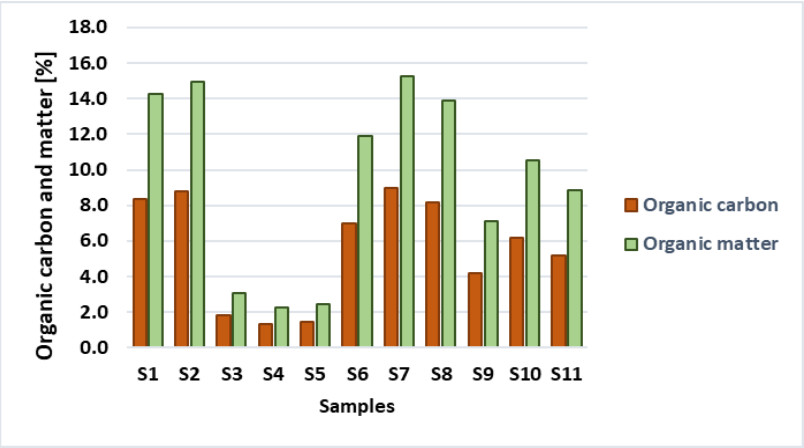


Figure 5. 3. Representation of the results obtained of the organic carbon and matter.

The samples with the highest organic carbon content are S1, S2, S7, and S8, and the sample with the lowest organic carbon content are S3, S4, and S5.

Samples S1, S2, S7, and S8, have the highest percentage of organic matter, thus the bigger resistance to acidification, and higher resistance to the changes in pH (Queensland Government, 2022). Samples S3, S4, and S5 have the least percentage of organic matter.

Montalto is in the green part of the map in Figure 5.4, that indicates the organic carbon value expected would be superior to 2.7 %. S3, S4, and S5, don't have values higher than 2.7 %, the rest of samples do.

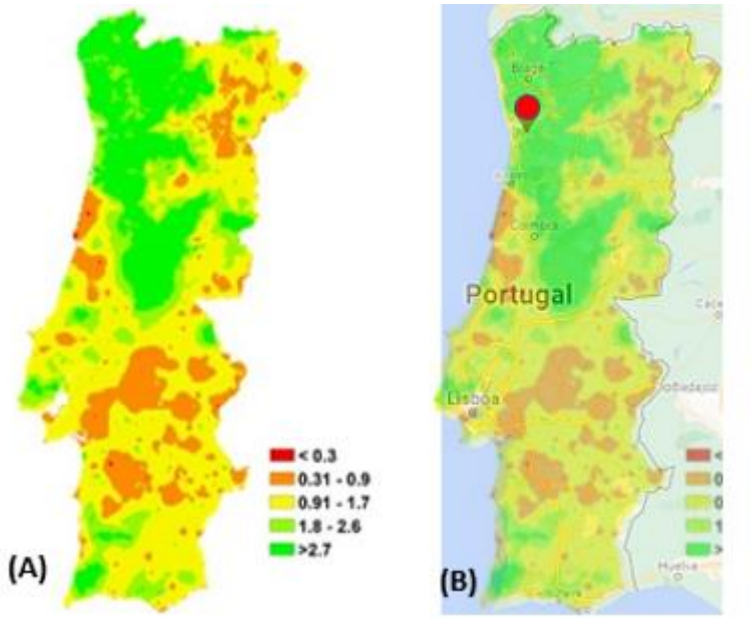


Figure 5. 4. (A) Soil organic carbon map (InfoSolo, 2020) and (B) Google maps.

These three samples might have been collected from locations where tailings were placed, the lower organic carbon in these locations agrees with that possibly.

5.1.4.1 Statistical analysis of the results of organic carbon

The statistical study was also performed with the results of the organic carbon (Table 5.11.) were and the results obtained in A3 in the XRF (A3 soil size particles correspond with the granulometry used in this test).

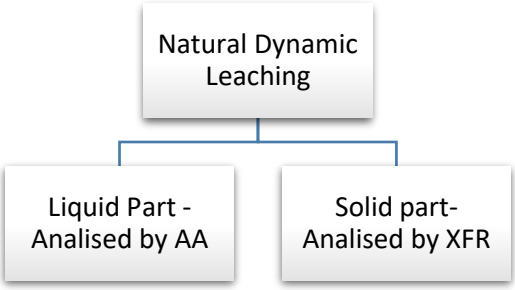
Table 5. 11. Spearman correlation with the percentage of organic carbon.

Variables _A3	Fe	K	Ca	Mn	Sb	Ti	Zn	As	Zr	Pb	Rb	Sn	Sr	Ba	Cu	Cr	Nb	OC [%]
OC [%]	-0.273	-0.209	-0.095	0.500	-0.229	0.378	-0.053	-0.073	0.208	0.400	**0.627**	0.075	-0.092	-0.094	0.400	-0.200	0.000	**1**

In Table 5.11. the Spearman correlation obtained between Rb and the percentage of organic carbon was 0.627, and between Ti and the percentage of organic carbon was 0.378. All the others presented negative values. Therefore, it was not possible to establish a correlation between the percentage of organic carbon and the different elements.

5.1.5. Natural dynamic leaching

The leaching process is normally evaluated by comparing the concentration of elements in the liquid and solid part (Nunes, 2015):



5.1.5.1 Analysis of the liquid part

In Figure 5.5., are represented the results obtained from the four measurements of pH and Eh, in each sample through the dynamic leaching process. The graphs are in a reduced size to highlight the different behavior of the pH (blue line) and Eh (orange line). This approach permits the observation and comparation of the trend of the behavior of these two parameters over time in the different samples promptly and clearly.

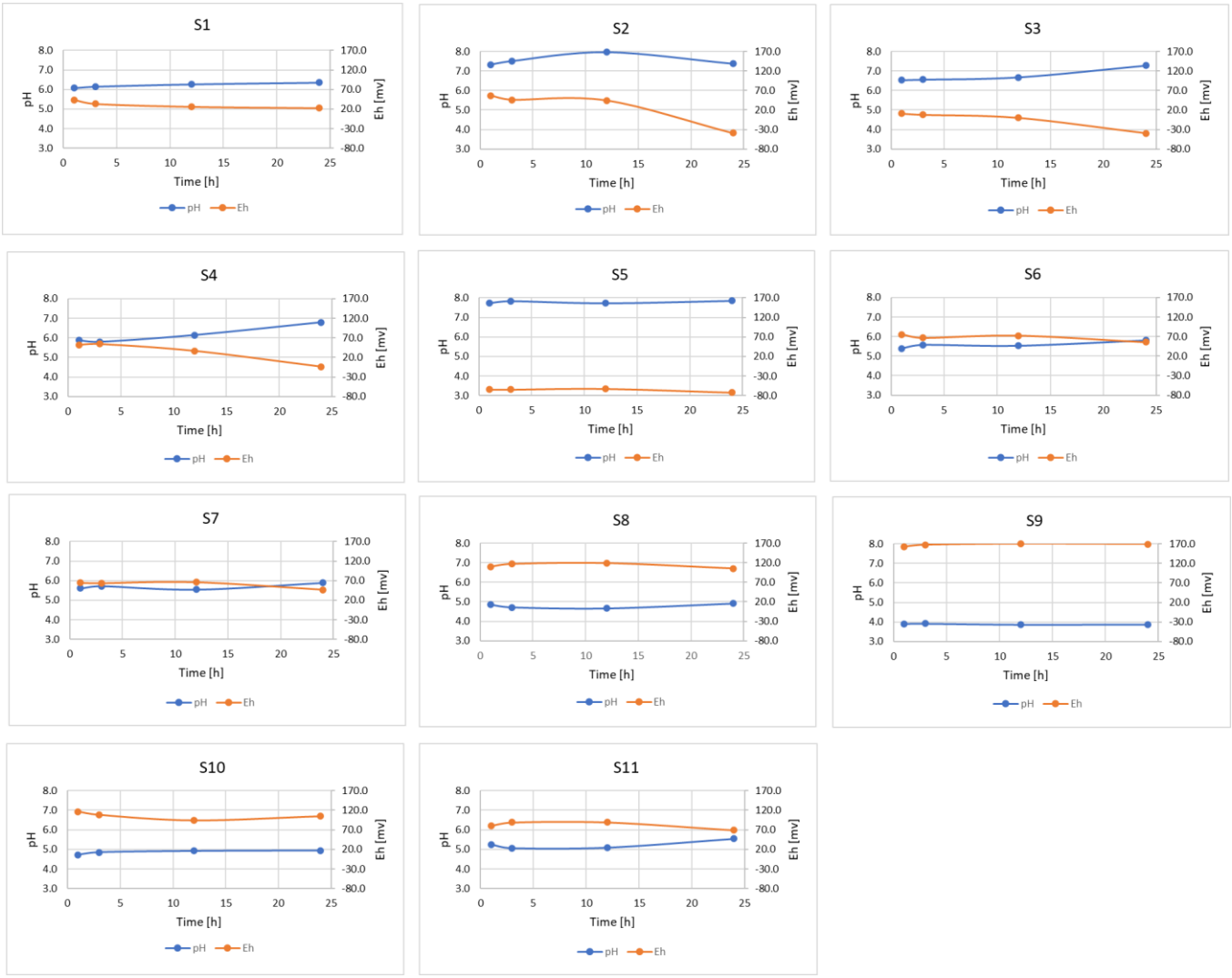


Figure 5. 5. pH vs Eh in the liquid phase of the leaching tests.

All the graph in Figure 5.5 have on x-axis the time in the hours, on the y-axis the measured pH values, and on the secondary, axis in the right-hand side, are the measured values of Eh in mV. The axes of the graphs have the same intervals.

Eh (redox potential) measures the electron activity. Positive values indicate oxidizing conditions, while negative values indicate electrons are available so is a reducing environment (Jardim, 2014). The sample with lowest Eh is S5, and highest S9. For the pH, S9 shows the lowest values, S2 and S5 the highest.

The graph in Figure 5.6. has in x-axis the time in hours and on y-axis the conductivity in µS/cm.

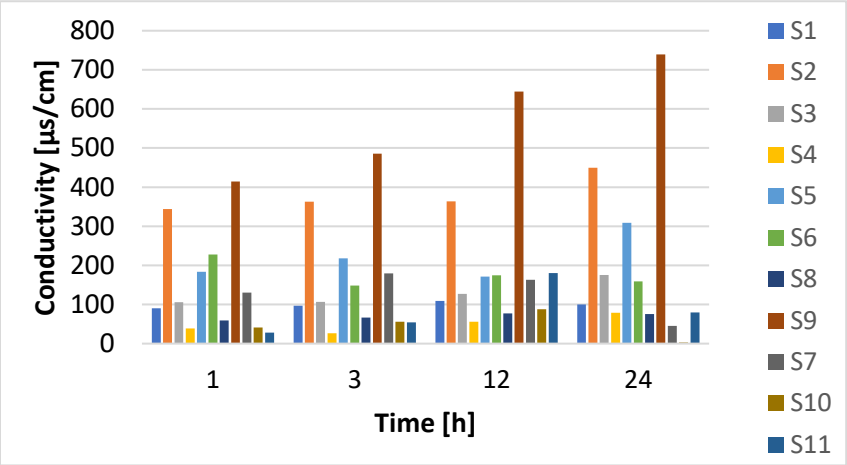


Figure 5. 6. Electrical conductivity of the liquid phase of leaching tests.

The samples with the highest conductivity are S2, S5 and S9. The conductivity shows a growing tendency, comparing the results after one hour to the results after 24 hours.

The graph in Figure 5.7, has on the x-axis the eleven samples and on the y-axis the concentration obtained using the atomic absorption for Fe, Sb, Pb, and Cu, of the liquid part resulted from the natural leaching.

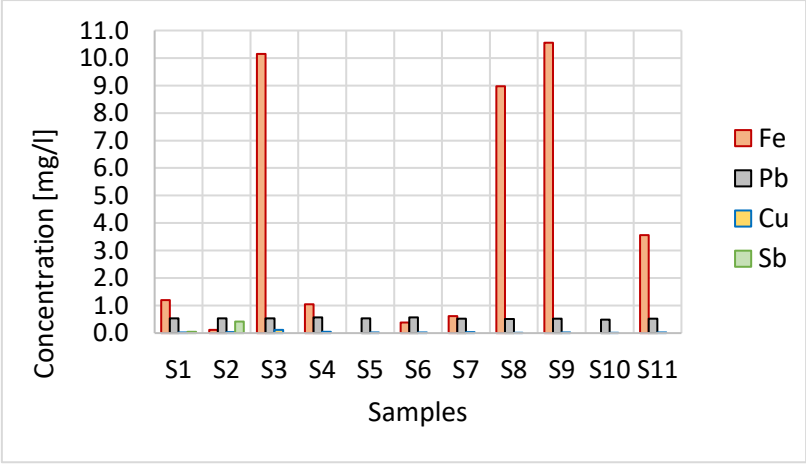


Figure 5. 7. Concentration obtained by the atomic absorption analysis.

The concentration found is also dependent on the concentration original found in the sample. The leaching was done with water and some elements are not soluble in these water conditions (pH, and temperature). Pb was the only element that was found in all samples. Sb was only detected on S2. Fe presented highest concentration in S3, S8, S9, and S11. Cu has the least concentration in all the samples.

5.1.5.2. Analysis of the solid part

As for the solid part sample S2 was where more elements were leached. Which means, part of the particle was "dissolved" and passed to the liquid form. From the elements that have been analyzed by atomic absorption, Fe shows indications of leaching in all samples except S6, and S10. Pb only in S2, Cu appears to have leached in S2, and S5, and Sb leached in S3, and S4.

With the results obtained from the element chemical analysis it's possible to compare them to the reference values for contaminated soils. Table 5.12. shows the comparison between the reference values and the elements found in the soil before leaching.

Table 5. 12. Comparison of the sample values obtained with the reference values (A4).

A4	Sb		Zn		As		Pb		Ba		Cu		Co		Ni	
Samples	[mg/kg]	±	[mg/kg]	±	[mg/kg]	±	[mg/kg]	±	[mg/kg]	±	[mg/kg]	±	[mg/kg]	±	[mg/kg]	±
S1	300	0.011	100	0.002	100	0.001	0	0.000	0	0.000	0	0.002	0	0.000	0	0.002
S2	1000	0.015	1300	0.029	400	0.003	300	0.002	700	0.105	100	0.005	0	0.000	100	0.004
S3	300	0.003	100	0.001	100	0.000	0	0.000	0	0.000	0	0.001	0	0.000	0	0.000
S4	3500	0.049	100	0.001	2000	0.014	0	0.000	0	0.000	0	0.000	0	0.000	0	0.000
S5	100	0.004	200	0.004	100	0.004	0	0.000	1100	0.081	100	0.002	0	0.000	0	0.000
S6	0	0.000	100	0.001	0	0.000	0	0.000	400	0.054	0	0.000	0	0.000	0	0.000
S7	0	0.000	100	0.000	100	0.000	0	0.000	400	0.050	0	0.000	0	0.000	0	0.000
S8	0	0.003	0	0.000	0	0.000	0	0.000	700	0.050	0	0.000	0	0.000	0	0.000
S9	0	0.000	100	0.001	0	0.000	0	0.000	1200	0.007	0	0.000	0	0.000	0	0.000
S10	0	0.000	0	0.001	0	0.000	0	0.000	0	0.000	0	0.000	0	0.000	0	0.000
S11	0	0.000	100	0.000	0	0.000	0	0.000	500	0.068	0	0.002	0	0.000	0	0.000
Reference values																
[mg/Kg]	1		290		11		45		210		62		22		37	

After leaching the comparison was performed again as showed in Table 5.13., for the same eight elements.

Table 5. 13. Comparison of the sample values obtained with the reference values (A5).

A5	Sb		Zn		As		Pb		Ba		Cu		Co		Ni	
Samples	[mg/kg]	±	[mg/kg]	±	[mg/kg]	±	[mg/kg]	±	[mg/kg]	±	[mg/kg]	±	[mg/kg]	±	[mg/kg]	±
S1	300	0.002	100	0.002	100	0.001	0	0.000	0	0.000	0	0.001	0	0.000	0	0.000
S2	1000	0.007	1100	0.014	300	0.001	200	0.001	0	0.000	0	0.003	0	0.000	0	0.002
S3	200	0.001	100	0.001	100	0.000	0	0.000	0	0.000	100	0.002	800	0.012	400	0.007
S4	3000	0.025	0	0.000	2000	0.006	0	0.000	0	0.000	100	0.000	400	0.003	300	0.001
S5	100	0.003	100	0.001	100	0.000	0	0.000	0	0.000	0	0.002	0	0.000	0	0.000
S6	0	0.000	100	0.001	0	0.000	0	0.000	0	0.000	0	0.000	0	0.000	0	0.000
S7	0	0.003	100	0.000	0	0.002	0	0.000	0	0.000	0	0.000	0	0.000	0	0.000
S8	0	0.000	0	0.001	0	0.001	0	0.000	0	0.000	0	0.000	0	0.000	0	0.000
S9	0	0.000	100	0.000	0	0.000	0	0.000	400	0.057	0	0.000	0	0.000	0	0.000
S10	0	0.000	0	0.001	0	0.000	0	0.000	0	0.000	0	0.000	0	0.000	0	0.000
S11	0	0.000	100	0.001	0	0.000	0	0.000	0	0.000	0	0.003	0	0.005	0	0.003
Reference values																
[mg/Kg]	1		290		11		45		210		62		22		37	

Table 5.13 shows after the leaching process fewer contaminants have content above the recommended value. However, there was an increase in Cu, Co, and Ni in samples S3 and S4. These now are above the recommended values.

5.2. Water samples

In this section are presented the results obtained from the two water sampling campaigns. Is to be noted that more significance is given to the results obtained by the accredited laboratory.

5.2.1. Physical-chemical parameters

Table 5.14 indicates the physical chemical parameters of the samples collected by the SHS project research team.

Table 5. 14. Water physical-chemical parameters of the samples from the first sampling campaign.

Water samples		W1	W2	W3	W4	W5	W6	W7	W8	W9	W10
Field	pH	6.9	7.3	4.5	7.4	5.9	6.6	4.8	7.3	7.3	7.3
	Conductivity [µs/cm]	206.0	265.0	310.0	576.0	294.0	463.0	415.0	166.6	165.6	313.0
	O2 [%]	0.0	76.4	73.7	69.0	75.7	57.2	69.3	58.5	47.9	57.2
Laboratory	pH	7.8	7.8	4.4	8.0	7.1	5.6	5.1	7.3	7.4	7.3
	Conductivity [µs/cm]	187.7	277.0	315.0	588.0	313.0	417.0	311.0	177.7	180.1	178.3
	O2 [%]	65.3	68.2	64.5	66.1	68.2	67.2	71.9	67.9	67.9	65.8

Comparing the pH values measured in the field with the values measured in the laboratory, there was an increase in the pH measured in laboratory. In the case of the conductivity, there were increases in W2, W3, W4, W5, W8, and W9 in the laboratory measurements. In W7, and W10 a measurement error occurred, there is a 25 % difference in W7 between what was measured in the field and the laboratory and a 45 % difference in W10. The recorded conductivity value in the field probably has not the stabilized value. The dissolved oxygen is always higher in the laboratory than in the field.

From the second sampling campaign is possible to observe the physical-chemical parameters in Table 5.15.

Table 5. 15. Water physical-chemical parameters of the samples from the second sampling.

	Water samples	W_1	W_2	W_3	W_4	W_5	W_6	W_8	W_9	W_10	W_11	W_13	W_14	W_15
Field	pH	6.7	5.7	4.1	7.3	5.4	6.6	7.3	7.1	7.1	3.5	7.2	6.9	7.3
	Conductivity [µS/cm]	196	98.6	293	562	300	437	199	197	196	445	235	196	204
	O2 [%]	16.9	77.4	59.2	88	57.1	95	97	96	97	87	90	98	98

All the samples from the Sousa River (W_8, W_9, W_10, W_14, W_15) have a neutral pH. W_11 has the lowest pH, and one of the highest electrical conductivity.

The samples with the same number were collected practically in the same place and have similar pH values except W_2. The conductivity values are very different in W_2 and W_10. The dissolved oxygen is more sensitive than the others, so it is normal that this one, of the three, shows the most differences.

5.2.2. Reference values for water

The parameters analyzed by the ALS laboratory were compared to the reference values indicated in the Decree-Law nº 236/98 appendix VI and XVI, and Decree-Law nº 306/2007 part I and II. In light green are the values that are under the reference values.

It was possible to conclude that none of the sample waters are suitable to be consumed by humans. In general, the values of manganese, zinc, and iron are above the reference value, as shown in Table 5.16 and Table 5.17. Some samples present worrying values in certain parameters, such as the arsenic concentration in sample W_1.

Table 5. 16. Comparison of parameters of groundwater samples with the reference values for drinking water from the Decree-Law nº 236/98 appendix VI.

		Groundwater samples							
		W_1	**W_2**	**W_3**	**W_4**	**W_5**	**W_13**	**MRV**	**MAV**
EC	**µS/cm**	196.0	98.6	293.0	562.0	300.0	235.0	400	
	±	11.0	5.4	16.0	31.0	17.0	13.0		
NH_4	**mg/L**	<0.1	<0.1	0.1	<0.1	<0.1	<0.1	0.05	
	±	-	-	0.0	-	-	-		
Cl^-	**mg/L**	12.4	15.8	11.6	19.5	37.9	11.2	25	
	±	1.9	2.4	1.7	2.9	5.7	1.7		
pH	**.**	6.7	5.7	4.1	7.3	5.4	7.2	6.5-8.5	
	±	0.4	0.4	0.4	0.4	0.4	0.4		
NO_3	**mg/L**	<2.0	<2.0	<2.0	2.6	26.4	<2.0	25	
	±	-	-	-	0.4	4.0	-		
SO_4	**mg/L**	<5.0	5.2	120.0	48.1	48.8	14.6	25	
	±	-	0.7	16.0	6.3	6.4	1.9		
NO_2	**mg/L**	<1.0E-02	<1.0E-02	<1.0E-02	<1.0E-02	<1.0E-02	<1.0E-02		0.1
	±	-	-	-	-	-	-		
Hg	**µg/L**	<1.1E-02	<1.1E-02	2.0E-02	<1.1E-02	3.3E-02	<1.1E-02	1	
	± [%]	10.0	-	10.0	-	10.0	-		
Ca	**mg/L**	7.8	3.8	13.2	32.3	6.5	13.5	100	
	± [%]	10.0	10.0	10.0	10.0	10.0	10.0		
Mn	**µg/L**	238.0	11.9	1150.0	7.8	39.2	210.0	20	
	± [%]	10.0	10.0	10.0	10.0	10.0	10.0		
Cu	**µg/L**	1.8	94.9	20.0	<5.0	24.7	<1.0	3000	
	± [%]	10.0	10.0	10.0	-	10.0	-		
Zn	**µg/L**	7.2	442.0	147.0	49.8	144.0	5.3	5	
	± [%]	10.0	10.0	10.0	10.0	10.0	10.0		
Pb	**µg/L**	0.5	4.7	2.1	0.9	2.0	<0.050		50
	± [%]	13.7	10.4	10.8	12.0	10.9	-		
Cd	**mg/L**	<4.0E-04	<4.0E-04	<4.0E-04	<4.0E-04	<4.0E-04	<4.0E-04		5
	± [%]	-	-	-	-	-	-		
Ni	**µg/L**	5.5	8.2	66.6	4.5	51.2	8.1		50
	± [%]	11.3	11.0	10.5	11.5	10.5	11.0		
Al	**mg/L**	1.3E-02	<1.E-02	1.5E+00	<1.E-02	1.8E-02	<1.0E-02	0.05	
	± [%]	10.0	-	10.0	-	10.0	-		
As	**µg/L**	618.0	<1.0	1.2	<1.0	<1.0	2.2		50
	± [%]	10.0	-	10.0	-	-	10.0		
Sb	**µg/L**	54.6	<1.0	<1.0	<1.0	<1.0	1.3		10
	± [%]	10.0	-	-	-	-	10.0		
Se	**ug/L**	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0		10
	± [%]	-	-	-	-	-	-		
Na	**mg/L**	9.7	12.2	12.0	66.5	27.2	11.1	20	
	± [%]	10.0	10.0	10.0	10.0	10.0	10.0		
K	**mg/L**	0.6	0.4	1.2	6.4	6.9	0.5	10	
	± [%]	10.0	10.0	10.0	10.0	10.0	10.0		
Mg	**mg/L**	13.6	3.3	14.7	20.6	14.2	19.9	30	
	± [%]	10.0	10.0	10.0	10.0	10.0	10.0		
Fe	**mg/L**	10.1	0.2	2.9	0.1	0.3	2.1	0.1	
	± [%]	10.0	10.0	10.0	10.0	10.0	10.0		

The groundwater samples, W_2, and W_13 have 87 % of the compared parameters below the reference values. There isn't a sample with less than 61 % of parameters below the reference values.

Table 5. 17. Comparison of parameters of surface water samples with the reference values for drinking water from the Decree-Law nº 236/98 appendix VI.

		Suface water samples								
		W_6	**W_8**	**W_9**	**W_10**	**W_11**	**W_14**	**W_15**	**MRV**	**MAV**
EC	**µS/cm**	437.0	199.0	197.0	196.0	445.0	196.0	204.0	400	
	±	24.0	11.0	11.0	11.0	25.0	11.0	11.0		
NH_4	**mg/L**	0.1	0.5	0.5	0.6	<0.1	0.6	0.5	0.05	
	±	0.0	0.1	0.1	0.1	-	0.1	0.1		
Cl^-	**mg/L**	14.4	26.6	26.4	26.5	12.6	26.6	26.8	25	
	±	2.2	4.0	4.0	4.0	1.9	4.0	4.0		
pH	**.**	6.6	7.3	7.1	7.1	3.5	6.9	7.3	6.5-8.5	
	±	0.4	0.4	0.4	0.4	0.4	0.4	0.4		
NO_3	**mg/L**	<2.0	31.6	31.7	31.5	<2.0	31.7	31.7	25	
	±	-	4.8	4.8	4.7	-	4.8	4.8		
SO_4	**mg/L**	184.0	14.1	14.1	14.0	151.0	14.1	14.1	25	
	±	24.0	1.8	1.8	1.8	20.0	1.8	1.8		
NO_2	**mg/L**	<1.0E-02	0.9	1.0	1.0	<1.0E-02	1.1	1.0		0.1
	±	-	0.2	0.2	0.2	-	0.2	0.2		
Hg	**µg/L**	1.4E-02	1.4E-02	<1.0E-02	1.2E-02	2.0E-02	3.4E-02	1.4E-02	1	
	± [%]	10.0	10.0	-	10.0	10.0	10.0	10.0		
Ca	**mg/L**	28.1	8.4	8.2	8.3	18.4	8.2	9.0	100	
	± [%]	10.0	10.0	10.0	10.0	10.0	10.0	10.0		
Mn	**µg/L**	2160.0	24.4	25.4	25.7	1680.0	21.1	30.5	20	
	± [%]	10.0	10.0	10.0	10.0	10.0	10.0	10.0		
Cu	**µg/L**	5.1	12.3	5.2	2.8	5.3	2.6	<2.0	3000	
	± [%]	10.0	10.0	10.0	10.0	10.0	10.0	-		
Zn	**µg/L**	72.6	9.0	9.5	9.9	126.0	18.1	8.7	5	
	± [%]	10.0	10.0	10.0	10.0	10.0	10.0	10.0		
Pb	**µg/L**	0.7	0.4	0.5	0.4	1.8	0.3	<1.0E-02		50
	± [%]	12.6	14.5	13.9	14.3	11.0	16.1	-		
Cd	**mg/L**	<4.0E-04	<4.0E-04	<4.0E-04	<4.0E-04	<4.0E-04	<4.0E-04	<2.0E-03		5
	± [%]	-	-	-	-	-	-	-		
Ni	**µg/L**	57.0	0.7	0.8	0.7	62.9	0.8	<5.0E-03		50
	± [%]	10.5	17.4	16.7	17.1	10.5	16.8	10.0		
Al	**mg/L**	0.1	0.1	0.1	0.1	0.7	0.1	0.2	0.05	
	± [%]	10.0	10.0	10.0	10.0	10.0	10.0	10.0		
As	**µg/L**	3.0	4.8	5.1	5.2	<1.0	4.9	<1.0E-02		50
	± [%]	10.0	10.0	10.0	10.0	-	10.0	-		
Sb	**µg/L**	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<2.0E-02		10
	± [%]	-	-	-	-	-	-	-		
Se	**ug/L**	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<3.0E-02		10
	± [%]	-	-	-	-	-	-	-		
Na	**mg/L**	11.6	22.0	21.6	21.2	9.7	21.7	22.0	20	
	± [%]	10.0	10.0	10.0	10.0	10.0	10.0	10.0		
K	**mg/L**	2.4	5.4	5.5	5.7	1.3	5.6	6.0	10	
	± [%]	10.0	10.0	10.0	10.0	10.0	10.0	10.0		
Mg	**mg/L**	22.8	3.3	3.3	3.3	17.0	3.3	3.5	30	
	± [%]	10.0	10.0	10.0	10.0	10.0	10.0	10.0		
Fe	**mg/L**	19.8	0.1	0.1	0.1	0.6	0.1	0.3	0.1	
	± [%]	10.0	10.0	10.0	10.0	10.0	10.0	10.0		

For the surface water samples, W_6, and W_11 had the most parameters, 65 % of them lower than the reference values.

From the results in Table 5.18 it is possible to observe that the samples W_2, W_4, W_5, and W_13, can be used for irrigation.

Table 5. 18. Comparison of groundwater sample parameters with reference values for irrigation from the Decree-Law nº 236/98 appendix XVI.

		Groundwater samples							
		W_1	**W_2**	**W_3**	**W_4**	**W_5**	**W_13**	**MRV**	**MAV**
Cl^-	**mg/L**	12.4	15.8	11.6	19.5	37.9	11.2	70	
	±	2	2	2	3	6	2		
pH	**.**	6.7	5.7	4.1	7.3	5.4	7.2		4.5--9
	±	0.4	0.4	0.4	0.4	0.4	0.4		
NO_3	**mg/L**	<2.0	<2.0	<2.0	2.6	26.4	<2.0	50	
	±	-	-	-	0.4	4	-		
SO_4	**mg/L**	<5.0	5.2	120.0	48.1	48.8	14.6	575	
	±	-	1	16	6.3	6.4	2		
Mn	**mg/L**	2.4E-01	1.2E-02	1.2E+00	7.8E-03	3.9E-02	2.1E-01		10
	± [%]	10	10	10	10	10	10		
Cu	**mg/L**	1.8E-03	0.1	2.0E-02	<5.0E-03	2.5E-02	<1.0E-03		5
	± [%]	10	10	10	-	10	-		
Zn	**mg/L**	7.2E-03	4.4E-01	1.5E-01	5.0E-02	1.4E-01	5.3E-03		10
	± [%]	10	10	10	10	10	10		
Pb	**mg/L**	4.8E-04	4.7E-03	2.1E-03	8.9E-04	2.0E-03	<5.0E-05		20
	± [%]	14	10	11	12	11	-		
Cd	**mg/L**	<4.0E-04	<4.0E-04	<4.0E-04	<4.0E-04	<4.0E-04	<4.0E-04		0.05
	± [%]	-	-	-	-	-	-		
Ni	**mg/L**	5.5E-03	8.2E-03	0.1	4.5E-03	0.1	8.1E-03		2
	± [%]	11.3	11	10.5	11.5	10.5	11		
Al	**mg/L**	1.3E-02	<1.0E-02	1.5	<1.0E-02	1.8E-02	<1.0E-02		20
	± [%]	10	-	10	-	10	-		
As	**mg/L**	0.6	<1.0E-03	1.2E-03	<1.0E-03	<1.0E-03	2.2E-03		10
	± [%]	10	-	10	-	-	10		
Se	**mg/L**	<1.E-03	<1.0E-03	<1.0E-03	<1.0E-03	<1.0E-03	<1.0E-03		0.05
	± [%]	-	-	-	-	-	-		
Fe	**mg/L**	10.1	0.2	2.9	0.1	0.3	2.1	5	
	± [%]	10	10	10	10	10	10		

Table 5. 19. Comparison of surface water sample parameters with reference values for irrigation from the Decree-Law nº 236/98 appendix XVI.

		Suface water samples								
		W_6	**W_8**	**W_9**	**W_10**	**W_11**	**W_14**	**W_15**	**MRV**	**MAV**
Cl^-	**mg/L**	14.4	26.6	26.4	26.5	12.6	26.6	26.8	70	
	±	2	4	4	4	2	4	4		
pH	**.**	6.6	7.3	7.1	7.1	3.5	6.9	7.3		4.5--9
	±	0.4	0.4	0.4	0.4	0.4	0.4	0.4		
NO_3	**mg/L**	<2.0	31.6	31.7	31.5	<2.0	31.7	31.7	50	
	±	-	5	5	5	-	5	5		
SO_4	**mg/L**	184.0	14.1	14.1	14.0	151.0	14.1	14.1	575	
	±	24	2	2	2	20	2	2		
Mn	**mg/L**	2.2E+00	2.4E-02	2.5E-02	2.6E-02	1.7E+00	2.1E-02	3.1E-02		10
	± [%]	10	10	10	10	10	10	10		
Cu	**mg/L**	5.1E-03	1.2E-02	5.2E-03	2.8E-03	5.3E-03	2.6E-03	<2.E-03		5
	± [%]	10	10	10	10	10	10	-		
Zn	**mg/L**	7.3E-02	9.0E-03	9.5E-03	9.9E-03	1.3E-01	1.8E-02	8.7E-03		10
	± [%]	10	10	10	10	10	10	10		
Pb	**mg/L**	7.0E-04	4.0E-04	4.6E-04	4.1E-04	1.8E-03	2.9E-04	<1.0E-05		20
	± [%]	13	15	14	14	11	16	-		
Cd	**mg/L**	<4.0E-04	<4.0E-04	<4.0E-04	<4.0E-04	<4.0E-04	<4.0E-04	<2.0E-03		0.05
	± [%]	-	-	-	-	-	-	-		
Ni	**mg/L**	5.7E-02	7.2E-04	7.9E-04	7.5E-04	6.3E-02	7.8E-04	<5.0E-06		2
	± [%]	10.5	17.4	16.7	17.1	10.5	16.8	10		
Al	**mg/L**	1.2E-01	6.9E-02	7.5E-02	7.4E-02	6.9E-01	5.1E-02	2.0E-01		20
	± [%]	10	10	10	10	10	10	10		
As	**mg/L**	3.0E-03	4.8E-03	5.1E-03	5.2E-03	<1.0E-03	4.9E-03	<1.0E-05		10
	± [%]	10	10	10	10	-	10	-		
Se	**mg/L**	<1.0E-03	<1.0E-03	<1.0E-03	<1.0E-03	<1.0E-03	<1.0E-03	<3.E-05		0.05
	± [%]	-	-	-	-	-	-	-		
Fe	**mg/L**	19.8	0.1	0.1	0.1	0.6	0.1	0.3	5	
	± [%]	10	10	10	10	10	10	10		

From the results in Table 5.19 it is possible to observe that the samples W_8, W_9, W_10, W_14, and W_15, can be used for irrigation.

5.2.3. Statistical analysis of water parameters

Using the elements found in the water samples collected in the second sampling by the ALS laboratory a statistical analysis was performed, with XLSAT. Table 5.20. presents the Spearman correlation obtained where is possible to observe the correlation between the elements found.

Table 5. 20. Spearman correlation of water chemical elements.

Variables	Ca	Mn	Cu	Zn	Pb	Ni	Al	As	Sb	Na	K	Mg	Fe	Hg
Ca	**1**	0.319	-0.431	-0.082	-0.127	0.181	0.309	-0.243	-0.087	-0.124	0.060	0.698	0.154	-0.070
Mn	0.319	**1**	0.055	0.011	0.116	0.599	0.552	0.051	0.288	-0.691	-0.313	0.549	0.896	0.333
Cu	-0.431	0.055	**1**	0.729	0.703	0.464	0.200	-0.199	-0.448	-0.033	-0.199	-0.331	0.044	0.301
Zn	-0.082	0.011	**0.729**	**1**	0.869	0.643	0.177	-0.520	-0.620	0.047	-0.005	0.143	-0.011	0.333
Pb	-0.127	0.116	**0.703**	**0.869**	**1**	0.746	0.030	-0.419	-0.289	-0.120	-0.184	0.206	0.176	0.072
Ni	0.181	**0.599**	**0.464**	**0.643**	**0.746**	**1**	0.155	-0.345	0.052	-0.536	-0.440	0.593	0.604	0.185
Al	0.309	**0.552**	0.200	0.177	0.030	0.155	**1**	0.006	-0.448	-0.205	0.099	0.028	0.326	0.527
As	-0.243	0.051	-0.199	-0.520	-0.419	-0.345	0.006	**1**	0.377	-0.249	-0.141	-0.356	0.011	-0.104
Sb	-0.087	0.288	-0.448	-0.620	-0.289	0.052	-0.448	0.377	**1**	-0.516	-0.507	0.210	0.463	-0.365
Na	-0.124	-0.691	-0.033	0.047	-0.120	-0.536	-0.205	-0.249	-0.516	**1**	0.803	-0.289	-0.729	0.090
K	0.060	-0.313	-0.199	-0.005	-0.184	-0.440	0.099	-0.141	-0.507	**0.803**	**1**	-0.022	-0.538	0.305
Mg	**0.698**	**0.549**	-0.331	0.143	0.206	**0.593**	0.028	-0.356	0.210	-0.289	-0.022	**1**	0.495	0.028
Fe	0.154	**0.896**	0.044	-0.011	0.176	**0.604**	0.326	0.011	**0.463**	-0.729	-0.538	**0.495**	**1**	0.084
Hg	-0.070	0.333	0.301	0.333	0.072	0.185	**0.527**	-0.104	-0.365	0.090	0.305	0.028	0.084	**1**

In Table 5.20 the correlation values above 0.5 are indicated in bold. Certain elements present a stronger association, above 0.7, such as Mn and Fe, Zn and Pb, Na and K, Cu and Zn, Cu and Pb.

The following graphs were obtained through the PCA analysis preformed in XLSTAT.

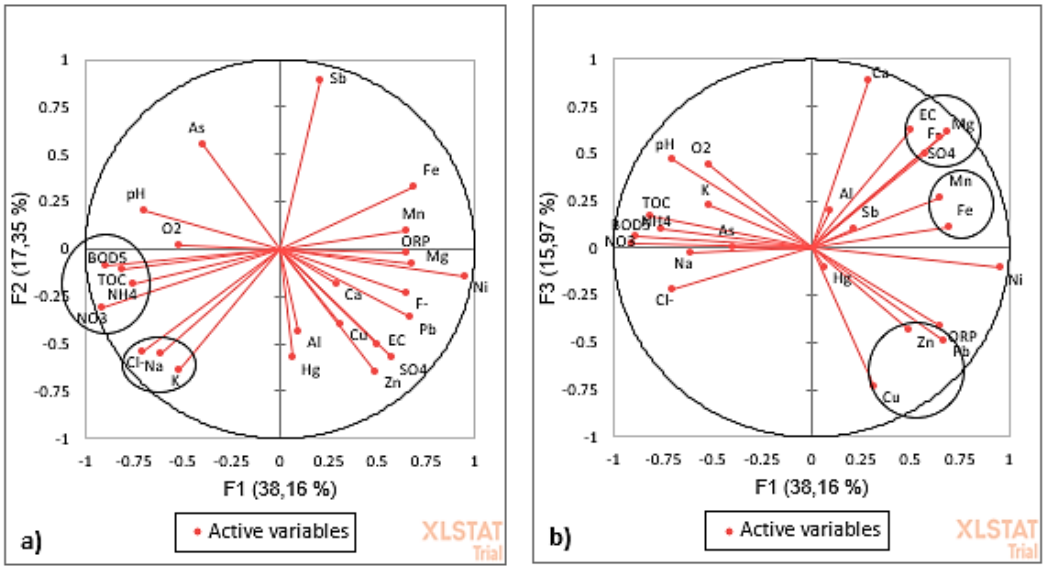


Figure 5. 8. Projection of the variables a) F1/F2 plane b) F1/F3 plane.

The variables in Figure 5.8. have different representation, the longer the line stronger is the representation. In graph a) NO_3, Ni, and Sb have strong representation, same situation in b) for Ni, Mg, and Ca.

There are two circles in Figure 5.8. a), the variables in each circle are correlated with each other. The circle on the left contains the variables $\mathrm{BOD5}$, TOC, $\mathrm{NH_4}$, and $\mathrm{NO_3}$, and on left lower circle Cl^-, Na, and K also show a strong correlation. In b) Zn, Cu, and Pb indicate a strong correlation, as well as Mn with Fe, and the last circle shows EC, Mg, SO_4, and F^-. The correlation between elements found in PCA is corresponding to the correlation observed in the Table 5.20.

Figure 5.9. shows the projection of the samples.

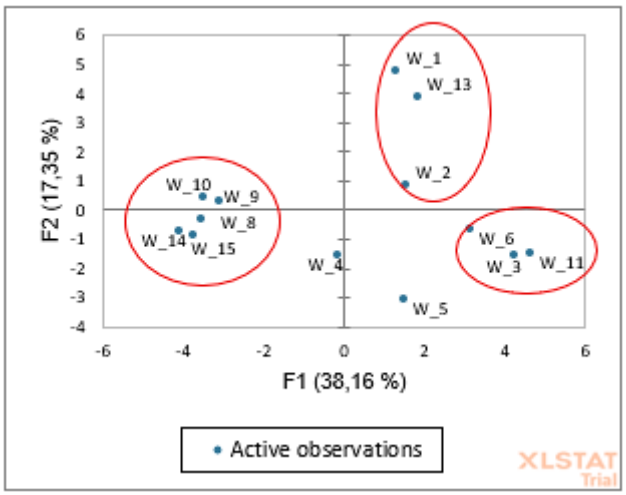


Figure 5. 9. Projections of the water samples with the plane F1/F2.

There are three red circles indicated in Figure 5. 9. The circle on the left has the samples collected from the river. On the top right circle are the samples collected from where the mine was located. Lastly, W_3, W_6, and W_11, these three samples show correlation and might have been collected from the same water line and may be influenced by the same elements.

The final graph (Figure 5.10.) has the projection of the variables and the samples together.

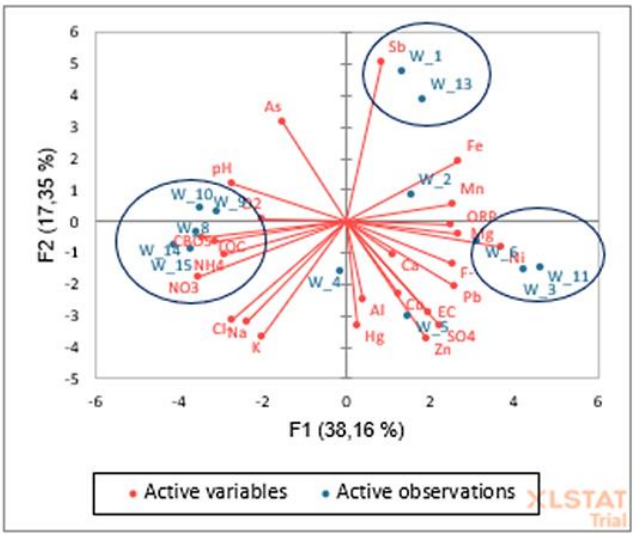


Figure 5. 10. Projection of the samples with the variables onto the F1/F2 plane.

A correlation can be observed between the samples from the river, which are in the left circle, and BOD5, TOC, NH_4, and NO_3. There is a correlation with Sb and two samples W_1, and W_13 that were collected from the mine site, which was expected since it was mostly a Sb exploitation. The samples in the circle on the right bottom side, show correlation with Mg and Ni.

5.2.4. Risk characterization

The Table 5.21 shows the scenario considered for the risk characterization. In the house where the sample W_1 was collected there are two adults and one child with less than six years old.

The reference doses RfD and the slope factor (SF or CPF) for the contaminants under analysis were consulted in the IRIS (Integrated Risk Information System) toxicological database recommended by the American Environmental Protection Agency (EPA).

Table 5. 21. Exposure scenario based on the sample W_1.

	Adults	Children
Weight [kg]	70	28
Skin surface area [cm^2]	18150	15125
Water consumption [L/day]	1.5	1
Duration of exposure [days]	0.02	0.02
As concentration [mg/L]	0.618	
Zn concentration [mg/L]	0.007	
Sb concentration [mg/L]	0.055	
Mn concentration [mg/L]	0.238	
RfD As [mg/kg.day]	3.0E-04	
RfD Zn [mg/kg.day]	0.300	
RfD Sb [mg/kg.day]	4.0E-04	
RfD Mn [mg/kg.day]	0.140	
Coefficient permeability [cm/day]	0.024	
Exposure period [days]	365	

Table 5.22. presents the results obtained for the dose, the hazard ratio, in case of water ingestion, for As, Zn, Sb, and Mn, and the risk intake of As.

Table 5. 22. Results obtained for adults and children in case of water ingestion.

	Adults	Children
As dose per water ingestion [mg/kg.day]	1.32E-02	2.21E-02
Zn dose per water ingestion [mg/kg.day]	1.54E-04	2.57E-04
Sb dose per water ingestion [mg/kg.day]	1.17E-03	1.95E-03
Mn dose per water ingestion [mg/kg.day]	5.10E-03	8.50E-03
Hazard ratio As	4.41E+01	7.36E+01
Hazard ratio Zn	5.14E-04	8.57E-04
Hazard ratio Sb	2.93E+00	4.88E+00
Hazard ratio Mn	3.64E-02	6.07E-02
Risk intake of As	1.99E-02	3.31E-02

The hazard ration should be less than one, in this case is higher than one with As, and Sb. The hazard ratio of As is forty four times higher than the limit (one) for the adult and seventy four times higher for the children. The hazard ratio of Sb in three times higher for the adult and five times higher for the children.

According to (Fiúza & Vila, 2020) the risk intake shouldn't be superior to 10^{-6}, and in this exposure scenario is higher, for adults the risk intake is 0.02, and for children 0.03, so this water is improper to be consumed due to the high risk of carcinogens by ingestion.

This sample was collected from the family property, this water presents a risk, should not be consumed. It is also important to consider that this water may have contact with other water lines and the Sousa River.

Table 5. 23. Results obtained for adults and children in case of dermal contact.

	Adults	**Children**
As dose by dermal contact [mg/kg.day]	2.20E-07	4.57E-07
Zn dose by dermal contact [mg/kg.day]	2.56E-09	5.33E-09
Sb dose by dermal contact [mg/kg.day]	1.94E-08	4.04E-08
Mn dose by dermal contact [mg/kg.day]	8.45E-08	1.76E-07
Hazard ratio As	7.32E-04	1.5E-03
Hazard ratio Zn	8.52E-09	1.8E-08
Hazard ratio Sb	4.85E-05	1.0E-04
Hazard ratio Mn	6.04E-07	1.3E-06

In this case, all hazard ratio values are less than one, as showed in Table 5.23., so in this exposure scenario the use of this water to shower, doesn't present a risk.

Chapter 6- Conclusions

6.1. Conclusions

The main goal of this dissertation was to assess the contamination state of the area where Montalto Sb mine was located. To achieve this goal twelve soil samples, and twenty-three water samples were collected and studied.

From the element chemical analysis of the soil samples, it was possible to observe that most samples have Mn and Zn, being Fe the element that always appears in higher content. The samples that present more contaminants are S1 and S2. These two samples were collected from the garden of a house where it takes place some agriculture and animal farming, so the contaminants found, may have a higher possibility of being exposed to humans.

The statistical analysis to the chemical elements of the soil showed a strong correlation between Sb and As, it seems that these two elements appear together naturally, which may be due to the geology of the area.

Using the soil textural triangle the samples S2, S3, S6, S8, S10, S11 were classified as sand, and S1, S4, S5, S7, S9, as loamy sand.

The soil pH values range from 3.7 to 7.2. The samples S1, S4, S6, S7, S8, S9, S10, and S11 have an acid pH. The samples S2, S3, and S5 are almost neutral. This statistical analysis indicates that the presence of Ca, Sb, Zn, Sn, and Cu in the soil might have influence on the pH.

The samples with the highest organic carbon content are S1, S2, S7, and S8, and the sample with the lowest organic carbon content are S3, S4, and S5. These three samples might have been collected from locations where tailings were placed, the lower organic carbon in these locations agrees with that possibility.

During the leaching process the sample S2 showed, in the results obtained with XRF, more evidence of leaching potential. From the elements that were analyzed with atomic absorption, Fe shows indications of leaching in all samples except S6, and S10. Pb only in S2, Cu appears to have leached in S2, and S5, and Sb leached in S3, and S4.

From the second water sampling all the samples from the Sousa River (W_8, W_9, W_10, W_14, W_15) have a neutral pH. W_11 has the lowest pH, and one of the highest electrical conductivity.

The samples collected from the river are very similar to each other, and have higher content of Na, Ca, and K.

It was possible to conclude that none of the sample waters, from the second sampling, are suitable to be consumed by humans. Samples W_1, W_3, W_6, W_11, can't be used for irrigation.

The statistical analysis of the water parameters showed that certain elements present a stronger association, above 0.7, such as Mn and Fe, Zn and Pb, Na and K, Cu and Zn, Cu and Pb. The PCA showed that some variables presented correlation BOD_5, TOC, NH_4, and NO_3, also Cl^-Cl-, Na, and K, and EC, Mg, SO_4, and F^-. There are three group of samples: the samples collected from the river (W_8, W_9, W_10, W_14, and W_15), the samples collected from where the mine was located (W_1, W_2, W_13), and lastly the samples, W_3, W_6, and W_11. These three samples show correlation and from the location of the samplings seems that they were collected from the same water line and might be influenced by the same elements. The PCA also reveals a correlation between the river samples and $BOD5$, TOC, NH_4, and NO_3. As well as the correlation between two samples W_1, and W_13 with Sb which was expected since it was mostly a Sb exploitation.

From the point of view of environmental risk to human health it was possible to conclude that the water sample W_1 has a high risk of carcinogens by ingestion, the hazard ratio of As is forty four times higher than the limit (one) for the adult, and seventy four times higher for the children. The hazard ratio of Sb in three times higher for the adult and five times higher for the children. In conclusion this water should not be consumed. In this exposure scenario, the hazard ratio of dermal contact are all less than one so it doesn't present a risk if the contact to this water is just dermal.

In conclusion the soil samples S1 and S2, collected from the property where the mine was located. In the case of S1, the concentration of arsenic is 400 mg/kg and reference value implemented by APA is 11 mg/kg, and the antimony concentration of 900 mg/kg when the reference value is 1 mg/kg. In the sample S2, the concentration of arsenic is 800 mg/kg and of antimony 1000 mg/kg. From the water samples from the second sampling, W_1 shows the highest risk to humans from its location and due to the concentration in arsenic of 618 µg/L and antimony of 54.6 µg/L, the reference values respectively are 50 µg/L, and 10 µg/L. The arsenic concentration in that water sample is more than twelve times higher than the recommend, and the antimony is more than five times. Measures should be taken so that this water is not in contact with other water lines or the river that flows close to the point where the sample was collected.

6.2. Future work

For future work a new sampling of soil samples would be necessary, with more samples to be able to further study the area. Add to the analysis performed during this dissertation, for example NAG, BOD, and COD adding valuable information. The results of the analysis of the water samples could be implemented in a software such as the Groundwater Modeling System (GMS) that allows the construction of a three-dimensional model. Also, a more complete and detailed hydrogeological study could be performed to further understand the area.

References

Fiúza, A., Leite, M., Vila, C., Dinis,M. L., Futuro, A., Gois, J. (2019). Bi-level depth assessment of an abandoned tailings dam aiming its reprocessing for recovery of valuable metals. Minerals Engineering, 133(November 2018), 1–9. https://doi.org/10.1016/j.mineng.2018.12.016

Analyses, D. of S. (n.d.). Correlation (Pearson, Kendall, Spearman). Retrieved July 1, 2022, from https://www.statisticssolutions.com/free-resources/directory-of-statistical-analyses/correlation-pearson-kendall-spearman/

APA. (2019). Valores De Referência Para O Solo. In Solos Contaminados - Guia Técnico (Vol. 2019).

Arnesen, G., Beck, P. S. A., & Engelskjon, T. (2018). Soil acidity, content of carbonates, and available phosphorus are the soil factors best correlated with alpine vegetation: Evidence from Troms, North Norway. Arctic, Antarctic, and Alpine Research, 39(2), 189–199. https://doi.org/10.1657/1523-0430(2007)39[189:SACOCA]2.0.CO;2

Batista, A. F. (2016). Análise Espacial das Mineralizações de Antimónio em Relação com Magmatismo Básico Filoniano e outras Características Geológicas no Distrito Auri – Antimonífero Dúrico - Beirão. Geology master dissertation. Faculdade de Ciências da Universidade do Porto.

Bolan, N., Kumar, M., Singh, E., Kumar, A., Singh, L., Kumar, S., Keerthanan, S., Hoang, S. A., El-Naggar, A., Vithanage, M., Sarkar, B., Wijesekara, H., Diyabalanage, S., Sooriyakumar, P., Vinu, A., Wang, H., Kirkham, M. B., Shaheen, S. M., Rinklebe, J., & Siddique, K. H. M. (2021). Antimony contamination and its risk management in complex environmental settings: A review. Environment International. https://doi.org/10.1016/j.envint.2021.106908

Cappuyns, V., Van Campen, A., & Helser, J. (2021). Antimony leaching from soils and mine waste from the Mau Due antimony mine, North-Vietnam. Journal of Geochemical Exploration, 220(September 2020), 106663. https://doi.org/10.1016/j.gexplo.2020.106663

Couto, H. (1993a). As mineralizações de Sb-Au. Geology PhD thesis (Volume I). Faculdade de Ciências da Universidade do Porto.

Couto, H. (1993b). As mineralizações de Sb-Au. Geology PhD thesis (Volume II). Faculdade de

Ciências da Universidade do Porto.

Couto, H. (2014). Ouro explorado pelos Romanos em Valongo: controlos das mineralizações auríferas. In Atas do 1º Congresso de Mineração Romana em Valongo. http://www.altorelevo.org/cmr/pdf/Couto 2015 CMR14_pp48_57.pdf

Dinis, M. L. (2018). Procedimentos Laboratoriais Impacte Ambiental Mineiro Mestrado em Engenharia de Minas e Geo-Ambiente, Faculdade de Engenharia da Universidade do Porto.

Dunnivant, F., & Anders, E. (2006). A basic introduction to pollutant fate and transport : an integrated approach with chemistry, model- ing, risk assessment, and environmental legislation. Wiley.

EPA. (2022). Reference Dose (RfD): Description and Use in Health Risk Assessments. https://www.epa.gov/iris/reference-dose-rfd-description-and-use-health-risk-assessments

European Commission. (2020). Study on the Eu's list of Critical Raw Materials - Critical Raw Materials Factsheets. In Critical Raw Materials Factsheets. https://doi.org/10.2873/11619

Fiúza, A., Leite, M., Vila, M., Dinis, M. L., Futuro, A., Gois, J., & Figueiredo, J. (2021). Quantitative Risk Assessment of Environmental Hazards Generated by a Tailings Embankment: case study Cabeço do Pião, Portugal. Boletin Geologico y Minero, 132(4), 465–486. https://doi.org/10.21701/bolgeomin.132.4.006

Fiúza, A. (n.d.). Hidromineralurgia , Mestrado em Engenharia de Minas e Geo-Ambiente, Faculdade de Engenharia da Universidade do Porto.

Fiúza, A. (2015). Impacte Ambiental Mineiro. Master in Mining and Geo-Environmental Engineering, Faculdade de Engenharia da Universidade do Porto.

Fiúza, A., & Vila, C. (2020). Risco Ambiental: análise sistemática estruturada. ISBN: 9789724086903. Almedina.

Fonseca, B. (2019). Avaliação da contaminação associada às escombreiras das minas de Rio de Frades - Arouca. Master dissertation in Geology. Faculdade de Ciências da Universidade do Porto.

Gonçalves, E. J. dos S. (2013). Hidrogeologia das áreas de Valongo, de Paredes e de Arouca, no contexto do Anticlinal de Valongo. Geosciences PhD thesis. [Faculdade de Ciências da Universidade do Porto]. https://repositorio-aberto.up.pt/handle/10216/69292

Gondomar, M. de. (n.d.). Geoportal Gondomar. Retrieved January 17, 2022, from https://ws.cm-gondomar.pt:81/geoportal

González-Alvarez, M. ., Aboal-Somoza, M., & Bermejo-Barrera, P. (2012). Preliminary Findings on the Antimony Levels of Quiroga River Water in the Vicinity of a Long-Abandoned Stibnite Mine. Water Environment Research, 84. https://doi.org/10.2175/106143011x13203533157316

INE. (2021). Censos. Retrieved January 18, 2022, from. https://www.ine.pt/scripts/db_censos_2021.html

Jardim, W. F. (2014). Medição e interpretação de valores do potencial redox (EH) em matrizes ambientais. Retrieved July 11, 2022, from. Instituto de Química, Universidade Estadual de Campinas, Campinas - SP, Brasil. https://www.scielo.br/j/qn/a/rXscfXjzdqVyG688PLZprLC/?lang=pt

Laerd statistics. (n.d.). Spearman's Rank-Order Correlation. Retrieved June 22, 2022, from https://statistics.laerd.com/statistical-guides/spearmans-rank-order-correlation-statistical-guide.php

Leite, M. (1987). Fragmentação e classificação de rochas e minérios. Texto de apoio, Licenciatura em Engenharia de Minas da Faculdade de Engenharia da Universidade do Porto.

Meteoblue. (n.d.). Mudanças climáticas Covelo. Retrieved January 18, 2022, from https://www.meteoblue.com/pt/climate-change/covelo_portugal_2740327

Minitab, L. (2021). Interpretar todas as estatísticas e gráficos para Correlação. Retrieved June 22, 2022, from. https://support.minitab.com/pt-br/minitab/20/help-and-how-to/statistics/basic-statistics/how-to/correlation/interpret-the-results/all-statistics-and-graphs/

Nunes, C. (2015). Co- Deposição em Pasta de Resíduos de Tratamento de Minérios de Ouro com Incorporação de Cinzas de Carvão. Master dissertation in Mining and Geo-Environmental Engineering. Faculdade de Engenharia da Universidade do Porto.

Pennock, D., Yates, T., & Braidek, J. (2008). Chapter 1: Soil Sampling Designs. In M. R. Carter & E. G. Gregorich (Eds.), Soil Sampling & Methods of Analysis (2nd ed.). Canadian Society of Soil Science.

Queensland Government. (2022). Soil Carbon. Retrieved February 6, 2022, from. https://www.qld.gov.au/environment/land/management/soil/soil-properties/carbon

Reuter, H. I., Lado, L. R., Hengl, T., & Montanarella, L. (2010). Continental-scale digital soil mapping using European soil profile data: soil pH.

Rodrigues, A. (2009). Dispersão e Contaminação por Pb , Zn e As , associada à escombreira mineira de Terramonte (Castelo de Paiva – Portugal). Master's dissertation. Faculdade de Ciências da Universidade do Porto.

Silva, G. (2017). A Indústria Mineira no Distrito do Porto no final do século XIX: o antimónio nos concelhos de Valongo e Gondomar. Master thesis in Risks, Cities and Spatial Planning, Faculdade de Letras da Universidade do Porto.

Sousa, A. (2017). Breve História da Exploração Mineira em Gondomar. Research done in Seminar II, Degree in History, Arts and Heritage, Universidade Aberta.

Sousa, A. C. (2014). Remoção de arsénio e antimónio de soluções aquosas por biossorção. Master dissertation in Environmental Engineering, Faculdade de Engenharia da Universidade do Porto. Faculdade de Engenharia da Universidade do Porto.

Tao, Y., Su, H., Li, H., Zhu, Y., Shi, D., Wu, F., & Sun, F. (2021). Ecological and human health risk assessment of antimony (Sb) in surface and drinking water in China. Journal of Cleaner Production, August. https://doi.org/10.1016/j.jclepro.2021.128514

Vila, C. (2014). Quimodinâmica e Análise de Risco. Texto de apoio Mestrado Engenharia do Ambiente, Faculdade de Engenharia da Universidade do Porto.

Vila, C. (2021). Protocolos experimentais, laboratórios de Engenharia do Ambiente II, Faculdade de Engenharia da Universidade do Porto.

Attachments

I-Chemical analysis of the soil samples performed in XRF

Table I- Results obtained in the XRF analysis (A1).

A1	Samples	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	S11
Fe	[%]	5.83	5.01	4.94	4.09	5.31	3.18	3.66	3.01	41.20	3.26	5.09
	±	1.E-01	4.E-01	5.E-01	5.E-02	1.E-01	3.E-02	3.E-01	8.E-02	5.E-01	4.E-02	5.E-02
K	[%]	2.09	1.80	2.08	0.00	1.74	0.00	0.00	0.00	0.53	2.30	0.00
	±	5.E-02	2.E-02	8.E-02	0.E+00	2.E-01	0.E+00	0.E+00	0.E+00	7.E-02	1.E-01	0.E+00
Ca	[%]	0.43	1.17	0.79	0.00	1.26	0.00	0.00	0.00	0.06	0.00	0.00
	±	1.E-02	5.E-02	2.E-01	0.E+00	1.E-01	0.E+00	0.E+00	0.E+00	5.E-02	0.E+00	0.E+00
Mn	[%]	0.13	0.09	0.09	0.04	0.03	0.04	0.04	0.03	0.06	0.00	0.03
	±	3.E-03	8.E-03	6.E-02	2.E-02	3.E-03	4.E-03	2.E-02	3.E-02	1.E-02	0.E+00	6.E-03
Sb	[%]	0.09	0.15	0.04	0.57	0.02	0.00	0.00	0.00	0.00	0.00	0.00
	±	1.E-03	1.E-03	7.E-03	1.E-01	2.E-03	0.E+00	0.E+00	3.E-03	0.E+00	0.E+00	0.E+00
Ti	[%]	0.60	0.46	0.50	0.42	0.55	0.55	0.52	0.56	0.15	0.72	0.68
	±	3.E-02	5.E-02	4.E-02	6.E-02	3.E-02	6.E-02	4.E-02	4.E-02	9.E-03	3.E-02	4.E-02
Zn	[%]	0.03	0.22	0.02	0.01	0.02	0.01	0.01	0.00	0.01	0.00	0.01
	±	1.E-03	6.E-02	1.E-03	1.E-03	2.E-03	1.E-03	2.E-03	0.E+00	1.E-03	0.E+00	0.E+00
As	[%]	0.03	0.05	0.01	0.15	0.01	0.00	0.01	0.00	0.00	0.00	0.00
	±	1.E-03	2.E-03	1.E-03	7.E-03	2.E-03	0.E+00	1.E-03	1.E-03	0.E+00	0.E+00	0.E+00
Zr	[%]	0.03	0.02	0.03	0.02	0.02	0.03	0.03	0.02	0.01	0.04	0.03
	±	1.E-03	2.E-03	2.E-03	2.E-03	1.E-03	8.E-03	4.E-03	2.E-03	2.E-03	1.E-03	1.E-03
Pb	[%]	0.03	0.05	0.00	0.03	0.00	0.00	0.00	0.00	0.01	0.00	0.00
	±	1.E-03	3.E-03	0.E+00	2.E-02	7.E-03	0.E+00	0.E+00	0.E+00	1.E-03	0.E+00	0.E+00
Rb	[%]	0.02	0.02	0.02	0.01	0.01	0.03	0.03	0.01	0.01	0.02	0.01
	±	0.E+00	2.E-03	1.E-03	1.E-03	0.E+00	0.E+00	2.E-03	3.E-03	1.E-03	0.E+00	0.E+00
Sn	[%]	0.01	0.02	0.02	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	±	2.E-03	1.E-03	1.E-02	4.E-03	4.E-03	3.E-03	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00
Sr	[%]	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.03	0.00
	±	0.E+00	1.E-03	0.E+00	1.E-03	1.E-03	0.E+00	1.E-03	4.E-03	1.E-03	2.E-03	0.E+00
Ba	[%]	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.11	0.00	0.00
	±	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00	1.E-02	0.E+00	0.E+00
Cu	[%]	0.01	0.01	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.01
	±	2.E-03	2.E-03	1.E-03	1.E-03	1.E-03	0.E+00	0.E+00	1.E-03	0.E+00	0.E+00	1.E-03
Co	[%]	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00
	±	0.E+00	4.E-03	8.E-03	0.E+00	0.E+00	0.E+00	0.E+00	2.E-03	1.E-02	0.E+00	0.E+00
Cr	[%]	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.00	0.00
	±	0.E+00	0.E+00	0.E+00	0.E+00	5.E-03	0.E+00	0.E+00	0.E+00	4.E-03	0.E+00	0.E+00
Ni	[%]	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	±	2.E-03	6.E-03	0.E+00	1.E-03	0.E+00	0.E+00	0.E+00	1.E-03	0.E+00	0.E+00	0.E+00
Nb	[%]	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00
	±	0.E+00	0.E+00	1.E-03	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00

Table II- Results obtained in the XRF analysis (A2).

A2	Samples	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	S11
Fe	[%]	6.30	5.62	4.73	5.03	5.26	4.05	3.41	2.86	38.27	3.10	5.30
	±	1.E-01	4.E-01	2.E-01	4.E-02	5.E-02	2.E-01	9.E-01	2.E-02	1.E+00	4.E-02	4.E-02
K	[%]	0.64	2.19	2.00	0.00	1.95	0.00	0.00	0.00	0.82	2.11	1.94
	±	9.E-01	2.E-01	1.E-01	0.E+00	8.E-02	0.E+00	0.E+00	0.E+00	2.E-02	6.E-02	3.E-02
Ca	[%]	0.11	1.23	0.62	0.00	1.16	0.00	0.00	0.00	0.00	0.00	0.00
	±	2.E-01	8.E-02	6.E-02	0.E+00	3.E-02	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00
Mn	[%]	0.14	0.11	0.04	0.03	0.04	0.05	0.05	0.00	0.04	0.00	0.02
	±	4.E-03	9.E-03	3.E-03	2.E-03	1.E-03	1.E-02	1.E-02	0.E+00	2.E-03	0.E+00	7.E-03
Sb	[%]	0.09	0.10	0.04	0.68	0.01	0.00	0.00	0.00	0.00	0.00	0.00
	±	3.E-02	7.E-03	6.E-03	1.E-01	4.E-03	0.E+00	0.E+00	2.E-03	0.E+00	0.E+00	0.E+00
Ti	[%]	0.52	0.63	0.48	0.50	0.48	0.58	0.47	0.58	0.23	0.73	0.82
	±	2.E-02	6.E-02	1.E-03	1.E-02	1.E-03	1.E-02	1.E-01	1.E-02	1.E-03	1.E-02	1.E-02
Zn	[%]	0.04	0.19	0.02	0.01	0.02	0.01	0.01	0.00	0.01	0.00	0.01
	±	3.E-03	1.E-02	1.E-03	0.E+00	1.E-03	1.E-03	4.E-03	0.E+00	1.E-03	0.E+00	0.E+00
As	[%]	0.04	0.08	0.02	0.24	0.01	0.01	0.00	0.00	0.00	0.01	0.00
	±	1.E-03	8.E-03	1.E-03	5.E-03	0.E+00	1.E-03	3.E-03	1.E-03	0.E+00	1.E-03	0.E+00
Zr	[%]	0.04	0.03	0.03	0.02	0.02	0.08	0.05	0.02	0.01	0.05	0.07
	±	4.E-03	2.E-03	3.E-03	1.E-03	3.E-03	2.E-03	2.E-02	3.E-03	1.E-03	1.E-02	3.E-03
Pb	[%]	0.04	0.06	0.00	0.06	0.00	0.00	0.00	0.00	0.01	0.00	0.00
	±	2.E-03	2.E-03	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00	5.E-03	0.E+00	0.E+00
Rb	[%]	0.02	0.02	0.01	0.01	0.01	0.03	0.02	0.01	0.01	0.01	0.01
	±	1.E-03	0.E+00	1.E-03	0.E+00	1.E-03	2.E-03	7.E-03	1.E-03	1.E-03	2.E-03	1.E-03
Sn	[%]	0.01	0.01	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	±	3.E-03	1.E-03	2.E-03	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00
Sr	[%]	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.02	0.01
	±	1.E-03	0.E+00	0.E+00	0.E+00	0.E+00	1.E-03	3.E-03	1.E-03	1.E-03	3.E-03	0.E+00
Ba	[%]	0.04	0.00	0.09	0.00	0.00	0.00	0.00	0.00	0.15	0.06	0.00
	±	5.E-02	0.E+00	7.E-02	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00	2.E-02	8.E-02	0.E+00
Cu	[%]	0.02	0.02	0.01	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.00
	±	2.E-03	2.E-03	0.E+00	1.E-03	2.E-03	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00	1.E-03
Co	[%]	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.03	0.00	0.00
	±	0.E+00	3.E-03	4.E-03	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00	2.E-03	0.E+00	0.E+00
Cr	[%]	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.00	0.00
	±	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00	1.E-02	0.E+00	0.E+00
Ni	[%]	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	±	1.E-03	2.E-03	0.E+00	1.E-03	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00
V	[%]	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00
	±	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00	1.E-02	0.E+00	0.E+00

Table III- Results obtained in the XRF analysis (A3).

A3	Samples	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	S11
Fe	[%]	4.88	4.92	4.37	3.59	6.09	3.31	3.58	4.86	22.81	5.73	4.98
	±	2.E-01	3.E-01	1.E-01	2.E-01	3.E-01	9.E-02	6.E-02	4.E-02	4.E+00	2.E-01	1.E+00
K	[%]	0.65	2.46	0.00	1.61	2.09	0.00	0.00	0.00	0.42	2.05	0.67
	±	9.E-01	2.E-01	0.E+00	1.E-01	1.E-01	0.E+00	0.E+00	0.E+00	6.E-01	6.E-02	9.E-01
Ca	[%]	0.05	1.20	0.00	0.28	0.94	0.00	0.00	0.00	0.00	0.00	0.00
	±	8.E-02	5.E-02	0.E+00	3.E-02	2.E-01	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00
Mn	[%]	0.07	0.07	0.03	0.01	0.04	0.05	0.06	0.00	0.04	0.00	0.01
	±	4.E-03	5.E-03	7.E-03	1.E-03	8.E-03	9.E-03	2.E-03	0.E+00	8.E-03	0.E+00	1.E-02
Sb	[%]	0.03	0.09	0.02	0.43	0.02	0.00	0.00	0.00	0.00	0.00	0.00
	±	7.E-03	9.E-02	8.E-03	4.E-02	4.E-03	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00
Ti	[%]	0.46	0.42	0.34	0.35	0.50	0.53	0.50	0.51	0.29	0.64	0.43
	±	8.E-03	1.E-02	3.E-02	7.E-03	2.E-02	2.E-02	3.E-02	1.E-02	5.E-02	2.E-02	1.E-01
Zn	[%]	0.01	0.12	0.01	0.01	0.02	0.01	0.01	0.00	0.01	0.00	0.01
	±	2.E-03	1.E-02	1.E-03	1.E-03	1.E-03	1.E-03	1.E-03	0.E+00	1.E-03	0.E+00	5.E-03
As	[%]	0.01	0.04	0.01	0.22	0.01	0.00	0.01	0.00	0.00	0.00	0.00
	±	0.E+00	3.E-03	1.E-03	1.E-02	1.E-03	2.E-03	0.E+00	2.E-03	0.E+00	0.E+00	0.E+00
Zr	[%]	0.02	0.02	0.01	0.02	0.02	0.03	0.02	0.02	0.02	0.04	0.02
	±	3.E-03	2.E-02	2.E-03	1.E-03	2.E-03	1.E-03	3.E-03	1.E-03	4.E-03	1.E-03	5.E-03
Pb	[%]	0.00	0.04	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	±	0.E+00	3.E-02	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00
Rb	[%]	0.01	0.02	0.01	0.01	0.01	0.03	0.03	0.01	0.01	0.01	0.01
	±	1.E-03	2.E-03	1.E-03	1.E-03	1.E-03	1.E-03	1.E-03	0.E+00	0.E+00	0.E+00	4.E-03
Sn	[%]	0.00	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	±	3.E-03	1.E-02	3.E-03	6.E-03	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00
Sr	[%]	0.00	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.02	0.00
	±	1.E-03	1.E-02	1.E-03	1.E-03	1.E-03	0.E+00	0.E+00	0.E+00	2.E-03	0.E+00	2.E-03
Ba	[%]	0.00	0.00	0.00	0.00	0.00	0.04	0.00	0.00	0.12	0.00	0.00
	±	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00	5.E-02	0.E+00	0.E+00	3.E-02	0.E+00	0.E+00
Cu	[%]	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	±	0.E+00	3.E-03	0 ± 0	1.E-03	2.E-03	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00	2.E-03
Co	[%]	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	±	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00
Cr	[%]	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00
	±	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00	1.E-02	0.E+00	0.E+00
Ni	[%]	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	±	0.E+00	4.E-03	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00
Nb	[%]	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00
	±	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00	1.E-03

Table IV- Results obtained in the XRF analysis, before leaching (A4).

A4	Samples	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	S11
Fe	[%]	4.87	4.91	4.45	3.64	5.29	3.33	3.73	5.04	25.34	5.66	6.30
	±	6.E-02	5.E-01	8.E-02	4.E-01	1.E+00	1.E-01	1.E-02	2.E-02	2.E+00	2.E-02	1.E-01
K	[%]	0.00	2.15	0.00	0.00	1.83	0.00	0.00	0.00	0.89	2.00	2.26
	±	0.E+00	2.E-01	0.E+00	0.E+00	5.E-01	0.E+00	0.E+00	0.E+00	6.E-01	1.E-01	1.E-01
Ca	[%]	0.00	1.11	0.00	0.00	0.79	0.00	0.00	0.00	0.02	0.00	0.03
	±	0.E+00	1.E-01	0.E+00	0.E+00	2.E-01	0.E+00	0.E+00	0.E+00	3.E-02	0.E+00	4.E-02
Mn	[%]	0.07	0.07	0.03	0.02	0.03	0.04	0.07	0.01	0.04	0.00	0.02
	±	3.E-03	1.E-02	6.E-03	2.E-02	8.E-03	8.E-03	5.E-03	9.E-03	3.E-03	0.E+00	7.E-03
Sb	[%]	0.03	0.10	0.03	0.35	0.01	0.00	0.00	0.00	0.00	0.00	0.00
	±	1.E-02	2.E-02	3.E-03	5.E-02	4.E-03	0.E+00	0.E+00	3.E-03	0.E+00	0.E+00	0.E+00
Ti	[%]	0.45	0.38	0.35	0.37	0.45	0.48	0.51	0.00	0.36	0.65	0.56
	±	1.E-02	2.E-02	8.E-03	3.E-02	1.E-01	1.E-02	4.E-02	1.E-02	5.E-02	1.E-02	2.E-02
Zn	[%]	0.01	0.13	0.01	0.01	0.02	0.01	0.01	0.00	0.01	0.00	0.01
	±	2.E-03	3.E-02	1.E-03	1.E-03	4.E-03	1.E-03	0.E+00	0.E+00	1.E-03	1.E-03	0.E+00
As	[%]	0.01	0.04	0.01	0.20	0.01	0.00	0.01	0.00	0.00	0.00	0.00
	±	1.E-03	3.E-03	0.E+00	1.E-02	4.E-03	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00
Zr	[%]	0.02	0.02	0.02	0.01	0.02	0.02	0.03	0.02	0.02	0.03	0.02
	±	3.E-03	1.E-03	0.E+00	1.E-03	6.E-03	3.E-03	4.E-03	3.E-03	3.E-03	2.E-03	1.E-03
Pb	[%]	0.00	0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	±	0.E+00	2.E-03	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00	0.00
Rb	[%]	0.01	0.02	0.01	0.01	0.01	0.03	0.03	0.01	0.01	0.01	0.01
	±	1.E-03	1.E-03	1.E-03	1.E-03	4.E-03	1.E-03	4.E-03	1.E-03	2.E-03	0.E+00	1.E-03
Sn	[%]	0.00	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	±	3.E-03	2.E-03	4.E-03	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00
Sr	[%]	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.02	0.01
	±	1.E-03	1.E-03	0.E+00	0.E+00	2.E-03	1.E-03	2.E-03	1.E-03	2.E-03	1.E-03	0.E+00
Ba	[%]	0.00	0.07	0.00	0.00	0.11	0.04	0.04	0.07	0.12	0.00	0.05
	±	0.E+00	1.E-01	0.E+00	0.E+00	8.E-02	5.E-02	5.E-02	5.E-02	7.E-03	0.E+00	7.E-02
Cu	[%]	0.00	0.01	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00
	±	2.E-03	5.E-03	1.E-03	0.E+00	2.E-03	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00	2.E-03
Co	[%]	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	±	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00
Cr	[%]	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00
	±	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00	1.E-02	0.E+00	0.E+00
Ni	[%]	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	±	2.E-03	4.E-03	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00
Nb	[%]	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00
	±	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00

Table V- Results obtained in the XRF analysis, after leaching (A5).

A5	Samples	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	S11
Fe	[%]	3.92	4.06	3.85	2.51	4.98	3.57	3.37	4.98	18.98	6.31	5.85
	±	3.E-01	2.E-01	8.E-02	7.E-02	3.E-01	3.E-01	7.E-02	4.E-01	3.E-01	4.E-01	1.E-01
K	[%]	2.12	2.35	2.28	1.36	2.26	0.00	0.00	1.85	1.49	1.81	1.99
	±	7.E-02	1.E-01	4.E-02	2.E-01	3.E-01	0.E+00	0.E+00	1.E-01	4.E-02	8.E-02	8.E-03
Ca	[%]	0.07	1.08	0.17	0.06	0.69	0.00	0.00	0.00	0.00	0.00	0.00
	±	5.E-02	1.E-01	7.E-03	9.E-02	1.E-01	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00
Mn	[%]	0.05	0.04	0.03	0.01	0.02	0.03	0.04	0.00	0.03	0.00	0.01
	±	5.E-03	2.E-03	8.E-03	1.E-03	1.E-02	4.E-03	8.E-03	0.E+00	2.E-03	0.E+00	7.E-03
Sb	[%]	0.03	0.10	0.02	0.30	0.01	0.00	0.00	0.00	0.00	0.00	0.00
	±	2.E-03	7.E-03	1.E-03	3.E-02	3.E-03	0.E+00	3.E-03	0.E+00	0.E+00	0.E+00	0.E+00
Ti	[%]	0.50	0.41	0.34	0.31	0.58	0.57	0.48	0.54	0.43	0.58	0.53
	±	2.E-02	5.E-03	2.E-02	1.E-02	4.E-02	3.E-02	2.E-02	6.E-02	2.E-02	1.E-02	4.E-02
Zn	[%]	0.01	0.11	0.01	0.00	0.01	0.01	0.01	0.00	0.01	0.00	0.01
	±	2.E-03	1.E-02	1.E-03	0.E+00	1.E-03	1.E-03	0.E+00	1.E-03	0.E+00	1.E-03	1.E-03
As	[%]	0.01	0.03	0.01	0.20	0.01	0.00	0.00	0.00	0.00	0.00	0.00
	±	1.E-03	1.E-03	0.E+00	6.E-03	0.E+00	0.E+00	2.E-03	1.E-03	0.E+00	0.E+00	0.E+00
Zr	[%]	0.02	0.02	0.02	0.01	0.02	0.03	0.03	0.02	0.02	0.03	0.02
	±	2.E-03	0.E+00	1.E-03	0.E+00	1.E-03	6.E-03	3.E-03	2.E-03	2.E-03	4.E-03	1.E-03
Pb	[%]	0.00	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	±	0.E+00	1.E-03	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00
Rb	[%]	0.02	0.02	0.01	0.01	0.01	0.03	0.03	0.01	0.01	0.01	0.01
	±	1.E-03	1.E-03	0.E+00	0.E+00	1.E-03	1.E-03	1.E-03	1.E-03	1.E-03	1.E-03	0.E+00
Sn	[%]	0.00	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	±	0.E+00	2.E-03	3.E-03	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00
Sr	[%]	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.02	0.01
	±	1.E-03	0.E+00	0.E+00	0.E+00	0.E+00	1.E-03	0.E+00	1.E-03	0.E+00	1.E-03	0.E+00
Ba	[%]	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.04	0.00	0.00
	±	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00	6.E-02	0.E+00	0.E+00
Cu	[%]	0.00	0.00	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	±	1.E-03	3.E-03	2.E-03	0.E+00	2.E-03	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00	3.E-03
Co	[%]	0.00	0.00	0.08	0.04	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	±	0.E+00	0.E+00	1.E-02	3.E-03	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00	5.E-03
Cr	[%]	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00
	±	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00	1.E-03	0.E+00	0.E+00
Ni	[%]	0.00	0.00	0.04	0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	±	0.E+00	2.E-03	7.E-03	1.E-03	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00	3.E-03
Nb	[%]	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00
	±	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00	0.E+00

II-Particle size analysis

Procedure (Leite, 1987):

1. Weight the entire sample
2. Select and remove to a separate basin the bigger particles
3. Discover the size of these particles by testing the largest sieves individually
4. Weight of the largest particles
5. Place the rest of the sample into the first series
6. Leave sieving for 15 minutes
7. Weight the material that is in each sieve
8. The material below 0.600mm is used in the next series

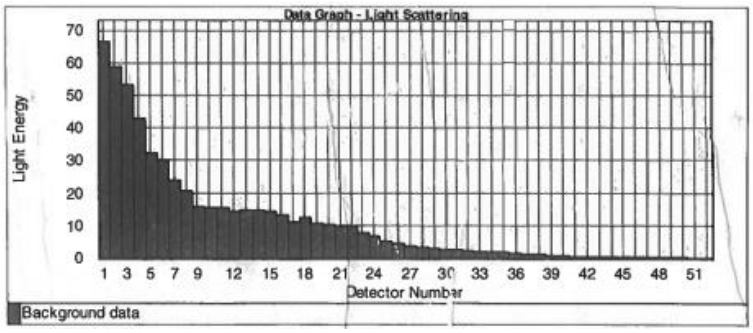
9. Leave the second series sieving for 15 minutes
10. Repeat step 7
11. Save the material below 0.075 mm separate
12. Repeat for all eleven samples

Procedure granulometer:

- Connect the optical bench and the dispersion unit.
- Check if the container is full or nearly full.
- Check that the reading windows are clean.
- Turn on the computer and start the Mastersizer 2000 program.

Manual measurements:

- With the program window already open, open a new worksheet as follows:
    - Go to **File** and select new.
    - Name the result sheet and save it in the desired extension.
    - Go to **Measure** and select **Manual** mode.
    - Click on **Accessory** and check if the dispersion tank is full. If it is not full, click on **Fill.**
    - Define the **Stirrer** and **Pump** to the values in the mead of the scale.
    - Do **Align** (when the icon is available).
    - In **Option**, click on **Measurement** and select the analysis time of 5s and the background time for 10s.
    - Select the option of average in the end.
    - In the same window click on **Measurement** and define limits of 5%-10% for finer and medium particles and 5%-12% for bigger particles.
    - Go to **Document** and identify the sample.
    - Press **Start**, to obtain the Background:



    - **Add sample** until it reaches the limit established.

- The results are in the **Report Analysis**.
- Do **clean**

III- Soil pH determination

Materials:

- Distilled water
- CaCl2 solution at 0.01M
- Solid sample
- Analytical balance
- 50mL beaker
- Mechanical stirrer
- pH meter

Procedure (Dinis, 2018):

1. Weigh a sample of 20 g of dry soil
2. Place the sample to a 50 mL beaker
3. Add 20 ml of distilled water
4. Place the beaker on a stirrer and let stir at moderate speed for 20 minutes
5. Let the solution stand for 30 minutes and measure the pH by introducing the electrode into the clarified fraction. Take note of the value and display it as pH1
6. Take a new sample of 10 g of the same soil. Transfer it to a beaker of 50 ml
7. Add 20 mL of 0,01 M CaCl2
8. Repeat steps 4 and 5
9. Indicate the pH as pH2
10. Compare the two values

IV- Organic Carbon and organic matter in a soil

Materials (Vila, 2021):

- Solution of potassium dichromate (K2Cr2O7) → 0.167 mol/L; 49.04 g/L
- Concentrated sulfuric acid → 96%
- Ferrous ammonium sulfate → 0.5 mol/L

- Ferroin or Orth phenanthroline indicator solution

Procedure (Vila, 2021):

1. Weight a quantity of sieved soil (to give between 5 and 10 mg of organic carbon) into an Erlenmeyer flask. The sample size will vary between 0.2 to 1g, depending on the organic matter content.
2. Add 5mL of the potassium dichromate solution using a pipette; then add 10mL of concentrated sulfuric acid.
3. Mix immediately by shaking the flask for about 1 minute, then let it stand by placing the Erlenmeyer flask in a beaker for 30 minutes. Cool with ice before titrating.
4. Add 15mL of distilled water and three drops of Ferroin.
5. Titrate with the ferrous ammonium sulfate solution until the color changes to greenish-brown.

V- Natural dynamic leaching

Materials (Nunes, 2015):

- Analytic scale.
- Beaker 600mL.
- pH, temperature, conductivity, total dissolved solids, dissolved oxygen equipment.
- Magnetic stirrer.
- Filter
- XRF equipment.
- Analytik jena.
- Distilled water.
- Dry soil.

Procedure (Nunes, 2015):

A- Leaching preparation:

1. Weight 50g of dry soil.
2. Place the soil in a 600 mL beaker.
3. Measure the parameters of the distilled water (pH, temperature, conductivity, total dissolved solids, dissolved oxygen)
4. Add 500 mL of distilled water to the beaker.

B- Leaching:

5. Set the agitation speed to 200 rpm.
6. Take note of the time of the beginning of the reaction.
7. Let it stir for 1h.
8. Turn off the stirrer and remove the beaker.
9. Leave decanting for 15 minutes.
10. Measure all the referred parameters and take note of the value.
11. Let it stir for 3h.
12. Repeat set 8, 9, and 10.
13. Let it stir for 24h.
14. Repeat set 8, 9, and 10.

C- Filtration:

15. With a funnel, filter to a 600mL beaker.
16. Take a sample of the solution and identify it.

D- Drying process:

17. Place the moist soil in the oven and let it dry for 24h at 60 ºC.
18. Determine the chemical composition of the solid part with the XRF analyzer.
19. Determine the chemical composition of the liquid part using atomic absorption.